The Israel Chemical Society
Celebrates its
90th Anniversary

April 3, 2024

BOOK OF ABSTRACTS

The Israel Chemical Society
Celebrates its
90th Anniversary

The 87th Annual Meeting of The Israel Chemical Society

Timetable

April 3, 2024

Smolarz Auditorium, Tel Aviv University

8:30-9:00	**Registration**	Poster mounting and exhibition	Light breakfast
09:00-9:20		Opening Session	
9:20-9:50	Chair: **Prof. E. Keinan**	**Prof. Lucio Frydman,** Weizmann Institute *Nuclear Magnetic Resonance or Magnetic Resonance Imaging? Let's take both*	ICS Prize of 2022 Excellence
09:50-10:10	Chair: **Dr. N. Shpigel**	**Prof. Oded Hod**, Tel Aviv University *Layered Ferroelectricity: from Geometric Measures to First-Principles Calculations*	
10:10-10:30		**Prof. Leeor Kronik,** Weizmann Institue *Understanding optical properties of biogenic and bio-inspired molecular crystals: a first principles perspective*	
10:30-10:50		**Prof. Sharon Ruthstein**, Bar-Ilan University *The correlation between the gating mechanism of the human copper transporter, Ctr1, and the development of innovative biomarkers*	
10:55-11:35	Coffee Break		
11:35-11:55	Chair: **Dr. Z. Nairoukh**	**Prof. Eylon Yavin**, The Hebrew University *FIT-PNAs as RNA sensors for Ovarian cancer diagnostics*	
11:55-12:15		**Prof. Doron Pappo**, Ben Gurion University *Redox-Active 3rd-Transition Metal Catalysts for Dehydrogenative C–H Bond Coupling*	ICS-Adama Prize 2023
12:15-12:35		**Dr. Raya Sorkin,** Tel Aviv University *Membrane tension and membrane (hemi) fusion*	
12:35-12:55		**Prof. Ori Gidron,** The Hebrew University *Aromatic Materials – A Twisted Tale*	ICS Young Scientist Prize 2022
13:00-14:30	Lunch, Posters Session, Exhibition, Gender Equality Power Hour (with **Prof. Mindy Levine**)		
13:30-14:30	General Assembly		
14:30-15:00	Chair: **Prof. E. Keinan**	**Prof. Shlomo Magdassi,** The Hebrew University *From Gutenberg Bible to 4D printing*	ICS Prize of 2022 Excellence
15:00-15:20	Chair: **Prof. A. Salomon**	**Prof. Galia Maayan**, Technion *Bio-inspired electrocatalytic water oxidation*	
15:20-15:40		**Prof. Dan Meyerstein**, Ariel University *The Mechanisms of the Fenton and Fenton-Like Reactions*	
15:40-16:00		**Prof. Malachi Noked**, Bar-Ilan University *Mitigating Electrode Material Degradation through Advanced Surface Modification Techniques*	ICS Young Scientist Prize 2023
16:05-16:30	Coffee Break		
16:30-16:50	Chair: **Prof. D. Golodnitsky**	**Prof. David Eisenberg**, Technion *Porous Materials: The Next Frontier in Energy Research*	
16:50-17:10		**Prof. Emanuel Peled,** Tel Aviv University *Lithium and sodium metal batteries*	
17:10-17:30		**Prof. Idan Hod**, Ben Gurion University *Molecular Manipulation of Heterogeneous Electrocatalysis Using Metal-Organic Frameworks*	ICS Young Scientist Prize 2022
17:30-18:00		**Prof. Abhishek Dey**, IACS, Kolkata, India *Factors Deciding the Selectivity of O_2, NO, CO_2 and SO_2 Reduction*	
18:00-18:45	**Reception**		
18:45	**ICS Award Ceremony**		

BARGAL · tzamal D-CHEM LABORATORIES · ELDAN NEOPHARM GROUP · TECHNION Israel Institute of Technology · Ben-Gurion University of the Negev · WEIZMANN INSTITUTE OF SCIENCE · האוניברסיטה העברית בירושלים THE HEBREW UNIVERSITY OF JERUSALEM · TEL AVIV UNIVERSITY · ARIEL UNIVERSITY

Lectures

Lectures

Speaker and affiliation	Title	Page
Prof. Lucio Frydman Department of Chemical and Biological Physics, Weizmann Institute, 7610001 Rehovot, Israel	Nuclear Magnetic Resonance or Magnetic Resonance Imaging? Let's take both	6
Prof. Oded Hod School of Chemistry, Tel Aviv University, 6997801, Tel Aviv , Israel.	Layered Ferroelectricity: from Geometric Measures to First-Principles Calculations	7
Prof. Leeor Kronik Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovoth, Israel	Understanding optical properties of biogenic and bio-inspired molecular crystals: a first principles perspective	8
Prof. Sharon Ruthstein The Chemistry Department and the Institute of Nanotechnology and Advanced Materials, Faculty of Exact Sciences, Bar Ilan University, Israel.	The correlation between the gating mechanism of the human copper transporter, Ctr1, and the development of innovative biomarkers	9
Marah Daas[a], Sheethal Thomas Mannully[a], Tamar Perri[b], Reuven Reich[a], and Prof. Eylon Yavin[a] [a] The Institute for Drug Research, The School of Pharmacy, The Hebrew University of Jerusalem, Hadassah Ein-Kerem, Jerusalem 9112002, Israel. [b] Department of Gynecologic Oncology, Hadassah Medical Center, Hadassah Ein-Kerem, Jerusalem 9112002, Israel	FIT-PNAs as RNA sensors for Ovarian cancer diagnostics	10
Prof. Doron Pappo Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel	Redox-Active 3rd-Transition Metal Catalysts for Dehydrogenative C–H Bond Coupling	11
Petr Shendrik[#1,3], Gonen Golani[#2], Raviv Dharan[1,3], Ulrich S. Schwarz[2] and Dr. Raya Sorkin[1,3*] [1] School of Chemistry, Raymond & Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, Israel. [2] Institute for Theoretical Physics and BioQuant Center for Quantitative Biology, Heidelberg University, Heidelberg, Germany. [3] Center of Physics and Chemistry of Living Systems, Tel Aviv University, Tel Aviv, Israel.	Membrane tension and membrane (hemi)fusion	12

Lectures

Nuclear Magnetic Resonance or Magnetic Resonance Imaging? Let’s take both

Lucio Frydman

Department of Chemical and Biological Physics, Weizmann Institute, 7610001 Rehovot, Israel

E-mail: lucio.frydman@weizmann.ac.il

No chemist needs to be reminded about the importance of nuclear magnetic resonance (NMR). When used in its spectroscopic mode, where chemically distinct sites give origin to individual peaks or simple multiplets, NMR is simply “the eyes” with which the chemist views structures. Whether applied in the pharmaceutical or synthetic industries, whether on basic or applied research, nearly no product arising from a chemical process or no natural product isolated for potential applications in medicine or technology, is trusted today without an NMR elucidation. NMR is no less important in the clinic today, where it is employed to localize the position and properties of water molecules throughout tissues using magnetic resonance imaging (MRI). A particularly promising window could be opened by the combination of NMR’s spectroscopic ability with MRI’s capacity to map objects non-invasively in 3D, into a joint magnetic resonance spectroscopic imaging (MRSI) experiment. MRSI can then image the metabolites supporting life within organisms, thus shedding light about health and helping to signal and prognose the onset disease. The fate of MRSI-based metabolic techniques, however, hinges in overcoming NMR’s sensitivity problem, as well as the long durations of these high-dimensional experiments. We are currently exploring a number of complementary approaches to alleviate these related challenges; ongoing developments describing these efforts will be presented.

Acknowledgements: This award lecture is dedicated to the 24 graduate students and 40 postdocs that, with the assistance of uninterrupted ISF funding, have accompanied me since immigrating to Israel and joining the Weizmann Institute 23 years ago.

Layered Ferroelectricity: from Geometric Measures to First-Principles Calculations

Oded Hod*[a]

[a] *School of Chemistry, Tel Aviv University, 6997801, Tel Aviv , Israel.*

E-mail: odedhod@tauex.tau.ac.il

The ability to locally switch confined electric polarization is vital in modern technologies, aiming to complement or replace traditional magnetic components toward storing, retrieving, and processing large volumes of information. Non-centrosymmetrically stacked layered materials have recently emerged as promising candidates for vertical polarization switching via lateral interlayer shifts – a mechanism known as Slidetronics.[1] In this presentation, I will elucidate the microscopic origins of polarization in layered materials; demonstrate that it is dictated by interlayer registry;[2] explain its cumulative nature[3] and its saturation behavior;[4] show that it can emerge also in intrinsically non-polar systems, such as graphitic interfaces;[5] and extend the notion of slidetronics to the quasi-one-dimensional case of facetted nanotubes (see Fig. 1).[6]

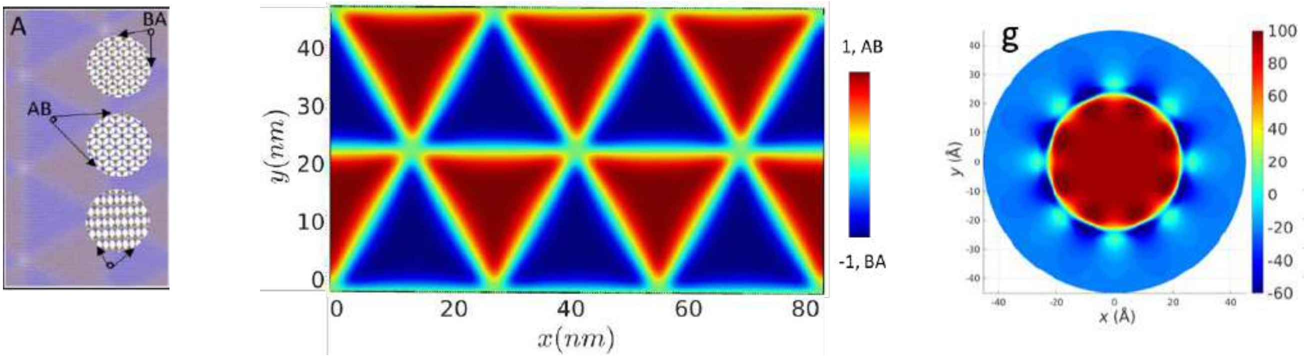


Figure 1: Polarization patterns in low-dimensional systems. Left: Surface reconstruction patterns in a marginally twisted *h*-BN bilayer. Middle: Local polarization registry index patterns in a marginally twisted *h*-BN bilayer.[2] Right: electrostatic potential difference map (in meV) calculated at the (001) cross section of a (55,0)@(63,0) double-walled boron nitride zigzag nanotube.[5]

References:

1. M. Vizner Stern, Y. Waschitz, W. Cao, I. Nevo, K. Watanabe, T. Taniguchi, E. Sela, M. Urbakh, O. Hod, and M. Ben Shalom, "Interfacial Ferroelectricity by van der Waals Sliding", *Science* **2021**, *372*, 1462-1466.

2. W. Cao, O. Hod, and M. Urbakh, "Interlayer Registry Dictates Interfacial 2D Material Ferroelectricity", *ACS Appl. Mater. Interfaces* **2022** *14*, 57492-57499.

3. S. Deb, W. Cao, N. Raab, K. Watanabe, T. Taniguchi, M. Goldstein, L. Kronik, M. Urbakh, O. Hod, M. Ben Shalom, "Cumulative Polarization in Conductive Interfacial Ferroelectrics", *Nature* **2022**, *612*, 465-469.

4. W. Cao, S. Deb, M. Vizner Stern, N. Raab, M. Urbakh, O. Hod, L. Kronik, M. Ben Shalom, "Polarization Saturation in Multi-Layered Interfacial Ferroelectrics", submitted (2023).

5. S. Salleh Atri, W. Cao, B. Alon, N. Roy, M. Vizner Stern, V. Falko, M. Goldstein, L. Kronik, M. Urbakh, O. Hod, M. Ben Shalom, "Spontaneous Electric Polarization in Graphene Polytypes", *Adv. Phys. Res.* **2024**, 2300095 (1-6).

6. W. Cao, M. Urbakh, and O. Hod, “Nanotube Slidetronics”, *J. Phys. Chem. Lett.* **2024**, *15*, 9–14.

Understanding optical properties of biogenic and bio-inspired molecular crystals: a first principles perspective

Leeor Kronik[a]

[a] *Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovoth, Israel*

E-mail: leeor.kronik@weizmann.ac.il

Molecular crystals are crystalline solids composed of molecules bound together by relatively weak intermolecul nteractions, typically consisting of van der Waals interactions and/or hydrogen bonds. These crystals play an importa role in many areas of science and engineering, ranging from biology and medicine to electronics and photovoltaic Therefore, much effort has been dedicated to understanding their structure and properties.

Here, I focus on our recent progress in explaining and even predicting optical properties in biogenic and bio-inspire molecular crystals based on first principles electronic structure calculations. I will examine structure-function relation as well as implications for biology and for bio-inspired optical materials. Throughout, I will highlight the insights gaine from a successful interaction between theory and experiment – particularly with the experimental groups of Adda Weiner, Leiserowitz, and Oron (Weizmann Institute), Gazit (Tel Aviv University), and Harris (U Cardiff).

The correlation between the gating mechanism of the human copper transporter, Ctr1, and the development of innovative biomarkers

Sharon Ruthstein

The Chemistry Department and the Institute of Nanotechnology and Advanced Materials, Faculty of Exact Sciences, Bar Ilan University, Israel.
E-mail: Sharon.ruthstein@biu.ac.il

ı the last couple of years, my lab has been exploring the cellular copper cycle in eukaryotic and prokaryotic systems sing various biophysical and biochemical methods. Dysfunction of the copper regulation system can lead to eurological diseases, cancer, and cell death, it is essential to understand every little detail in the copper cycle to be ble to control it according to specific needs.

:tr1 is a high affinity copper transporter, is a homotrimer integral membrane protein that provides the main route for ellular copper uptake. Together with a sophisticated copper transport system, Ctr1 regulates Cu(I) metabolism in ukaryotes. Despite its pivotal role in normal cell function, the molecular mechanism of copper uptake and transport ia Ctr1 remains elusive. Using electron paramagnetic resonance (EPR), UV-visible spectroscopy, and all-atom imulations, we resolved the Cu(II) and Cu(I) binding sites to full-length human Ctr1 (hCtr1), and elucidated how metal inding at multiple distinct sites affects the hCtr1 conformational dynamics [1-3]. The molecular level knowledge gained n this transporter, was then used to develop a novel 64Cu(II)-based radiotracer for detection of hypoxic conditions in ımors. This radiotracer integrates into the cellular copper cycle and presents high affinity towards Ctr1, allowing active ptake by the cell. *In-vitro* as well as *in-vivo* PET-MRI imaging experiments on mice with breast cancer tumors showed igh tumor to muscle (T/M) ratio with clearly delineated tumor boundaries. As compared with the 64Cu-ATSM and 18F-DG tracers, our radiotracer offered a superior T/M ratio and could clearly report on the tumor state, indicating high ensitivity to hypoxic tissues. This study illustrates the importance of molecular level knowledge on the chemical and iological cellular mechanism for the development of the next generation of diagnostic and therapeutic compounds.

eferences:

] Hofmann, L., and Ruthstein, S. (2022) EPR Spectroscopy Provides New Insights into Complex Biological Reaction Mechanisms, *J Phys Chem B 126*, 7486-7494.
2] Janos, P., Aupic, J., Ruthstein, S., and Magistrato, A. (2022) The conformational plasticity of the selectivity filter methionines controls the in-cell Cu(I) uptake through the CTR1 transporter, *QRB Discov 3*, e3.
3] Walke, G., Aupic, J., Kashoua, H., Janos, P., Meron, S., Shenberger, Y., Qasem, Z., Gevorkyan-Airapetov, L., Magistrato, A., and Ruthstein, S. (2022) Dynamical interplay between the human high-affinity copper transporter hCtr1 and its cognate metal ion, *Biophys J 121*, 1194-1204.

FIT-PNAs as RNA sensors for Ovarian cancer diagnostics

Marah Daas[a], Sheethal Thomas Mannully[a], Tamar Perri[b], Reuven Reich[a], and Eylon Yavin*[a]

[a] *The Institute for Drug Research, The School of Pharmacy, The Hebrew University of Jerusalem, Hadassah Ein-Kerem, Jerusalem 9112002, Israel.*
[b] *Department of Gynecologic Oncology, Hadassah Medical Center, Hadassah Ein-Kerem, Jerusalem 9112002, Israel.*

E-mail: eylony@ekmd.huji.ac.il

The PNAs (peptide nucleic acid) are synthetic DNA analogs that have been used for therapeutic (antisense) and diagnostic purposes.[1] One diagnostic approach relies on the introduction of a cyanine dye replacing a natural base in the PNA sequence (FIT-PNA: forced intercalation-PNA). [2] Such a surrogate base, when introduced into FIT-PNA, fluoresces only upon FIT-PNA hybridization to the complementary target DNA/RNA.

Ovarian carcinoma is the fifth leading cause of cancer-related deaths among women and is typically diagnosed at a late stage of the disease.

Herein, we report the development of FIT-PNAs designed to detect an over-expressed long non-coding RNA in OC, namely, ANRIL (Antisense Non coding RNA in the INK4 locus). To improve the sensitivity of our probe[3] , we introduced a cyclopentane modified PNA monomer (cpPNA)[4] adjacent to our cyanine dye (BisQ) in the PNA sequence. Apart from lighting up in OC cell lines after simple incubation of the cpFIT-PNA probes, we show that spraying omentum tissue (the site for OC metastisis) taken from OC patinets with our RNA probes results in a flourescent signal within minutes. These findings upon a new pardigm for cancer diagnostics that may be translated to the clinic.

Acknowledgements: We thank the Len & Susan Mark Initiative for Ovarian and Uterine/MMMT Cancers - Phase III grant from the Israel Cancer Research Fund (grant No. 21-305-MI) for financial support.

References:

1. Egholm, M.; Buchardt, O.; Christensen, L.; Behrens, C.; Freier, S. M.; Driver, D. A.; Berg, R. H.; Kim, S. K.; Norden, B.; Nielsen, P. E., PNA hybridizes to complementary oligonucleotides obeying the Watson-Crick hydrogen-bonding rules. *Nature* **1993,** *365* (6446), 566-8.
2. Bethge, L.; Jarikote, D. V.; Seitz, O., New cyanine dyes as base surrogates in PNA: Forced intercalation probes (FIT-probes) for homogeneous SNP detection. *Bioorganic & Medicinal Chemistry* **2008,** *16* (1), 114-125.
3. Tepper, O.; Zheng, H. C.; Appella, D. H.; Yavin, E., Cyclopentane FIT-PNAs: bright RNA sensors. *Chem. Commun.* **2021,** *57* (4), 540-543; **2023**, 59, 11593-11593.
4. Pokorski, J. K.; Witschi, M. A.; Purnell, B. L.; Appella, D. H., (S,S)-trans-cyclopentane-constrained peptide nucleic acids. a general backbone modification that improves binding affinity and sequence specificity. *J Am Chem Soc* **2004,** *126* (46), 15067-15073.

Redox-Active 3rd-Transition Metal Catalysts for Dehydrogenative C–H Bond Coupling

Doron Pappo

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
Email: pappod@bgu.ac.il

The metal-catalyzed dehydrogenative coupling is a powerful reaction for preparing new C–C or C–X (X = N or O) bonds from strong C–H bonds, while reducing O2 or ROOR to two ROH molecules. The process includes a key coupling step of highly reactive radical species; therefore, controlling the regio-, chemo-, and stereo-selectivity for designated transformations presents a significant challenge. In this talk, I will present our group's approach to enabling precise control over selectivity based on a mechanistically driven catalyst design that has led to the development of redox-active iron[1-5] and cobalt[6] complexes and copper[7] clusters, each facilitating dehydrogenative coupling reactions with unique selectivity.

Selected references:

(1) Dyadyuk, A.; Vershinin, V.; Shalit, H.; Shalev, H.; More, N. Y.; Pappo, D. A Chiral Iron Disulfonate Catalyst for the Enantioselective Synthesis of 2-Amino-2′-hydroxy-1,1′-binaphthyls (NOBINs). *J. Am. Chem. Soc.* **2022**, *144* (8), 3676-3684.
(2) Ben-Lulu, M.; Gaster, E.; Libman, A.; Pappo, D. Synthesis of Biaryl-Bridged Cyclic Peptides via Catalytic Oxidative Cross-Coupling Reactions. *Angew. Chem. Int. Ed.* **2020**, *59*, 4835-4839.
(3) Shalit, H.; Libman, A.; Pappo, D. meso-Tetraphenylporphyrin Iron Chloride Catalyzed Selective Oxidative Cross-Coupling of Phenols. *J. Am. Chem. Soc.* **2017**, *139* (38), 13404-13413.
(4) Narute, S.; Parnes, R.; Toste, F. D.; Pappo, D. Enantioselective Oxidative Homocoupling and Cross-Coupling of 2-Naphthols Catalyzed by Chiral Iron Phosphate Complexes. *J. Am. Chem. Soc.* **2016**, *138* (50), 16553-16560.
(5) Libman, A.; Shalit, H.; Vainer, Y.; Narute, S.; Kozuch, S.; Pappo, D. Synthetic and Predictive Approach to Unsymmetrical Biphenols by Iron-Catalyzed Chelated Radical-Anion Oxidative Coupling. *J. Am. Chem. Soc.* **2015**, *137* (35), 11453.
(6) Gaster, E.; Kozuch, S.; Pappo, D. Selective Aerobic Oxidation of Methylarenes to Benzaldehydes Catalyzed by N-Hydroxyphthalimide and Cobalt(II) Acetate in Hexafluoropropan-2-ol. *Angew. Chem. Int. Ed.* **2017**, *56* (21), 5912-5915.
(7) Libman, A.; Ben-Lulu, M.; Gaster, E.; Bera, R.; Shames, A. I.; Shaashua, O.; Vershinin, V.; Torubaev, Y.; Pappo, D. Multicopper Clusters Enable Oxidative Phenol Macrocyclization (OxPM) of Peptides. *J. Am. Chem. Soc.* **2023**, *145* (38), 21002-21011.

Membrane tension and membrane (hemi)fusion

Petr Shendrik[#1,3], Gonen Golani[#2], Raviv Dharan[1,3], Ulrich S. Schwarz[2] and Raya Sorkin[1,3*]

1 School of Chemistry, Raymond & Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, Israel.

2 Institute for Theoretical Physics and BioQuant Center for Quantitative Biology, Heidelberg University, Heidelberg, Germany.

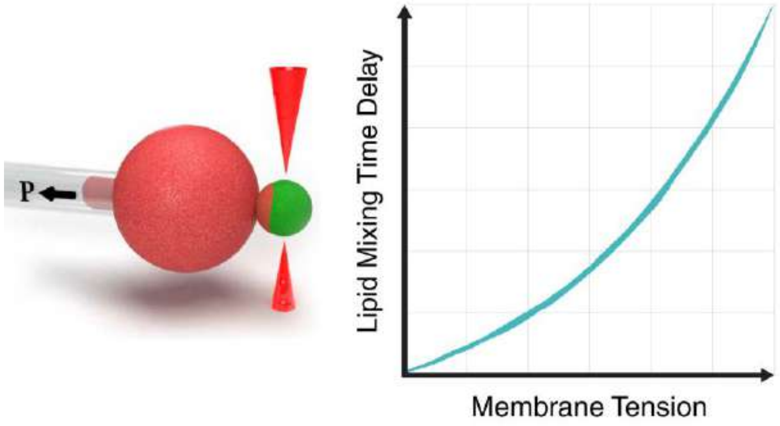
3 Center of Physics and Chemistry of Living Systems, Tel Aviv University, Tel Aviv, Israel.

**Corresponding author*

#These authors contributed equally

E-mail: (rsorkin@tuaex.tau.ac.il)

Fusion of biological membranes is fundamental in various physiological events. The fusion process involves several intermediate stages, with energy barriers that are tightly dependent on the mechanical and physical properties of the system, one of which is membrane tension. As previously established, the late fusion intermediates, including the hemifusion diaphragm and pore expansion, are enhanced by membrane tension. However, the current understanding of how the energy barrier of earlier fusion stages is affected by membrane tension is lacking. Here, we apply a newly developed experimental approach combining micropipette aspirated GUVs and optically trapped membrane-coated beads, revealing that membrane tension inhibits lipid mixing. We show that lipid mixing is 6 times slower under tension of 0.12 mN/m compared to tension-free membranes. Furthermore, using continuum elastic theory, we calculate the dependence of hemifusion stalk formation energy on the membrane tension and inter-membrane distance and find an increase in the corresponding energy barrier to be 1.5 kBT in our setting, which can explain the increase in lipid mixing time delay. Finally, we show that tension can be a significant factor in the stalk energy if the pre-fusion inter-membrane distance is in the order of several nanometers, while for membranes that are tightly docked, tension has a negligible effect.



Scheme or Figure 1: Membrane tension inhibits lipid mixing

Acknowledgements: We thank the ISF, NSF-BSF and ERC-StG for financial support.

References:

1. Membrane Tension Inhibits Lipid Mixing by Increasing the Hemifusion Stalk Energy Shendrik P., Golani G., Dharan R., Schwarz U. S., and Sorkin R., ACS Nano, 17, 19, 18942–18951, (2023)

Aromatic Materials – A Twisted Tale

Ori Gidron*

Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Edmond J. Safra Campus, 9190401 Jerusalem, Israel

E-mail: ori.gidron@mail.huji.ac.il

Twisting small aromatic molecules out of planarity can give rise to new electronic, optical and magnetic properties. One of the greatest challenges is to induce helicity to a π-conjugated backbone without disturbing the π-conjugation, with helicenes being the most well-known example of such systems. While helicenes became a common structural motif in polyaromatic systems, polymers and even metallacycles, their para-fused analogs, twisted acenes (twistacenes), are significantly less explored.

We have previously introduced the first helically-locked twistacenes, which are conformationally stable at different twisting angles depending on the tether length. This allowed us to systematically monitor the effect of twisting on electronic and chiroptical properties of acenes.[1] In this talk, I will present our recent progress in the inclusion of helically-locked twistacenes in π-conjugated materials, from helical π-conjugated polymers with tunable twist (Figure 1),[2] helitwistacenes and other aromatics.[3] The controllable twisting of these systems allowed us to formulate design principles for increasing the intensity of circularly polarized light absorption and emission. In addition, using twistacene monolayers, we provide evidence that the spin polarization is directly connected with the strength of their chiroptical properties.[4]

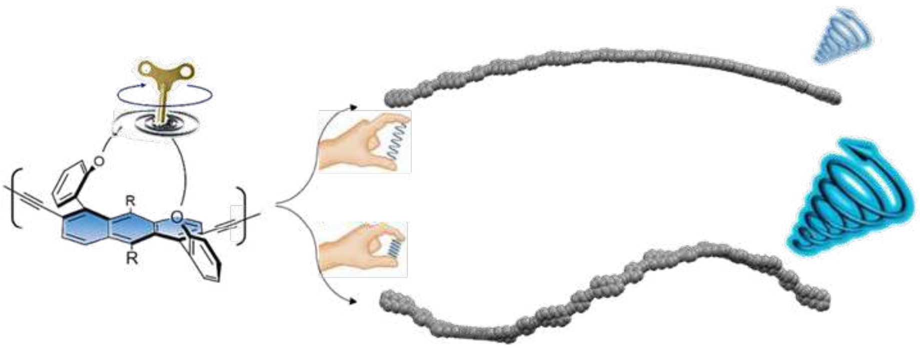


Figure 1: Tuning the chiroptical properties of acenes by controlling the degree of twisting.

References:

1. Bedi, A.; Gidron, O.* *Acc. Chem. Res.* **2019**, *52*, 2482.
2. Bedi, A.; Armon, A.; Diskin-Posner, Y.; Bogoslavsky, B.; Gidron, O.*, *Nat. Commun.* **2022**, *13*, 451.
3. Shioukhi, I.; Batchu, H.; Schwartz, G.; Minion, L.; Deree, Y.; Bogoslavsky, B.; Shimon, L.; Wade, J.; Hoffman, R.; Fuchter, M. J.; Markovich, G.; Gidron, O.* *Angew. Chem. Int. Ed.* **2024**, e202319318.
4. Metzger, S. T.; Batchu, H.; Kumar, A.; Fedotov, D.; Goren, N.; Bhowmick, D. K.; Shioukhi, I.; Yochelis, S.; Shapiro, I.; Naaman, R.*; Gidron, O.*; Paltiel, Y.* *J. Am. Chem. Soc.* **2023**, *145*, 3972.

From Gutenberg Bible to 4D printing

Shlomo Magdassi

The Hebrew University of Jerusalem, Institute of Chemistry, Jerusalem, Israel
Magdassi@mail.huji.ac.il

Abstract

Additive manufacturing , which is considered as the next industrial revolution, enables the fabrication of objects and devices through printing processes. It already has a great impact on a variety of fields, for example in the automotive, electronics, medical , food and aerospace industries. The lecture will focus on the development of new organic and ceramic materials for coatings, and for 2D, 3D and 4D printing, and their utilization in a variety of printing technologies. Recent progress in the general field of functional printing and applications will be presented, including : Conductive materials for printed electronics, stretchable materials for soft robotics , printed solar cells, 3D printing based on wood waste and recyclable polymers, new nanoparticles for printing in water, self-healing materials and bioprinting.

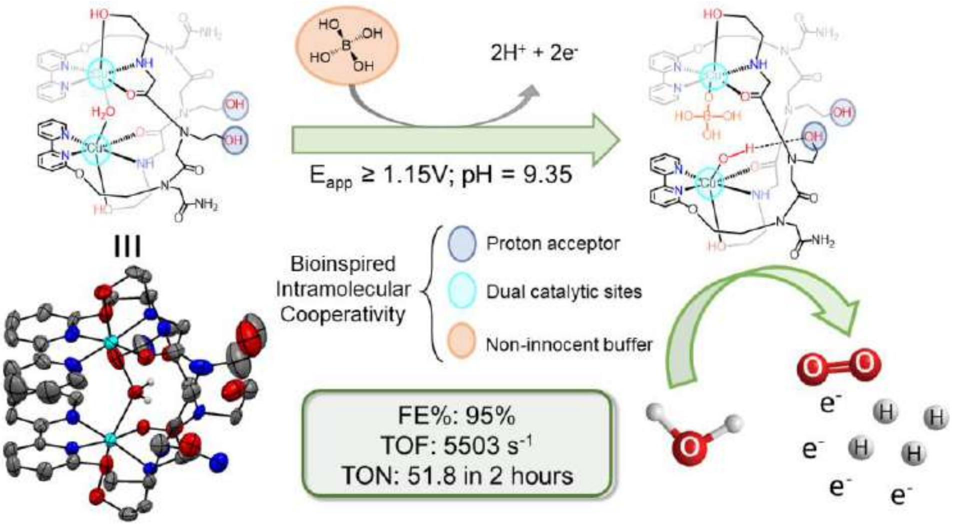
Bio-inspired electrocatalytic water oxidation

Galia Maayan*[a]

[a] Schulich Faculty of Chemistry, Technion- Israel Institute of Technology, Haifa, Israel, 32000

E-mail: gm92@technion.ac.il

Cooperative catalysis is a key to many successful transformations as it lays in the foundation of enzymatic activity. Enzymatic catalysis is largely based on cooperativity between a metal center and functional organic molecules located at its surrounding folds. This cooperativity leads to the creation of catalytic pockets, which enable enzymes' high specificity and efficiency. Inspired by this biological concept, we are developing molecules that aim to mimic enzymatic cooperativity. Thus, we use two different approaches for the design of intramolecular catalytic systems in which both the catalytic group(s) and the non-reacting components are tethered in close proximity to each other, aiming to address current challenges in the catalytic activation of small molecules. Our first approach is to mimic the structure of the oxygen evolving center, a manganese complex near photosystem II in plants and bacteria, within the context of its protein environment, aiming to mimic its function. In my talk I will present such complexes and demonstrate the role of the organic ligands, surrounding the metallic catalytic core, in the electrocatalytic water oxidation activity. Our second approach is to incorporate several functional side chains within peptoids, *N*-substituted glycine oligomers, for mimicking a second coordination sphere about embedded metal centers. Peptoids can be efficiently generated by a solid-phase method that enables the inclusion of innumerable functional groups at specified *N*-positions along their spine. Thus, they can be used as a tool for studying the cooperativity between catalytic groups placed on one scaffold. In my talk I will show how we utilized this approach for the construction of peptoids that catalyze oxidation transformation, specifically electrochemical water oxidation, with high turn-over-numbers *via* intramolecular cooperativity.



Acknowledgements: We thank the Israel Ministry of Energy and Grand Technion Energy Program for financial support.

References:

1. G. Maayan*, N. Gluz, G. Christou, *Nat. Catal.* **2018**, *1*, 48-54
2. T. Ghosh, G. Maayan, *Angew. Chem. Int. Ed.* **2019**, *58*, 2785–2790
3. N. Gluz, G. Christou and G. Maayan, *Chem. Eur. J.* **2021**, *27*, 6034–6043
4. N. Gluz, G. Ruan, G. Maayan, *Chem. Catal* **2024**, in press
5. T. Ghosh, P. Ghosh and G. Maayan, *ACS Catal.* **2018**, *8* (11) 10631-10640
6. Ruan, G. & Maayan G. *J. Am. Chem. Soc.* **2021**, *143* (28) 10614–10623

The Mechanisms of the Fenton and Fenton-Like Reactions

Dan Meyerstein

Chemical Sciences Department and the Radical Research Center, Ariel University, Ariel, Israel
and Chemistry Department, Ben-Gurion University, Beer-Sheva, Israel.
E-mail: danm@ariel.ac.il

The Fenton Reaction, $Fe(H_2O)_6^{2+} + H_2O_2$, and the Fenton Like Reactions, M^nL_k + ROOR', are of major importance due to their roles in biological systems, in advanced oxidation processes and in environmental processes. Recent results point out that the mechanisms of these reactions depend dramatically on the pH; the nature of the peroxide; the nature of the ligands L and on the nature of the central metal M. The source of these effects will be discussed. It is of importance to note that the intermediate oxidizing species formed differ in the different systems. In neutral solutions $OH^\cdot$ radicals are not formed in most systems studied.

Mitigating Electrode Material Degradation through Advanced Surface Modification Techniques

Malachi Noked
Chemistry department, Bar Ilan Institute for Nanotechnology and Advanced Materials(BINA), Bar Ilan University, Israel

E-mail: *Malachi.Noked@biu.ac.il*

Powering the vast majority of today's portable devices, batteries have propelled electronics into a transformative era of mobile energy, profoundly impacting our daily lives. Yet, the relentless quest for energy storage devices with enhanced performance poses a formidable challenge to the scientific community. This drive pushes researchers to explore novel chemistries and morphologies of electrode materials (EM), aiming to surpass current technology. The goal is to engineer electrochemical storage devices with superior energy density, enhanced power performance, and markedly prolonged stability..

Understanding fundamental degradation mechanisms of EMs, and their mitigation strategies, are challenged by constraints of the liquid electrolyte environment and the complexity of electrode/electrolyte interphase formation, namely the solid electrolyte interphase (SEI) layer which forms, grows, and changes (on the electrode interface) with battery usage. Accordingly, the research community is increasingly seeking new pathways to understand and control battery degradation, including new diagnostic and characterization methods as well as mitigation strategies (e.g., electrode surface treatments, electrolyte additives and artificial SEI layers).

In my talk I will demonstrate how surface modification of EMs, significantly suppress the degradation of the battery components (e.g. electrodes, and electrolyte) and facilitates long-term stability of the electrochemical device.
I will demonstrate how in our lab, we modify the surface of the EMs by either thin protection layer applied on its interface (using atomic/molecular layer deposition- M/ALD), or by surface reduction of high voltage cathode materials. I will farther show how we monitor *In-Operando* the degradation of the electrode\electrolyte interface using online electrochemical mass spectroscopy (OEMS), and will demonstrate the efficacy of our coating strategy in suppressing the degradation pathway of the EMs.

Porous Materials: The Next Frontier in Energy Research

David Eisenberg*[a]

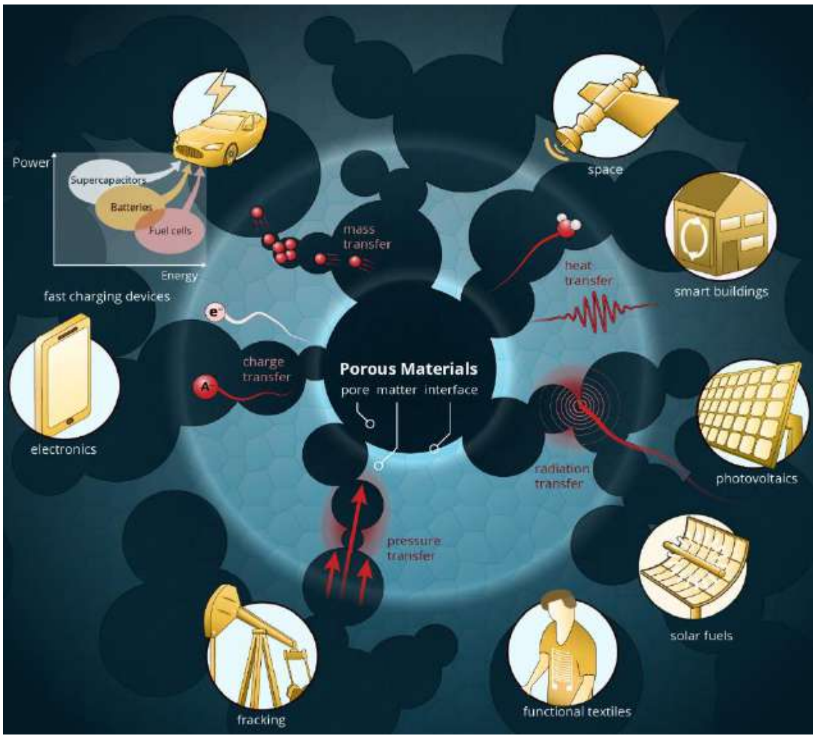
[a] *Schulich Faculty of Chemistry, the Grand Technion Energy Program, and the Resnick Sustainability Center for Catalysis, Technion–Israel Institute of Technology, Haifa 3200003, Israel*

E-mail: eisenberg@technion.ac.il

Porous materials are vital for society, playing an essential role in energy storage and conversion processes in solar, nuclear, electrochemical, thermal, and sub-surface energy sources and devices. A porous material consists of two phases, void and matter, which can conduct energy streams through the transfer of mass, charge, heat, radiation, and pressure. The high-area interface between these phases allows for these energy streams to meet and interconvert. As the number of pore design strategies grows, bringing about performance breakthroughs across the energy landscape, there is a growing need for a deeper, cross-disciplinary understanding of the multiple transfer processes in porous materials.

For instance, in porous electrodes, the ability to tune simultaneously mass and charge transfer in is used for increasing the power output, or recharging rate, of electrochemical devices such as supercapacitors, fuel cells, batteries, and electrolyzers. In the field of heat storage, pore-embedded phase change materials are enhanced by tuning pore sizes and apertures, improving heat conductivity without losing active matter. Tuning the porous structure of thermochemically reactive materials, used for storing high-temperature solar heat, enhances the simultaneous absorption of light, distribution of heat, and guides the reaction front evolution. In thermoelectric generators, pores are introduced to block phonon propagation, increasing the temperature difference needed for efficient energy conversion. In unconventional extraction of sub-surface energy, such as hydraulic fracturing of the soil for extracting oil, gas, or geothermal energy from low-porosity rock, the porosity evolves during operation, as it does in nuclear fuel pellets during fission reactions.

In this talk, we will take a bird’s view of the vital role of porosity across the landscape of energy technologies, establishing a paradigm of ‘energy streams’ to help bridge across disciplines and foster new research directions.



Lithium and sodium metal batteries

E. Peled

School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, Israel, 6997801

peled@tauex.tau.ac.il

Lithium and, more recently, sodium-ion high-energy batteries serve as primary power sources for energy storage and electric vehicles. These batteries typically consist of a graphite anode in the case of lithium and a hard carbon anode in the case of sodium, a non-aqueous electrolyte, and high-energy E intercalation compounds as cathodes (usually oxides of Ni, Co, and Mn, and LiFePO4). During the charging process, lithium or sodium intercalates into the anode structure, and during discharge, they deintercalate, migrate to the cathode, and intercalate there. One method to enhance the energy density of these batteries is to replace the carbon anode with lithium metal or sodium metal, resulting in post-Li-ion batteries known as lithium and sodium metal batteries (LMB, SMB, or MB). This substitution leads to weight, volume, and cost savings compared to using graphite or carbon electrodes. These metals have extremely high theoretical specific capacities (3860 and 1165 mAh g−1 for Li and Na, respectively), resulting in approximately 40% higher energy density compared to lithium or sodium-ion batteries. The electrolyte in these batteries can be composed of either liquid or solid materials. Another family of metal batteries with higher energy density is the anode-free metal batteries (AFMBs). In AFMBs, no lithium or sodium is present on the current collector of the anode; instead, all the metal cations remain in the cathode. In other words, these batteries are assembled in the discharge state, with the cathode fully lithiated or sodiated. During charging, lithium or sodium deintercalates from the cathode and plates onto the current collector. Another crucial point is that, in all kinds of lithium and sodium batteries, the anode is entirely covered by a solid electrolyte interphase (SEI), which acts as an electronic insulator and a metal cation conductor. The quality of the SEI determines the performance, safety, dendritic growth, and durability of the MBs. At present, LMBs exhibit better properties than SMBs. The coulombic efficiency during the deposition/stripping of sodium is much lower than that of lithium, and the sodium SEI impedance is much larger than that of lithium. Additionally, the cycle life of LMB is longer than that of SMB. Unfortunately, the present properties of MBs are not adequate for most practical applications.

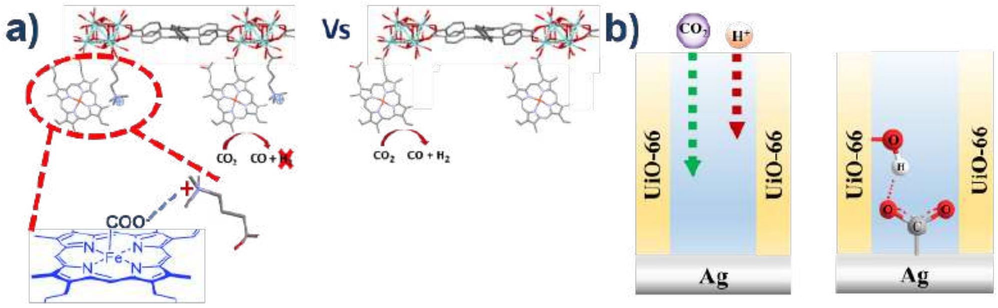
Molecular Manipulation of Heterogeneous Electrocatalysis Using Metal-Organic Frameworks

R. Shimoni,[1] A. Ghatak, [1] S. Shankar Golla, [1] S. Mukhopadhyay,[1] I. Liberman,[1] I. Hod*[1]

[1] Department of Chemistry at Ben-Gurion University of the Negev (BGU), Beer-Sheva, Israel

Electrocatalytically driven reactions that produce alternative fuels and chemicals are considered as a useful means to store renewable energy in the form of chemical bonds. in recent years there has been a significant increase in research efforts aiming to develop highly efficient electrocatalysts that are able to drive those reactions. Yet, despite having made significant progress in this field, there is still a need for developing new materials that could function both as active and selective electrocatalysts.

In that respect, Metal–Organic Frameworks (MOFs), are an emerging class of hybrid materials with immense potential in electrochemical catalysis. Yet, to reach a further leap in our understanding of electrocatalytic MOF-based systems, one also needs to consider the well-defined structure and chemical modularity of MOFs as another important virtue for efficient electrocatalysis, as it can be used to fine-tune the immediate chemical environment of the active site, and thus affect its overall catalytic performance. Our group utilizes Metal-Organic Frameworks (MOFs) based materials as a platform for imposing molecular approaches to control and manipulate heterogenous electrocatalytic systems. In this talk, I will present our recent study on electrocatalytic schemes involving MOFs, acting as: a) electroactive unit that incorporates molecular electrocatalysts, or b) non-electroactive MOF-based membranes coated on solid heterogenous catalysts.



References:

[1] Shimoni, R.; Zhuocheng Shi, Z.; Binyamin, S.; Yang, Y.; Liberman, I.; Ifraemov, R.; Mukhopadhyay, S.; Zhang, L.; Hod, I., Angewandte Chemie Int.Ed., 2022, 10.1002/anie.202206085.

[2] Mukhopadhyay, S.; Shimoni, R.; Liberman, I.; Ifraemov, R.; Rozenberg, I.; Hod, I., Angewandte Chemie Int.Ed., 2021, 60, 13423–13429.

[3] Liberman, I.S; Shimoni, R.S; Singh, C.P.PD; Hod, I., Journal of the American Chemical Society, 2020, 142 (4), 1933-1940.

[4] Shimoni, R.; He, W.; Liberman, I.; Hod, I., Journal of Physical Chemistry C, 2019, 123, 9, 5531-5539.

Factors Deciding the Selectivity of O_2, NO, CO_2 and SO_2 Reduction.

Abhishek Dey

School of Chemical Sciences, Indian Association for the Cultivation of Science, 2A Raja SC Mullick Road, West Bengal, India, 700032

E-mail: abbeyde@gmail.com

The talk will describe the intermediates involved in the multiple electron and multiple proton reduction of small molecules like O_2 , NO (NO_2^-), CO_2 and SO_2 . These intermediates are either observed in solution during stoichiometric reaction or in-operando using spectro-electrochemistry and characterized using a combination of spectroscopic techniques like EPR, Mossbauer, FTIR and resonance Raman spectroscopy. These transient intermediates are found to determine the selectivity of ne^-/nH^+ reduction of these small molecules which allows predictive design of catalysts for the purpose. While the reactions are very different,there seems to be certain commonalities in these reaction intermediates which can be taken advantage of when designing catalysts for selective reduction of these small molecules.

References

1. P. Saha, Sk Amanulla and A. Dey, Acc. Chem. Res., 2022, 55, 134–144

2. S. Chatterjee, K. Sengupta, B. Mondal, S. Dey and A. Dey Acc. Chem. Res. 2017, 50,

1744-1753.

3. P. Saha, S. Barman, Sk Amanulla and A. Dey ACS Catalysis, 2023, 13, 13181-13194

Posters

Contents

Bioinorganic Chemistry

Poster no. P_BC_01

A novel approach towards nitrile-substituted corrole: Versatile precursors for click chemistry and beyond

Azad Saini[a], Zeev Gross*[a]

[a] *Schulich Faculty of Chemistry, Technion- Israel Institute of Technology, Haifa 3200003, Israel.*
Email: *chr10zg@.technion.ac.il*

Corroles, i.e., contracted porphyrins, have gained substantial attention due to their unique electronic and photophysical properties, making them a suitable choice for catalysis and medical applications.[1,3,5] Upon systematically adjusting the electronic effects via substitution at *meso*- or *β*-positions on corrole macrocycle, the fine-tuning of fundamental properties (*absorbance, emission, redox potential, HOMO-LUMO gap etc.*) for the corresponding metal complexes can be achieved.[2] We now introduce a versatile precursor of the azide-nitrile click chemistry for potential chemical modifications. While there have been no previously reported examples of corroles with *meso*-C substituted nitriles, we now present a facile approach for the synthesis of 5,10,15--triscyanocorrole, (H_3-**1**). Hydrolysis of 5,10,15-tris(trifluoromethyl)corrole by an aqueous ammonia solution afforded H_3-**1**, due to a rare CF_3 to CN transformation. The free base corrole and several of its metal complexes were characterized by UV-Vis, IR, and NMR spectroscopy. This allows for investigating how the physical and chemical properties of corroles are affected by C_6F_5, CF_3, and CN substitution of the *meso*-C position.

The structure of the redox-active cobalt and photoactive phosphorus complexes **1**-$Co^{III}(py)_2$ and **1**-$P^V(OH)_2$, respectively, were determined by X-ray crystallography. Electrochemical characterization of **1**-$Co^{III}(py)_2$ with a strongly red shifted Soret band unveiled the reversible Co^{II}/Co^{I} couple at -1.1 V vs. Ag/AgCl, more facile by 460 mV and less facile by 320 mV as the *meso*-C substituent is varied from C_6F_5 to CN to CF_3. The photophysical property of **1**-$P^V(OH)_2$ was analyzed using fluorescence emission spectroscopy, with excitation at 423 nm, revealing a highly intense band at 598 nm. The quantum yields of H_3-**1** and **1**-$P^V(OH)_2$ were measured using tetraphenylporphyrin as a reference and were found to be 13% and 24% respectively.

References:

1. A. Mahammed, Z. Gross, *J. Am. Chem. Soc.* **2023**, 145, 23, 12429–12445
2. H. Lei, X. Li, J. Meng, H. Zheng, W. Zhang, R. Cao., *ACS Catal.* **2019**, 9, 5, 4320–4344
3. J. Y. Shin, S. H. Kim, S. Lee, Y. S. Lee, W. S. Han, K. Y. Wang, *Chem. Phys. Lett.* **2021**, 763, 138165
4. P. Yadav, S. Khoury, N. Fridman, V. K. Sharma, A. Kumar, M. Majdoub, A. Kumar, Y. Diskin-Posner, A. Mahammed, Z. Gross, *Angew. Chem. Int. Ed.* **2021**, *60*, 12829
5. R. D. Teo, J. Y. Hwang, J. Termini, Z. Gross, H.B. Gray, *Chem Rev.* **2017**,117, 4, 2711-2729

Poster no. P_BC_02

Designing Ligands for Guanine-Quadruplexes Using Hemopeptides

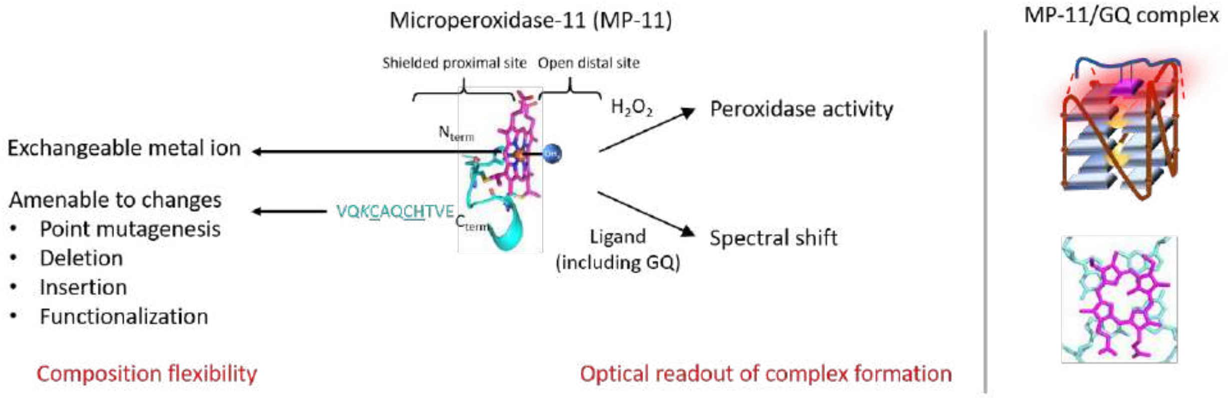
Leen Massalha, Nurit Adiram and Eyal Golub*

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

E-mail: Eyal.golub@biu.ac.il

Guanine quadruplexes are a large family of non-canonical secondary structures, which are globular guanine-rich secondary DNA or RNA structures that are a relatively common structural feature across eukaryotes, prokaryotes, and viruses. These structures are abundant in the human genome with more than 700,000 putative sites and are especially enriched at promoters, flanking the transcription start site, and at the 5`-end of the first intron. Indeed, GQs have been reported to regulate various cellular processes and their formation in cells have been associated with multiple diseases and syndromes. Accordingly, designing ligands for specific GQ sequences is important to allow us to study the effect of the different sequences independently and understand their role.

While various ligands have been developed in the past, they are often tightly binding but lack in specificity. This is due to the fact that they mostly target the two large aromatic surfaces at the edges of GQs that are common to all GQ sequences. Herein we present the repurposing of a semi-natural hemopeptide, i.e., microperoixdase-11 (MP-11), as a versatile ligand for GQs. MP-11 is the product of the cytochrome-c proteolytic digestion, comprised of a short 11-mer peptide chain that is covalently tethered to a heme group. Similarly to the parent heme molecule, MP-11 exhibits a clear preference towards GQs over dsDNA where, specifically, a topological selectivity towards parallel GQs is observed with increased affinities as compared to the bare heme. Importantly, the modular nature of MP-11 offers a versatile platform for ligand design. As the metallopeptide can be recombinantly expressed in cells, the peptide chain can be subjected to pronounced mutagenesis with the heme moiety serving as a GQ-specific anchor. Thus, the sequence of the peptide chain can be varied without jeopardizing the inherent affinity of the ligand towards GQs, allowing us to explore various peptide-heme constructs for selective GQ binding. Moreover, the affinity of the porphyrin can also be attenuated as the heme-bound iron can be replaced with other metal ions. Accordingly, MP-11 represents a promising model for the systematic design of GQ ligands.



Scheme or Figure 1: Versatility of MP-11 as a ligand for guanine quadruplexes.

Poster no. P_BC_03

Biomolecules-Functionalized TiIV -Phenolato Complexes as Potential Anticancer Drugs

Karin Pichhadze and Edit Y. Tshuva*

The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel

E-mail: Edit.tshuva@mail.huji.ac.il

The disruption of normal cell growth lies at the core of cancer development, which encompasses nearly 100 different types and remains a prominent cause of mortality. Cisplatin, a prominent and potent chemotherapy treatment, exhibits significant toxicity, and potentially indues resistance in cancer cells. Consequently, the search for alternative metal-based drugs has arisen, with titanium(IV) emerging as an attractive candidate owing to its bio-compatibility and activity against cisplatin-resistant cancer cells. Titanium(IV) complexes, including titanocene dichloride and budotitane, showcased potent anticancer activity across various cell lines with reduced side effects, entering clinical trials as pioneering non-platinum metal complexes. However, their clinical progress was curtailed mainly due to hydrolysis susceptibility. To counter this, our group employed bis(phenolato) ligands, stabilizing Ti(IV) compounds. The first generation comprised diaminobis(phenolato)-salan ligand-based complexes with labile isopropoxo ligands, bolstering complex stability through the chelate effect. This was followed by a second generation featuring diaminobis(phenolato)-bis(alkoxo) ligands devoid of labile counterparts, thereby further enhancing the stability.

Herein we will describe our endeavors to synthesize anti-cancer titanium(IV) complexes that have been functionalized with biomolecules, such as dopamine, cannabinoids and steroids. These modifications aim to enhance tumor targeting and delivery capabilities, while also elaborating on the therapeutic effects of titanium compounds alone. Striving toward this objective, meticulous multi-step synthesis methods were methodically developed, demonstrating promising results for both dopamine and sex steroids. Additionally, the conducted cytotoxicity evaluations toward human ovarian A2780 cell line on the obtained ligands and complexes, have showcased notable anti-tumor potential.

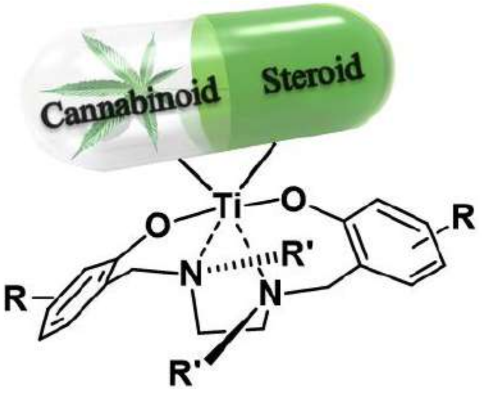


Figure 1. Illustration of the desired Ti(IV)-Salan complexes functionalized with cannabinoids or steroids biomolecules.

Acknowledgements: We thank the Israel Innovation Authority for financial support.

Poster no. P_BC_04

Ti(IV) Phenolato Hexacoordinate Complexes as Anticancer Chemotherapy: Functionality Toward ER, Folate and HER2 Targeting

Mohammad Taha and Edit Y. Tshuva*

The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel

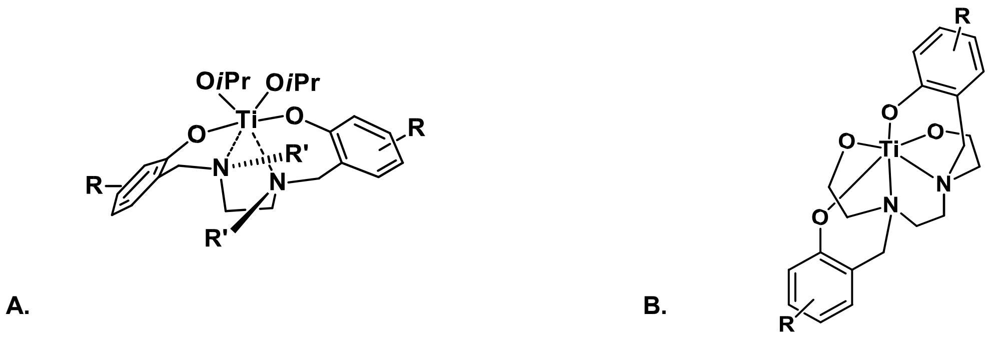
E-mail: Edit.tshuva@mail.huji.ac.il

Cisplatin is the first metal-based anticancer drug. It is effective, but suffers from two limitations: (a) it is toxic, which is a common feature of many chemotherapies; and (b) it is not widely active because some cancer cells can develop resistance to the treatment, limiting the potential use. Titanium is a good alternative to platina because, although titanium is not considered an essential metal for the human body, it has biocompatible features. Nevertheless, the low stability of titanium complexes reported previously in water limited their potential use in anticancer therapy.

In our group we aim to develop titanium-based complexes of enhanced stability and potency in anticancer therapy. The first family of compounds that we have analyzed is based on a tetradentate diaminobis-phenolato ligand system (scheme 1.A). Complexes of this family were more stable that previous compounds but decomposed within several hours in water. In an attempt to further enhance the stability of titanium(IV) complexes in aqueous media, we employed a single hexadentate diaminobis-phenolato-bis-alkoxo ligand to give singly ligated complexes (scheme 1.B). Complexes of this type are highly stable and highly cytotoxic, but lack suficient water solubility.

PhenolaTi, a leading complex of this family (m,p –methyl substituted) demonstrated significant activity toward all cell lines tested in the NCI-60 panel of the NIH. In particular. Colon, lung, and ovarian human cancer cells were identified as most sensitive for phenolaTi. In vitro studies of these complexes in presence of endoplasmic reticulum (ER) stress inhibitor, and upregulation of genes associated with the function of ER, suggested that the cytotoxic activity of phenolaTi involves ER stress; Nevertheless, knowledge of their exact mechanism of activity is still lacking.

Herein we present: (1) the synthesis of complexes of enhanced solubility; and (2) our studies of their spectrum of activity through targeting to common receptors for colon, lung, and ovarian human cancer cells, and to the ER, suspected as a target, for mechanistic analysis.



Scheme 1. A. tetradentate diaminobis-phenolato ligand based complexes, B. Single hexadentate diaminobis-phenolato-bis-alkoxo ligand based complexes.

Acknowledgements: We thank the Israel Innovation Authority for financial support.

References:

1. Taha, Mohammad, and Edit Y. Tshuva. "Phenolato Ti (iv) hexacoordinate complexes for anticancer chemotherapy: enhancement of solubility, hydrolytic stability, and cytotoxicity." *Dalton Transactions* (2023).

Poster no. P_BC_05

Chemical Engineering of Artificial Transcription Factors Using an Orthogonal Palladium(II) Strategy

Xiaoxi Lin[1], Omer Harel[1], and Muhammad Jbara[1]*

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv,
69978 Israel
*Correspondence to: jbaram@tauex.tau.ac.il

Site-selective functionalization strategies are in high demand to prepare well-defined homogeneous proteins for basic research and biomedical applications.[1] In this regard, cysteine-based reactions have enabled a broad set of transformations to produce modified proteins for various applications.[2] However, these approaches were mainly employed to modify a single reactive site with a specific transformation. Achieving site-selectivity or multiple transformations, essential for preparing complex biomolecules, remains challenging. Here we demonstrate the power of combining palladium(II)-mediated C-S bond formation and C-S bond cleavage reactions to selectively edit desired cysteine sites in complex and uniquely modified proteins.[3] We developed an orthogonal palladium(II) strategy for rapid and effective diversification of multiple cysteine sites, e.g., 3-6 residues with various transformations. Importantly, we employed our approach to prepare 10 complex analogs, including modified, stapled, and multimeric proteins on a milligram scale. Furthermore, we also synthesized a focused library of stabilized artificial transcription factors that displayed enhanced stability and potent DNA binding activity. Our approach enables rapid and effective protein editing and opens new avenues to engineer new biomolecules for fundamental research and therapeutic applications.

[1] O. Harel and M. Jbara. Chemical Synthesis of Bioactive Proteins. *Angew. Chem., Int. Ed.*, **2023**, 62.

[2] O. Harel and M. Jbara. Posttranslational Chemical Mutagenesis Methods to Insert Posttranslational Modifications into Recombinant Proteins. *Molecules*. **2022**, 27(14):4389.

[3] X. Lin, R.V. Nithun, O. Harel and M. Jbara. Enabling Peptide Ligation at Mimics of Aromatic Junctions via Native Chemical Ligation and Palladium-Mediated S-Arylation. *Org. Lett.*, **2023**, 25, 4715–4719.

Poster no. P_BC_06

Copper Mediated Site-selective Cysteine and Selenocysteine bioconjugation for Peptides and Proteins

Jian Huang, Yao Cai, Zhenguang Zhao, and Norman Metanis*

Institute of Chemistry, The Hebrew University of Jerusalem, Safra Campus, Givat Ram, Jerusalem, Israel 91940

E-mail: (jian.huang@mail.huji.ac.il, yao.cai@mail.huji.ac.il, zhenguang.zhao@mail.huji.ac.il, metanis@mail.huji.ac.il)

Protein post-translational modifications (PTMs) play a prominent role in expanding proteins function and enable the precise modification of proteins with a diverse range of functional moieties. Nevertheless, synthesizing covalent conjugates of a peptide or protein and a complex small molecule is often challenging with the available chemical tools. However, such conjugates may have clinical value as they can direct small-molecule toxins to certain tissues, widen therapeutic windows and tune pharmacokinetic and pharmacodynamic properties often beyond the capabilities of each component alone. Based on previous research from our lab and peer publications, we propose a peptides and proteins modification method to achieve regio- and chemoselective chemical modifications with the assistance of copper catalysis in aqueous solutions and under ambient conditions to achieve late-stage functionalization of cysteine and/or selenocysteine residue containig peptides and proteins.

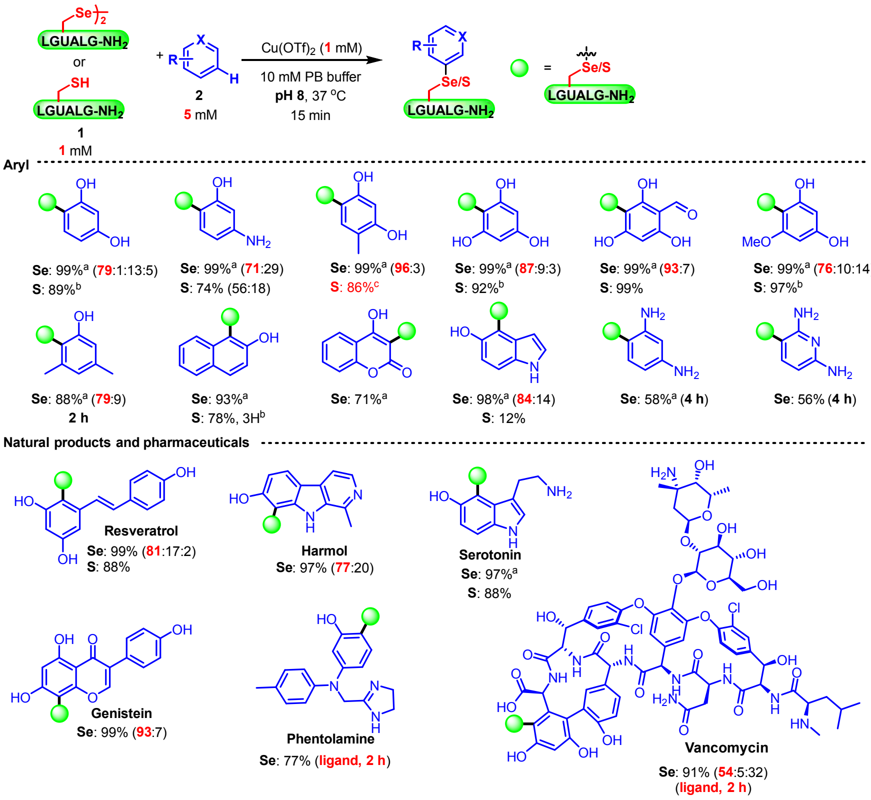


Figure 1: The substrate scope of compounds for the modification of Sec and Cys with model peptide

Acknowledgements: We thank the CSC for financial support....

References:

1. Cohen, D. T. et al. A chemoselective strategy for late-stage functionalization of complex small molecules with polypeptides and proteins. Nat Chem 11, 78-85 (**2019**). https://doi.org/10.1038/s41557-018-0154-0.

2. Zhao, Z., Shimon, D. & Metanis, N. Chemoselective Copper-Mediated Modification of Selenocysteines in Peptides and Proteins. J Am Chem Soc 143, 12817-12824 (2021). https://doi.org/10.1021/jacs.1c06101.

Bridging Chemistry and Biology

Poster no. P_BCB_01

Zirconium-Coated β-Cyclodextrin Nanomaterial for efficient Biofilm Eradication

Akanksha Gupta[1,2], , John H. T. Luong[3], Aharon Gedanken[1,2*]

[1]*Department of Chemistry, Faculty of Exact Sciences, Bar-Ilan University, Ramat-Gan, 5290002, Israel*

[2]*Bar-Ilan Institute for Nanotechnology and Advanced Materials (BINA), Bar-Ilan University, Ramat-Gan, 5290002, Israel*

[3]*School of Chemistry, University College Cork, Cork T12 YN60, Ireland*

* Corresponding author: gedanken@mail.biu.ac.il, Fax: +972-3-7384053; Tel: +972-3-5318315

Abstract

Beta-cyclodextrin (βCD), a cyclic oligosaccharide, served as a scaffold for the synthesis of a new class of antimicrobial and anti-biofilm agents. Under alkaline treatment, zirconyl chloride ($ZrOCl_2.8H_2O$) became a zirconia gel and formed a stable complex with βCD, referred to as Zr- βCD. The Zr- βCD complex was highly active in ROS (reactive oxygen species) formation via H_2O_2 decomposition and its surface with numerous hydroxyl groups played a role of an ionic sponge to capture the charged reaction intermediates including superoxide ($O_2^{-\bullet}$) and hydroxyl radical ($^{\bullet}OH$). The reactive oxygen species, especially $^{\bullet}OH$ radicals, are harmful to living microorganisms because of their kinetic instability, high oxidation potential, and chemical non-selectivity. Therefore, $^{\bullet}OH$ radicals can engage in fast reactions with virtually any adjacent biomolecules. In the presence of hydrogen peroxide, the Zr- βCD complex with cationic and hydrophobic moieties interacted with the anionic bacterial membrane of four common pathogens: two gram-positive (*Staphylococcus aureus* and *S. epidermidis*) and two gram-negative (*Escherichia coli* and *Klebsiella pneumoniae*). The Zr-βCD-H_2O_2 also eradicated more than 99% of the biofilm of these four pathogens. Since the acquisition of resistance to the oxidation of $^{\bullet}OH$ is difficult, the results suggest that this βCD-based nanomaterial may be a promising agent to target both drug-resistant Gram-positive and Gram-negative bacteria. With no cytotoxicity and exceptional antimicrobial activity, this material should be considered an appropriate antibacterial and antimicrobial agent for mature biofilm eradication.

Poster no. P_BCB_02

Bi-functional and molecular glue degraders of the oncogenic

Aseel Kashkush, Raphael I. Benhamou

The Institute for Drug Research of the School of Pharmacy, Faculty of Medicine, The Hebrew University of Jerusalem, Jerusalem, Israel

E-mail:Aseel.kashkush@mail.huji.ac.il

Abstract

The interaction between proteins and RNA is essential for regulating multiple steps of gene expression. This interaction of RNA-binding proteins with RNAs can vary under different cellular conditions, and such variability may be associated with various diseases, including cancer. The highly conserved RNA-binding protein (RBP) Lin28, known for its interaction with and suppression of the tumor suppressor miRNA let-7, has emerged as a significant oncogenic factor, driving tumor progression and metastasis across various cancer types. In this study, we employed a small molecule capable of binding to Lin28, thereby preventing its inhibition of let-7 activity. To enhance the efficacy of this molecule, we utilized two approaches: the Proteolysis Targeting Chimera (ProTaC) and molecular glue methods. Through these techniques, we developed a series of bifunctional molecules and molecular glues capable of degrading Lin28 in cells. These novel degraders, exhibiting high pharmacological properties, were evaluated in ovarian and placental cancers, which are known for their elevated levels of Lin28a directly associated with their oncogenic properties. Encouragingly, our designed molecules effectively mitigated Lin28-associated disease characteristics. This innovative strategy, combining molecular glue and ProTaC technology for the targeted degradation of RBPs, holds promise in opening new avenues for modulating RNA and addressing associated diseases with small molecules.

Poster no. P_BCB_03

Morphogenesis of biological crystals

Assaf Gal *[a]

[a]*Dept. of Plant and Environmental Sciences, Weizmann Institute of Science, Rehovot, ISRAEL.*

E-mail: assaf.gal@weizmann.ac.il

Directing crystal growth into complex morphologies is challenging, as crystals tend to adopt thermodynamically stable morphologies. Yet, many organisms form crystals with intricate morphologies that are under strict biological control. In our work, we study unicellular organisms that precipitate exquisite calcium carbonate crystals within specialized organelles (Fig. 1). Using state-of-the-art electron tomography, we investigate the native-state environment in which the crystals grow and the various stages of their development in 3D. We find that biological control over crystal growth is rooted in tight control over the chemical environment close to the forming crystal. When crystals grow in a solution-like environment they have simple habits. On the other hand, confined cellular volumes can drive crystal growth into a transport-limited regime where highly anisotropic shapes prevail. These findings suggest that a pivotal controller of biological crystallization is the confined crystallization volume, which gives rise to localized growth kinetics that yield complex crystalline morphologies.

Fig. 1: The delicate calcium carbonate crystals that encase the cell of a marine organism.

References:

[1] Kadan, Y.; Tollervey, F.; Varsano, N.; Mahamid, J.; Gal, A. Intracellular nanoscale architecture as a master regulator of calcium carbonate crystallization in marine microalgae, Proc. Natl. Acad. Sci. USA 2021, e2025670118.

[2] Avrahami, E. M.; Houben, L.; Aram, L.; Gal, A. Complex Morphologies of Biogenic Crystals Emerge from Anisotropic Growth of Symmetry-Related Facets. Science 2022, 376 (6590), 312–316.

[2] Ben-Joseph, O.; de Haan, D.; Rechav, K.; Shimoni, E.; Levin-Zaidman, S.; Langer, G.; Probert, I.; Wheeler, G. L.; Gal, A. Crystallization of Coccolith Calcite at Different Life-Cycle Phases Exhibits Distinct Degrees of Cellular Confinement. Small Struct. 2023, 2200353.

Poster no. P_BCB_04

Conformational analysis of toxins affinity and selectivity to K channel – NMR/MD study

C. Timsit-Shmueli, I. Sher, J. Chill, D. T. Major

Department of Chemistry, Bar-Ilan University, Ramat Gan

E-mail: chenshmueli14@gmail.com, jordan.chill@biu.ac.il, inbalasher87@gmail.com, dan-thomas.major@biu.ac.il,

Potassium (K+) channels are common ion channels among membrane proteins that form selective pores controlling a wide variety of cell functions. Toxins of the sea-anemone K+ channel (SAK-I) family, including ShK, AeTX-K, HmK, and Hui1, inhibit K+ channels by interacting with their pore regions in a specific manner. Here we combine experimental and computational methods to probe our hypothesis that bound conformations of toxins deviate from their free state structures, and that minor conformers contribute to channel specificity and affinity.

Using relaxation dispersion (RD) experiments, sensitive to *μ*s-ms motions typical of conformational equilibria, we establish the presence of a lowly-populated conformer in ShK and Hui1, while for HmK dispersion is not seen due to significantly faster exchange. We also conducted experiments under hydrostatic pressure (prNMR), in which Hui1 was most sensitive to pressure, with conformational changes appearing at the N-terminal turn and the two α-helices. This is an agreement with the change in binding mode observed for the D14Q mutant of HmK. In a complementary approach, by metadynamics-metainference simulation we generated a probability-weighted trajectory of ShK, Hui1 and HmK dynamics with sampling of low-probability structures. Focusing on disulfide isomerization, we found that the (-) χ3 conformer of 12-28 rota-isomers is preferred for the ShK and Hui1 toxins, compared to HmK where there is no preference. In addition, analysis of these trajectories reveals that exchange between rota-isomers is more facile for HmK, in agreement from RD experiments, and that this influences the positioning of helix-II of the toxin involved in channel binding. Thus, differences we are observing may explain the insertion of Arg24 or Lys22 into the channel pore by Hui1 and HmK, respectively. Extension of this treatment to the other toxins is underway for comparison between their conformational behaviors. We expect our synergistic NMR/MD approach to afford valuable information on the structural basis of toxin-channel interactions.

Acknowledgements:

We thank Drs. Adriaan Bax and Sai Chiliveri (NIDDK, NIH) for assistance with pressure NMR measurements, Drs. Keren Keinan-Adamsky, Hugo Gottlieb and Michal Afri for spectrometer maintenance support, and BSF grant 2017243 for funding this project.

References:

1.Sher, I. et al. Conformational flexibility in the binding surface of the potassium channel blocker ShK. ChemBioChem 15, (2014). 2.Löhr, T., Camilloni, C., Bonomi, M. & Vendruscolo, M. A Practical Guide to the Simultaneous Determination of Protein Structure and Dynamics Using Metainference. in Methods in Molecular Biology vol. 2022 (2019).

Poster no. P_BCB_05

A Bacterial Biofilm Polysaccharide Affects the Morphology and Structure of Calcium Oxalate Crystals

David N. Azulay,[a] Malachi Fraenkel,[a] and Liraz Chai*[a]

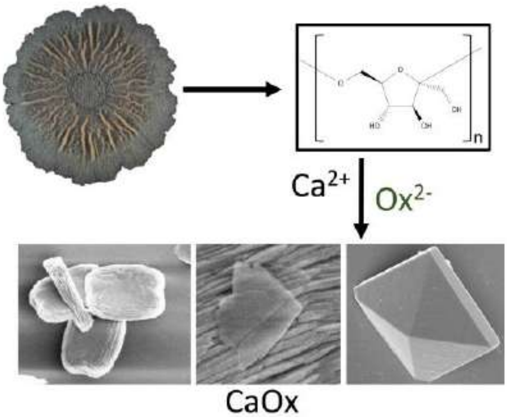
[a] Institute of Chemistry, The Hebrew University of Jerusalem and The Center for Nanoscience and Nanotechnology, Edmond J. Safra Campus, Jerusalem 91904, Israel

E-mail: liraz.chai@mail.huji.ac.il

Biomineralization describes the process of mineral precipitation from soluble precursors by living organisms. It is sometimes associated with single bacterial cells, for example, the formation of magnetosomes by magnetotactic bacteria, as well as with groups of bacterial cells that form biofilms and precipitate calcium carbonate ($CaCO_3$).

Recently, there has been growing evidence connecting isolated bacteria and bacterial biofilms with calcium oxalate (CaOx) formation in kidney stones. Therefore, in this study, we examined the effect of a principal exopolysaccharide bacterial biofilm component on the crystallization of CaOx. We observed that the exopolysaccharide, identified as levan, induced the formation of both octahedral CaOx dihydrate (COD, Weddellite) and pancake-like CaOx monohydrate crystals (COM, Whewellite) in a concentration-dependent manner. A combined analysis of the CaOx crystals that formed in the presence of levan, using scanning electron microscopy, Raman spectroscopy, and X-ray diffraction, indicated that levan affects both the nucleation and the growth of CaOx and that its interaction with CaOx is stereospecific.

Given the emerging relation between bacterial biofilms and kidney stones, which are prevalent within approximately 12% of the worldwide population, it is important to decipher the effect of biofilm extracellular polymers on the formation of CaOx crystals as it may assist in the development of future treatments to interfere with kidney stone formation.



Poster no. P_BCB_06

Towards NMR In-Cell Studies of WASp-Interacting Protein

Diana Egbaria, Inbal Sher, and Jordan Chill*

Department of Chemistry, Bar-Ilan University

E-mail: jordan.chill@biu.ac.il

We aim to investigate the complex interactions and regulatory mechanisms of Wiskott-Aldrich Syndrome Protein (WASp) and its important regulator, WASp-interacting protein (WIP), within the cellular environment. We wish to employ in-cell nuclear magnetic resonance (NMR) spectroscopy, offering a unique platform to explore the dynamic nature of intrinsically disordered proteins (IDPs) and their post-translational modifications (PTMs) in living cells. WIP is a 503-residue disordered 'hub' protein involved in multiple protein-protein interactions. In immune cells it mediates cytoskeletal processes by controlling actin remodeling and regulating the activity of WASp. Previously our investigations have focused on specific WIP interactions in a 'divide and conquer' approach, but it is clear that a comprehensive understanding of WIP biology on the molecular level requires its study in the native cellular environment. This is an outstanding challenge of structural biology today, particularly for NMR where signal is a limiting factor.

As an initial goal we have focused on preparing a deliverable WIP polypeptide that is isotopically labeled allowing in cell detection. Recombinant expression of WIP was previously unsucessful due to low yields and proteolytic degradation, and here we developed an improved protocol avoiding these issues (**Figure 1, left**). As a highly basic protein (pI over 11) WIP is difficult to handle and prone to non-specfic binding to resins and membranes, limiting our options throughout the purification process. We have succeeded in (i) producing a uniformly ^{15}N-labeled sample, confirmed by NMR to be soluble and amenable to cellular studies (**Figure 1, right**), and (ii) generating a fluorescently-labeled sample which will be needed for following the delivery of WIP into cells and its localization. Currently we are optimizing our isotopic labeling scheme for better targeting of the WASp-binding region of WIP, aiming for more selective ^{15}N and ^{19}F labeling options. Achieving these goals will be an important step towards studying the behavior of WIP in cells.

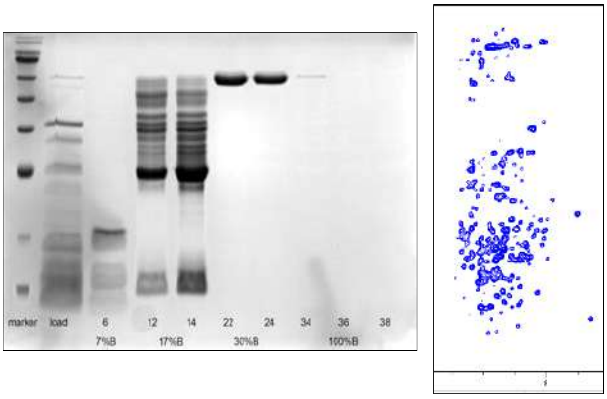


Figure 1: Left, SDS-PAGE analysis of the full-length WIP purification protocol, showing elution of >95% pure WIP (30% imidazole buffer off a Ni^{2+}-affinity column). **Right**, $^{1}H,^{15}N$-HSQC spectrum of 35 uM WIP in 20mM NaPi, 1mM DTT, pH 6.5, acquired at 278K for 4 hr.

Acknowledgements: We thank Ilana Kuzminski for her earlier work on WIP expression, Prof. Philipp Selenko (WIS) for guidance in preparation of in cell samples, Drs. Keren Keinan-Adamsky, Hugo Gottlieb and Michal Afri for spectrometer maintenance support, and the ISF (964/2019) for funding this project.

Poster no. P_BCB_07

Exploring Polymers and Small Molecules as Modulators of Molecular Crystals

Dolev Brenman-Begin[a], Zohar Eyal*[a], Rechael-Lynn Deis*[a], Anna-Eden Kossoy*[b], Iddo Pinkas*[b] and Dvir Gur*[a]

a Department of Molecular Genetics, Weizmann Institute of Science, Rehovot, Israel. b Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel.

E-mail: (dolev.brenman-begin@weizmann.ac.il)

In nature, organisms possess diverse types of organic and inorganic crystals with a broad spectrum of functionalities. These crystals undergo growth within specialized organelles. One of the most common organic materials used is the nucleobase guanine. The plate-like morphology of anhydrous guanine crystals is particularly intriguing due to its high anisotropic refractive index, in which the (100) crystallographic plane is constructed from H-bonded molecular layers which are stacked one on top of the other via π-π stacking interactions.

Prior work in our lab has revealed that biogenic guanine crystals in zebrafish do not follow the classical nucleation pathway; rather, they form via templated nucleation of multipole thin leaflets on top of an amyloid fiber, which serves as a template.[1] Furthermore, it has been shown that guanine crystals incorporate significant quantities of organic dopants, with hypoxanthine being the predominant component aside from guanine.[2] The influence of both amyloid fibers and organic dopants on the crystallization process, as well as their specific chemical interactions with the expanding crystals, remains to be elucidated.

In this study, we investigate the influence of polymers, serving as analogs of the amyloid fibers, and organic dopants, on the in-vitro formation of guanine crystals using a combination of spectroscopy and microscopy approaches. We show that the polarity of the side chains along the C-C polymer backbone affects the obtained crystal morphology. Specifically, we show that hydrophobic functional groups significantly decrease the growth rate along the π-π stacking direction, resulting in a plate-like morphology that mirrors the natural biogenic crystals. Furthermore, we show that an increase in the hypoxanthine levels results in crystals with broader width, more prominent (012) facets, and under-development of (010) facets (**Figure 1**). Considering that the expression of a crystallographic facet is inversely proportional to its growth rate, this suggests that hypoxanthine selectively hinders growth along the (012) plane.

These investigations can provide a deeper understanding of crystal formation mechanisms and the role of polymers and dopants on their properties. The knowledge gained from this research could lead to the development of novel techniques for controlling crystal morphology and properties, with potential applications in fields such as solid-state chemistry and materials science.

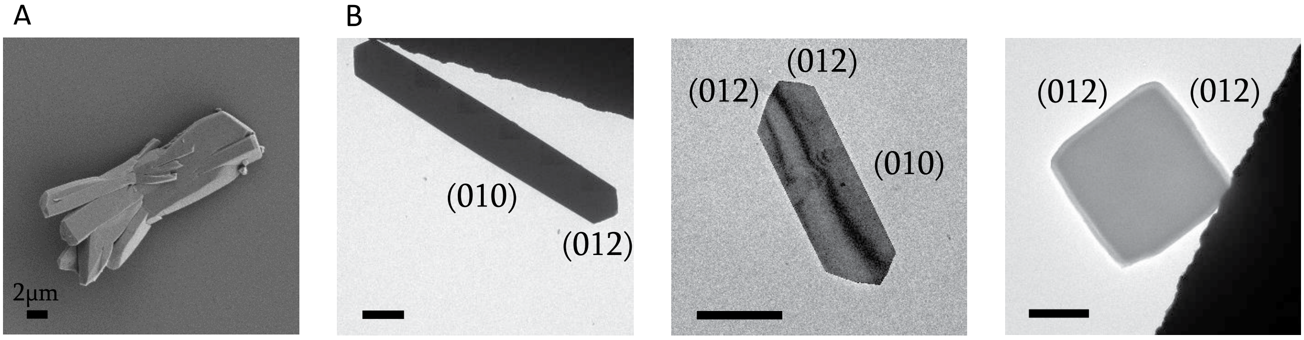


Figure 1. The effect of polymers and organic dopants on crystal morphology. A. A Scanning electron microscope image of pure guanine crystals, B. Transmission electron microscope images of guanine crystals formed with PVP-co-VA and increasing levels of hypoxanthine (left to right).

Poster no. P_BCB_08

Development of Fluorescent RIBOTACs to Investigate and Enhance Ribonuclease Recruitment

Elias Khaskia, Raphael I. Benhamou

The Hebrew University of Jerusalem, School of Pharmacy, Faculty of Medicine

E-mail: elias.khaskia@mail.huji.ac.il raphael.benhamou@mail.huji.ac.il

RNA-targeting small molecules have emerged as powerful tools for modulating gene expression with therapeutic potential in various diseases. Among them, RIBOTACs (ribonuclease-targeting chimeras) represent a promising class of molecules capable of selectively degrading RNAs by the recruitment of Ribonuclease (RNase). In this study, we report the development and application of novel fluorescent RIBOTACs for enhanced visualization and investigation of its RNase recruitment activity. This investigation sheds light on RNase L dynamics and its influence on RNA degradation pathways, facilitating the development of more effective degradation strategies. Additionally, leveraging the versatility of these conjugates, we explore applications such as real-time tracking of RIBOTAC localization, studying intracellular trafficking, and mechanisms of action. Moreover, the designed fluorescent probes are utilized for developing novel high-throughput fluorescence-based assays to identify small molecules that potentially bind and recruit RNase. Through this research, we aim to advance our understanding of protein-RNA biology and expedite the development of enhanced RNA-targeted degradation methods.

Poster no. P_BCB_09

De novo Semi-synthetic Platform for Monitoring Protein degradation in Live Cells

Mahdi Hasan, [a] Deepanjan Panda, [a] Guy Mann, [a] Ashraf Brik*[a]

[a] *Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa, 3200008 (Israel), E-mail: abrik@technion.ac.il*

Depletion or inactivation of proteins is a powerful tool for evaluating their involvement in cellular pathways and in medicine. Genetic manipulation such as the use of CRISPR or siRNA are commonly used approaches for such a goal. On the other hand, Inducible degron technologies were also developed to complement the genetic approaches, yet with the possibility to use small molecule to mediate protein degradation. Proteolysis targeting chimera (PROTAC) is promising for both the development of therapeutics and studying protein turnover in biological pathways. This method relies on a heterobifunctional molecule containing ligands for both a E3 ligase and protein of interest (POI) to induce its ubiquitination and subsequent degradation via the ubiquitin proteasome system (UPS). The development of PROTAC depends on a known POI binder and a suitable selection of an E3 recruiter. Although advanced progress has been made for the development of small molecule ligand for several proteins, developing a PROTAC requires significant efforts to optimize such a bifunctional molecule, containing a specific linker. Moreover, for many POIs there is a lack for a specific ligand to be used as part of the PROTAC, and the system requires extensive validation for the biological effect and its phenotype.

To overcome the limitation of PROTAC in studying the effect of knockdown of POI, several degron based technologies have been developed. Engineering degron technologies require a recombinant expression of a degron system, or genetically modifying the DNA to introduce the degrader to the POI. Moreover, these methods still restricted with the existing a few ligands for E3 ligases. Inspired by these important approaches we thought to design a novel platform that is more flexible and systematically can be manipulated as well as can be activated on demand. Here we report our first steps towards building such a platform based on SpyTag/SpyCatcher system that allows tagging the POI with E3 ligand in test-tube, followed by cell delivery to monitor its degradation via the UPS (Figure 1). We engineered Enhanced Green Fluorescent Protein tagged with SpyCatcher to enable its conjugation to a SpyTag peptide bearing a VHL E3 ligand, which was delivered to live cells to promote its degradation. This platform lays the ground for studying the degradation of endogenous proteins equipped with SpyTag and for tracking the degradation of post-translationally modified proteins in live cells.

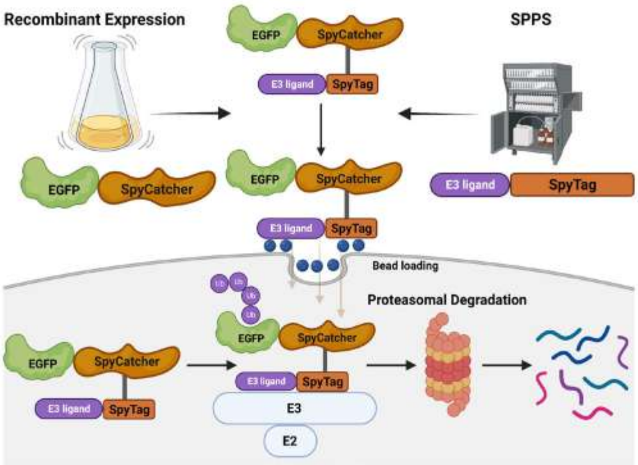


Figure 1. Schematic presentation of our strategy to engineer an exogenous EGFP conjugate using the SpyCatcher/SpyTag system and its delivery via bead loading to promote its degradation in live cells.

References:

1- Mahdi Hasan, Deepanjan Panda, Guy Mann, Ashraf Brik "De novo Semi-synthetic Platform for Monitoring Protein degradation in Live Cells." ChemBioChem (2023): e202300731.

Poster no. P_BCB_10

Polymorphism and structure of the bacterial extracellular matrix protein TasA

Mnar Ghrayeb, Aliza Ashman,[a] and Liraz Chai*[a]

[a] *Institute of Chemistry, The Hebrew University of Jerusalem,Edmond Safra Campus Givat Ram, Jerusalem 91904, Israel*

E-mail: (liraz.chai@mail.huji.ac.il)

Biofilms are surface-aggregates of microbial cells that encase themselves with extracellular matrix (ECM). The ECM is composed of secreted biopolymers, mainly proteins, and polysaccharides that help the cells to attach to surfaces and grant the biofilm significant mechanical strength and it is related to the increased resistance of biofilms to antibiotics activity. Even though it can serve as a target for anti-biofilm drugs, little is known about its composition and structure. In our model organism for biofilm formation, *Bacillus subtilis*, TasA is the major protein component of the ECM. It aggregates to form elongated fibers but their mechanism of formation and structure has not yet been determined. In a systematic study of TasA aggregation, we examine the effect of environmental conditions such as ionic strength, the type of metal ions, and pH on the morphology, aggregation kinetics as well as structure of TasA fibers. Our study shows that above a certain concentration of TasA it forms elongated fibers that can bundle up when increasing the NaCl concentration. These fibers bear an interesting nm-scale periodicity along the fiber axis. Recently, we have succeeded to solve the molecular structure of TasA fibers using Cryo-EM technique. In contrast to NaCl, the addition of Zinc ions to TasA solution leads to the formation of a fibrous hydrogel, with an antibacterial activity. The different morphologies of TasA fibers may be related to different functional roles in biofilms ranging from granting the biofilms with mechanical support to acting as an antibiotic agent.

Acknowledgements: we acknowledge the support of the Neubauer Foundation for the PhD fellowship.

References:

1. Ghrayeb, Mnar, Shahar Hayet, Neta Lester-Zer, Yael Levi-Kalisman and Liraz Chai. “Fibrilar Polymorphism of the Bacterial Extracellular Matrix Protein TasA.” *Microorganisms* 9 (2021)
2. Böhning, Jan, Mnar Ghrayeb, Conrado Pedebos, Daniel K. Abbas, Syma Khalid, Liraz Chai and Tanmay A. M. Bharat. “Donor-strand exchange drives assembly of the TasA scaffold in Bacillus subtilis biofilms.” *Nature Communications* 13 (2022)

Poster no. P_BCB_11

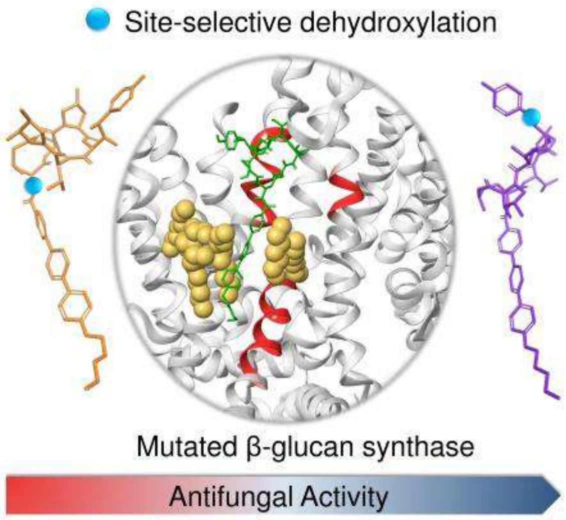
Reshaping Echinocandin Antifungal Drugs To Circumvent Glucan Synthase Point-Mutation-Mediated Resistance

Moriah Jospe-Kaufman,[a] Efrat Ben-Zeev,[b] Austin Mottola,[c] Anna Dukhovny,[c], Judith Berman,[c] Shmuel Carmeli,[a] and Micha Fridman*[a]

[a] School of Chemistry, Raymond & Beverly Sackler Faculty of Exact Sciences ,Tel Aviv University, Tel Aviv, 6997801, Israel. [b] The Whol Drug Discovery institute of the Nancy and Stephen Grand Israel National Center for Personalized Medicine, Weizmann Institute of Science, Rehovot, 7610001, Israel. [c] Shmunis School of Biomedical and Cancer Research, George S. Wise Faculty of Life Sciences, Tel Aviv University, Tel Aviv, 6997801, Israel

E-mail: (mfridman@tauex.tau.ac.il)

Echinocandins are a class of antifungal drugs that inhibit the activity of the β-(1,3)-glucan synthase complex, which synthesizes fungal cell wall β-(1,3)-glucan. Echinocandin resistance is linked to mutations in the *FKS* gene, which encodes the catalytic subunit of the glucan synthase complex. We present a molecular docking-based model that provides insights into how echinocandins interact with the target Fks protein: echinocandins form a ternary complex with both Fks and membrane lipids. We used reductive dehydration of alcohols to generate dehydroxylated echinocandin derivatives and evaluated their potency against a panel of *Candida* pathogens constructed by introducing resistance-conferring mutations in the *FKS* gene. We found that removing the hemiaminal alcohol, which drives significant conformational alterations in the echinocandins, reduced their efficacy. Conversely, eliminating the benzylic alcohol of echinocandins enhanced potency by up to two orders of magnitude, in a manner dependent upon the resistance-conferring mutation. Strains that have developed resistance to either rezafungin, the most recently clinically approved echinocandin, or its dehydroxylated derivative RZF-1, exhibit high resistance to rezafungin while demonstrating moderate resistance to RZF-1.These findings provide valuable insights for combating echinocandin resistance via selective chemical modifications.



Poster no. **P_BCB_12**

Peptoid Chelators With Two Binding Sites For ATP Extraction

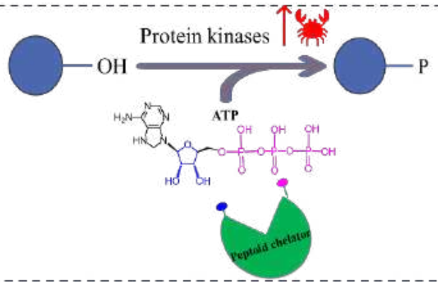
Nicole Vorobyov, [a] and Galia Maayan*[a]

[a] *Schulich Faculty of Chemistry, Technion- Israel Institute of Technology, Technion city, 3200008 Haifa, Israel*

E-mail: gm92@technion.ac.il

Adenosine triphosphate (ATP) is essential for a variety of cell functions such as catalytic activation of kinases that are involved in signal transduction and serving as DNA and RNA precursor for replication[1]. Considering the high replication and signal transduction rates in cancer cells, they express high dependency on ATP. Hence, chelating ATP may assist with harnessing cancer's replication and invasion[2,3]. ATP binding molecules mostly utilize one of two main binding modes[4] which are **metal binding mode** or **diol binding mode**. Metal binding mode is based on phosphates binding using terpyridine and dipicolylamine ligands coordinated to Zn^{2+}. Diol binding mode is based on the well-known phenyl boronic acid-diol interactions. Only one example that combines the two modes for ATP binding was investigated, using a self-assembled cyclodextrin structure[5]. Therefore, one important goal is to design and develop unique chelators that have high affinity to ATP. One way to meet this goal, is to utilize peptidomimetic oligomers, in which the two binding modes can be preorganized within their structures. **Peptoids[6]** (N substituted glycine oligomers) are biocompatible, stable, tunable peptidomimetic oligomers that can serve as suitable scaffolds to combine both the Zn^{+2}-terpyridine binding site and the phenyl boronic acid site on one stable preorganized backbone for efficient dual sited ATP chelation.

In this ongoing work, we designed and synthesized new water-soluble ATP binding peptoids library, that consists of three peptoids with both binding sites and two control peptoids with only one of the binding sites; terpyridine or phenyl boronic acid. All the peptoids were examined for their ATP binding ability by 1H-NMR, 31P-NMR, and ESI-MS. By using Nano ITC, we observed an improvement in the binding affinity of the dual binding peptoids compared to the controls, demonstrating the ability to improve the binding affinity to ATP by manipulating the peptoids preorganized structure, length and spacing between the sites.



- ➢Kinases levels are elevated in cancer
- ➢Kinases are crucial for cell signaling and depend on ATP
- ➢Chelating ATP may serve as possible kinase inhibitor
- ➢**Our goal: peptoid chelators** with two sites for strong binding

Scheme 1: Schematic represntation of the ATP binding peptoid chelator.

References:

1. Y. W. Jun, S. Sarkar, K. H. Kim, K. H. Ahn, ChemPhotoChem, 2019, 3, 214.
2. Vultaggio-Poma, Valentina, Alba Clara Sarti, and Francesco Di Virgilio, Cells, 2020, 2496.
3. Huang, L., Jiang, S., Shi, Y., Journal of hematology & oncology, 2020, 13, 1-23.
4. Huang, B., Liang, B., Zhang, R., Xing, D., Coordination Chemistry Reviews, 2022, 452, 214302.
5. Suzuki, Y., Masuko, M., Hashimoto, T., Hayashita, T., New Journal of Chemistry, 2023, 47(15), 7035-7040.
6. Zuckermann, R. N., Peptide Science, 2011, 96(5), 545-555.

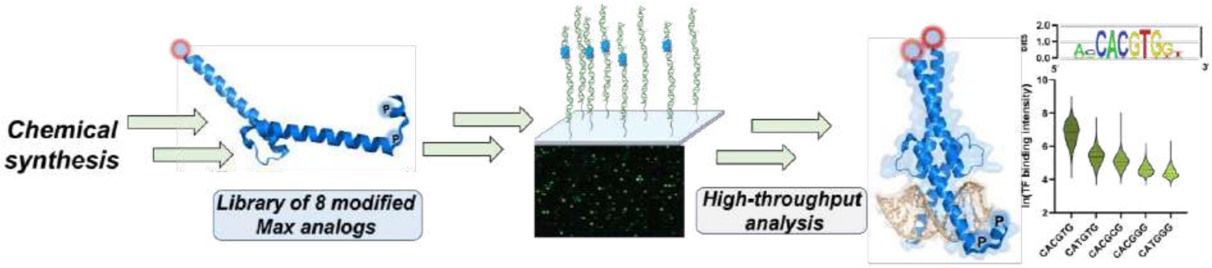
Poster no. P_BCB_13

Deciphering the Role of Posttranslational Modifications on the DNA-Binding Activity of Max Transcription Factor Using Chemical Protein Synthesis

Raj V. Nithun,[1] Shaimaa Habiballah,[1] Yumi Minyi Yao,[2] Xiaoxi Lin,[1] Omer, Harel,[1] Ariel Afek,[2]*
Muhammad Jbara[1]*

[1]School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University
[2]Department of Chemical and Structural Biology, Weizmann Institute of Science
*Correspondence to: ariel.afek@weizmann.ac.il, jbaram@tauex.tau.ac.il

Transcription factors (TFs) are important proteins that control the rate of gene transcription by interacting with specific DNA sites. TF activity is tightly regulated by dynamic post-translational modifications (PTMs); covalent modifications that can modulate TF-DNA interactions and impact gene expression.[1,2] Among these TFs, Max plays a pivotal role in controlling the expression of 15% of the human genome. The activity of Max is regulated by PTMs; Ser-phosphorylation and Lys-acetylation is considered one of the key regulatory mechanisms. In this study, we developed a practical synthetic strategy to prepare homogeneous full-length Max for the first time, to explore the impact of Max PTMs on its DNA binding activity.[3] We prepared a focused library of modified Max variants, with distinct modification patterns, including mono-phosphorylated, and doubly phosphorylated analogues as well as fluorescently labeled variants through solid phase peptide synthesis coupled native chemical ligation approach. Through comprehensive DNA binding analyses, we discovered that the phosphorylation position plays a crucial role in the DNA-binding activity of Max. Furthermore, in vitro high-throughput analysis using DNA microarrays revealed that the N-terminus phosphorylation pattern does not interfere with the DNA sequence specificity of Max. Our work provides insights into the regulatory role of Max's phosphorylation on the DNA interactions and sequence specificity, shedding light on how PTMs influence TF function.



1. O. Harel, M. Jbara, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217716
2. O. Harel, M. Jbara, M, Molecules, **2022,** 27, 4389
3. R. Nithun, Y. M. Yao, X. Lin, S. Habiballah, A. Afek, M. Jbara, *Angew. Chem. In. Ed.* **2023**, 62, e202310913

Poster no. P_BCB_14

Manipulating Engineered Cells with Biosynthesized Abiotic Nanomaterials for Solar-driven Reducing Power Enhancement

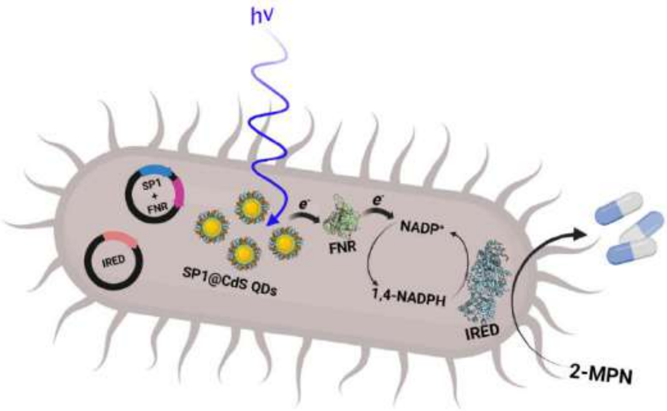
Oren Bachar[a], Matan M. Meirovich[a], Yara Zeibaq[a] and Omer Yehezkeli[a]

[a] *Faculty of Biotechnology and Food Engineering, Technion, Haifa, Israel.*

E-mail: orenchus@campus.technion.ac.il

We suggest a new concept for a self-sustained biotic-abiotic cyborg organism, which comprises a biological system with an add-on nano-based organelle. In this whole-cell biohybrid system, we use the distinctive structure of stable protein 1 (SP1) for the biosynthesis of various size-constrained inorganic nanomaterials in living systems. These nanomaterials are optically and electronically active NPs that can be utilized for various catalytic or photocatalytic processes.[1,2]

Here we show the biosynthesis of CdS NPs stabilized by a predesigned SP1 variant at ambient conditions.[3] The size controlled crystalline NPs were utilized for NADPH regeneration which was subsequently used for the activation of the imine reductase (IRED) enzyme (as depicted in the scheme). The system enabled the generation a vital product for the pharmaceutical industry. We extended this platform to a fully integrated photocatalytic NADPH regeneration system in a whole living bacterium.[4] In our recent results, we demonstrate the exclusive ability of SP1-expressing cells to biosynthesize photo-catalytically active CdS NPs. Finally, we demonstrate the use of the generated photo-active NPs in activating a solar driven cascade within a whole organism to produce fine chemicals. We attempt to investigate this new concept in a broader evolutionary perspective. The incorporation of biosynthetic capabilities of nanomaterials in living cells could allow new properties not only for the enhancement of a single enzymatic reaction, but also in the level of the whole organism.



Scheme: Representation of the semi-artificial photosynthesis in a whole *E. coli* using self-synthesized SP1-capped CdS QDs (SP1@CdS QDs) as photosensitizers for intracellular NADPH formation and enhanced biocatalysis.

References:

1. O. Bachar, M. Meirovich, R. Kurzion and O. Yehezkeli, In Vivo and in Vitro Protein Mediated Synthesis of Palladium Nanoparticles for Hydrogenation Reactions, 56, *Chem. Comm.*, **2020**, 11211–14.
2. O. Bachar, R. Cohen, M. Meirovich, Y. Cohen and O. Yehezkeli, Biotic-Abiotic hybrids for Bioanalytics and Biocatalysis, Current Opinion in Biotechnology, *COBIOT*, 81, **2023**, 102943.
3. O. Bachar, M. Meirovich, Y. Zeibaq, O. Yehezkeli, Protein-mediated Biosynthesis of Semiconductor Nanocrystals for Photocatalytic NAD(P)H Regeneration and Chiral Amine Production, *Angew. Chem. Int. Ed.*, 61, **2022**. e202202457.
4. O. Bachar, Matan M. Meirovich and O. Yehezkeli, Integrated Biotic-abiotic Solar Driven NADPH Regeneration Platform in E. coli for Chemical Biomanufacturing Applications, *Adv. Funct. Mater.* **2023**, 2314443

Poster no. P_BCB_15

Differential Substrate Sensing in Terpene Synthases from Plants and Microorganisms. Insights from Structural, Bioinformatic, and EnzyDock Analyses.

Renana Schwartz,*[a] Shani Zev,[a] Dan T. Major[a]

[a] *Department of Chemistry and Institute for Nanotechnology & Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel*

E-mail: (renana.kofman@biu.ac.il)

Terpene synthases (TPS) catalyze the first committed step in the formation of terpenoids, which comprise the largest class of natural products in nature. TPS employ a family of universal natural substrates, composed of isoprenoid units bound to a diphosphate moiety. The intricate structures generated by TPS are the result of a combination of initial substrate binding and folding in the active site, enzyme-controlled carbocation reaction cascades, and final reaction quenching. A key question in class I TPS that has yet to be addressed is the asymmetric nature of the diphosphate-$(Mg^{2+})_3$ cluster, which forms a critical part of the active site. In this asymmetric ion-cluster, two diphosphate oxygens protrude into the active site pocket, but only one of these coordinates a Mg^{2+}-ion indirectly via a water molecule. The substrate hydrocarbon tail, which eventually is molded into terpenes, can bind to either of these oxygens, yet to which of these oxygens is unknown. Here, we employ a combination of structural, bioinformatics, and EnzyDock docking tools to address this enigma. We bring initial data to suggest that this difference is rooted in evolutionary differences between TPS. We hypothesize that this alteration in binding, and subsequent chemistry, is due to TPS originating from plants or microorganisms. The current findings, which are based on a limited dataset, warrant further studies.

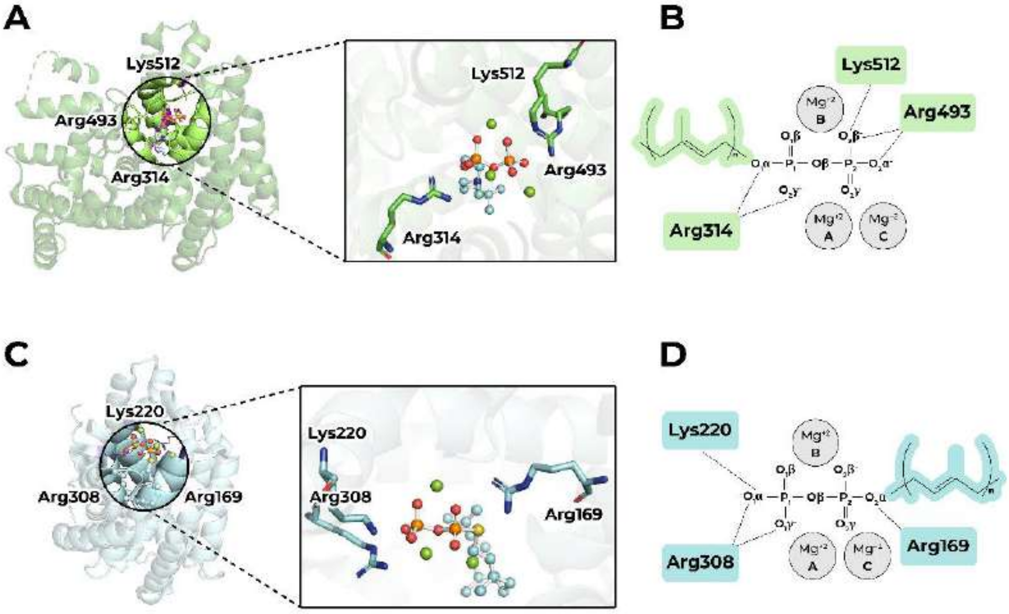


Figure 1: Top: (A) *Salvia officinalis* bornyl diphosphate synthases (BPPS), an example of a **plant TPS**, where the isoprenoid group is connected via O1α (PDB ID:1n21). **(B)** Naming convention for positively charged residues binding the diphosphate group for plant TPS follows the residue numbers in *Salvia officinalis* BPPS. **Bottom: (C)** *Aspergillus terreus* aristolochene synthase (AS), an example of a **microbial TPS**, where the isoprenoid group is connected via O2α (PDB ID: 4kux). **(D)** Naming convention for positively charged residues binding the diphosphate group for microbial TPS follows the residue numbers in *Aspergillus terreus AS*.

Acknowledgements: We thank the Israel Ministry of Science, Technology and Space and the National Institute of Health for financial support.

Poster no. P_BCB_16

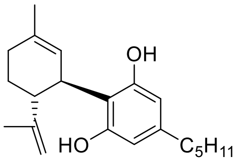
Design, synthesis, and characterization of novel hybrid cannabidiol: highly potent agents toward AAPH and Cu^{2+} -induced LDL oxidation

Eliav Peretz [a] and Sanaa Musa*[a]

[a] *Natural Compounds and Analytical Chemistry Laboratory, Migal- Galilee Research Institute and Tel-Hai academic college, Qiryat Shmona, Israel.*

E-mail: sanaa@migal.org.il

Natural product-based medicine plays a pivotal role in medicinal aspects, emphasizing the exploration of natural components found in medicinal plants as a fundamental basis for creating innovative bioactive compounds. In our research, we focus on a natural source of cannabidiol (**CBD**), a well-studied non-psychotropic component of plant-derived cannabinoids that has shown significant therapeutic potential for various diseases and disorders, including antioxidants and anti-inflammatory effects [1, 2].



(-)- Cannabidiol (CBD)

CBD's antioxidant capacity depends on the presence of the resorcinol group, responsible for transferring hydrogen atoms or electrons to the oxidants. Additionally, the limonene ring and the n-pentyl moiety contribute to the stability of the cation free radical or its semiquinone forms [2]. The antioxidant properties of the phytocannabinoids, including their ability to prevent Low-density lipoprotein (LDL) – oxidation, have been previously reported [3]. Studies have indicated that **CBD** can prevent the formation of conjugated dienes during LDL oxidation by extending the lag phase of the initial stages, albeit with moderate activity [4].

Herein, we describe the design and synthesis of novel hybrid derivatives based on the cannabidiol framework. These derivatives have demonstrated strong antioxidant properties against AAPH and Cu^{2+}-induced LDL oxidation.

References:

[1] Atalay, S., Jarocka-Karpowicz, I., and Skrzydlewska, E. (2020) Antioxidative and Anti-Inflammatory Properties of Cannabidiol, *Antioxidants 9*, 21.
[2] Borges, R. S., and da Silva, A. B. F. (2017) Chapter e12 - Cannabidiol as an Antioxidant, In *Handbook of Cannabis and Related Pathologies* (Preedy, V. R., Ed.), pp e122-e130, Academic Press, San Diego.
[3] Singla, S., Sachdeva, R., and Mehta, J. L. (2012) Cannabinoids and atherosclerotic coronary heart disease, *Clinical Cardiology 35*, 329-335.
[4] Musetti, B., González-Ramos, H., González, M., Bahnson, E. M., Varela, J., and Thomson, L. (2020) Cannabis sativa extracts protect LDL from Cu2+-mediated oxidation, *Journal of Cannabis Research 2*, 37.

Poster no. P_BCB_17

One-Pot Synthesis of RNA/DNA Building-Blocks from Prebiotic Substance via Heterogeneous (Photo)Catalysis

Shoval Gilboa, [a] Yaron Paz*[a]

[a] *Department of Chemical Engineering, Technion-Israel Institute for Technology, Haifa, Israel*

E-mail: shovalgilboa@campus.technion.ac.il

Throughout the years, many theories have been suggested on how life first emerged. The RNA world hypothesis suggests that in the primordial world, simple molecules were formed under appropriate conditions and then increased their complexity to form nucleotides, and eventually chains of RNA. The RNA molecule has an essential role in life; on the one hand, it can be self-replicated, allowing for genetic propagation. On the other, it functions as a catalyst in more complex reactions, such as protein synthesis.

Finding the suitable conditions for the formation of RNA building blocks, without enzyme intervention and in a one-pot reaction, is a big challenge in contemporary research. Moreover, the pathway for the integration of the nucleobase, sugar, and phosphate groups into a single entity is still unknown. In this work, cerium phosphate (CePO4), was used in the abiotic formation of RNA/DNA building blocks from the simple molecule formamide. This catalyst, which we term a Prometheus catalyst, serves several functions, such as reaction promoter, photocatalyst, phosphate donor, and an adsorption site for intermediates, thus increasing their stability and promoting high concentrations of different sub-groups in close proximity.

Experimental results show the successful one-pot synthesis of the complete nucleotides; adenosine cyclic monophosphate (cAMP), thymidine monophosphate (TMP), cytidine monophosphate (CMP), and guanosine monophosphate (GMP), along with the nucleosides uridine, thymidine cytidine, and other RNA/DNA building blocks from formamide, under heat, UV irradiation, and inert atmosphere. Additionally, the adsorption of these building blocks on the catalyst surface under environment similar to the environment in their formation was studied. Results were found to support the notion that adsorption of the sub-units of the building blocks assists the formation of nucleotides, and, at a later stage, may assist polymerization.

Based on the principle of Occam's razor, the one-pot reaction mentioned above represents a reasonable scenario in explaining the origin of life, and hence is of considerable interest to the community.

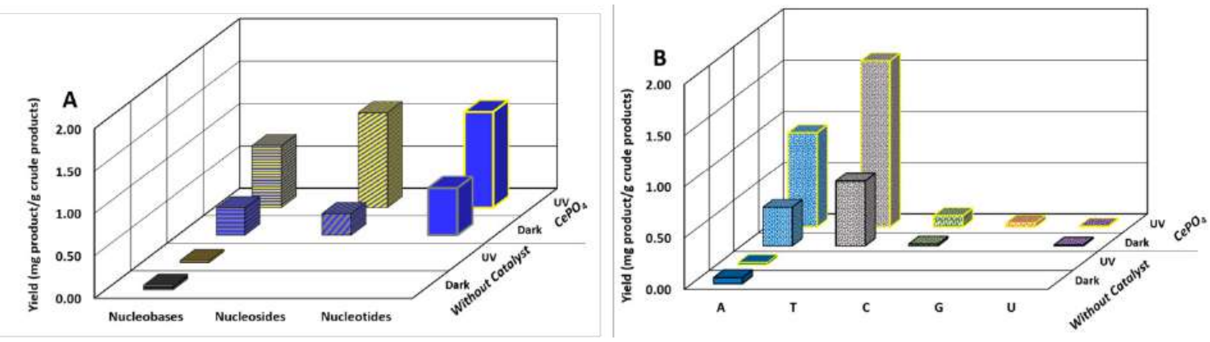


Figure 1: A) The total yield of different forms of the RNA/DNA building-blocks, categorized according to nucleobases, nucleosides and nucleotides, as obtained after 48 hours with and without $CePO_4$. (B) The total yield of RNA/DNA building blocks (nucleobases+ nucleosides+ nucleotides) categorized according to the type of nucleobases as obtained after 48 hours with and without $CePO_4$. The yield is given relative the total amount of products, summing up to formamide conversion of 13±3 % in all four cases.

Acknowledgements: The support of the Technion's PYS Fund is gratefully acknowledged.

Reference: Gilboa S, Panz L, Arbell N, Paz Y. Cerium Phosphate-Assisted Formation of Nucleosides and Nucleotides from Formamide in a One-Pot (Photo)catalytic Reaction. ChemRxiv. 2023; doi:10.26434/chemrxiv-2023-698l0-v2.

Poster no. P_BCB_18

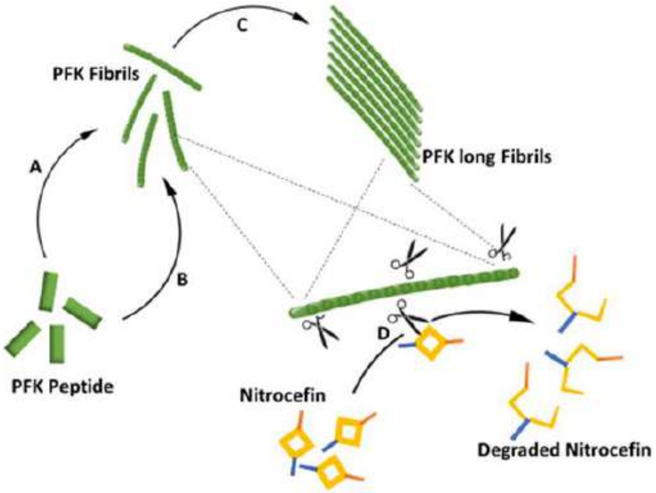
Short Synthetic Peptide Derived Functional Amyloids Catalyze β-Lactam Antibiotics

Sisira Mambram Kunnath[a] Elad Arad [a] and Raz Jelinek*[a]

[a] *Department of Chemistry, Ben-Gurion University of the Negev, Beersheba, Israel.*

E-mail: razj@bgu.ac.il

Amyloid fibrils, observed across diverse organisms, including animals, bacteria, and fungi, are typically linked to diseases and pathological conditions but also appear in native biological systems, playing roles in natural processes. The use of functional amyloid to degrade antibiotics is an emerging field, increasingly important as the abundance of antibiotic-resistant bacteria becomes a major health risk (1). This research delves into the fundamentals of antibiotic degradation by functional amyloids, emphasizing structural aspects of amyloid catalytic sites. The cationic peptide Pro-Lys-(Phe-Lys)5-Pro (PFK), A family of peptides featuring the sequence Pro-X-(Phe-X)5- Pro, denoted here as PFX, with X representing a charged amino acid (e.g., D, K, E) were shown to form β-sheet assemblies under certain ranges of pH values, peptide concentrations, and in the presence of specific ions or other molecules. The alternating hydrophobic–hydrophilic amino acid sequence induces the formation of bilayer-fibril structures in solutions, that under certain conditions, may also stabilize a hydrogel phase (2). Beta-lactam antibiotics are a class of antibiotics derived from the penicillin nucleus, having a beta-lactam ring in their chemical structure. β-lactams adsorb PFK fibrils and catalytically degraded through amide bond hydrolysis in the 4-member ring. The experiments presented below are designed to examine whether PFK fibrils, through active sites upon the fibril surface (schematically represented as "scissors"), catalyze the cleavage of the four-membered β-lactam ring, rendering the molecule functionally inactive. Specifically, we will be testing PFK fibril-mediated degradation of nitrocefin, a widely-studied β-lactam surrogate of penicillin (3). Hydrolysis of nitrocefin produces a shift of ultraviolet absorption inside the visible light spectrum from intact (yellow) nitrocefin (~380 nm) to degraded (red) nitrocefin (~500 nm) allowing visual detection of beta-lactamase activity on a macroscopic level and it will be monitored for 2 h. Methods for analyzing the structure can be done with TEM, CD, FTIR, ANS fluorescence, etc to determine the critical aggregation concentration (CAC).



Scheme: PFK fibrils catalytically degrade β-lactam antibiotics, (A- Incubation in DIW; B- Incubation in KCl solution; C- aging of PFK fibrils; D- catalytic degradation of Nitrocefin using PFK fibrils.)

References:

(1) Arad, E., Pedersen, K. B., Malka, O., Mambram Kunnath, S., Golan, N., Aibinder, P., ... & Jelinek, R. (2023). Staphylococcus aureus functional amyloids catalyze degradation of β-lactam antibiotics. Nature Communications, 14(1), 8198.
(2) Arad, E., Leshem, A. B., Rapaport, H., & Jelinek, R. (2021). β-Amyloid fibrils catalyze neurotransmitter degradation. Chem Catalysis, 1(4), 908-922.
(3) Arad, E., Yosefi, G., Kolusheva, S., Bitton, R., Rapaport, H., & Jelinek, R. (2022). Native Glucagon Amyloids Catalyze Key Metabolic Reactions. ACS nano, 16(8), 12889-12899.

Poster no. P_BCB_19

Rationally Designed Functionalization of Single-Walled Carbon Nanotubes for Real-Time Monitoring of Cholinesterase Activity and Inhibition in Plasma

Srestha Basu,*[a] Adi Hendler-Neumark,[a] and Gili Bisker [a,b,c,d]

[a]Department of Biomedical Engineering, Faculty of Engineering, Tel Aviv University, Tel Aviv 6997801, Israel

[b]Center for Physics and Chemistry of Living Systems, Tel Aviv University, Tel Aviv 6997801, Israel

[c]Center for Nanoscience and Nanotechnology, Tel Aviv University, Tel Aviv 6997801, Israel

[d]Center for Light-Matter Interaction, Tel Aviv University, Tel Aviv 6997801, Israel

***Presenting author**
Email ID: srestha.basu2012@gmail.com

Abstract: Enzymes play a pivotal role in regulating numerous bodily functions. Thus, there is a growing need for developing sensors enabling real-time monitoring of enzymatic activity and inhibition. We fluorometrically monitor the activity and inhibition of cholinesterase (CHE) enzymes in blood plasma using near-infrared (NIR) fluorescent single-walled carbon nanotubes (SWCNTs) as probes, strategically functionalized with myristoylcholine (MC) – the substrate of CHE. We observe a significant decrease in the fluorescence intensity of MC-suspended SWCNTs upon interaction with CHE, attributed to the hydrolysis of the MC corona phase of the SWCNTs by CHE. Complementary measurements for quantifying choline, the product of MC hydrolysis, reveal a correlation between the fluorescence intensity decrease and the amount of released choline, rendering the SWCNTs optical sensors with real-time feedback in the NIR biologically transparent spectral range. Moreover, when synthetic and naturally abundant inhibitors inhibit the CHE enzymes present in blood plasma, no significant modulations of the MC-SWCNT fluorescence are observed, allowing us to effectively detect CHE inhibition. Our rationally designed SWCNT sensors platform for monitoring of enzymatic activity and inhibition in clinically relevant samples is envisioned to not only advance the field of clinical diagnostics but also deepen further understanding of enzyme-related processes in complex biological fluids.

Reference:

1. **Basu, S**; Hendler-Neumark, A.; Bisker, G. Rationally Designed Functionalization of Single-Walled Carbon Nanotubes for Real-Time Monitoring of Cholinesterase Activity and Inhibition in Plasma. ***Small***, 2024 (Just accepted Manuscript).

Poster no. P_BCB_20

Enzymatic Activity Profiling Using an Ultra-Sensitive Array of Chemiluminescent Probes for Bacterial Classification and Characterization

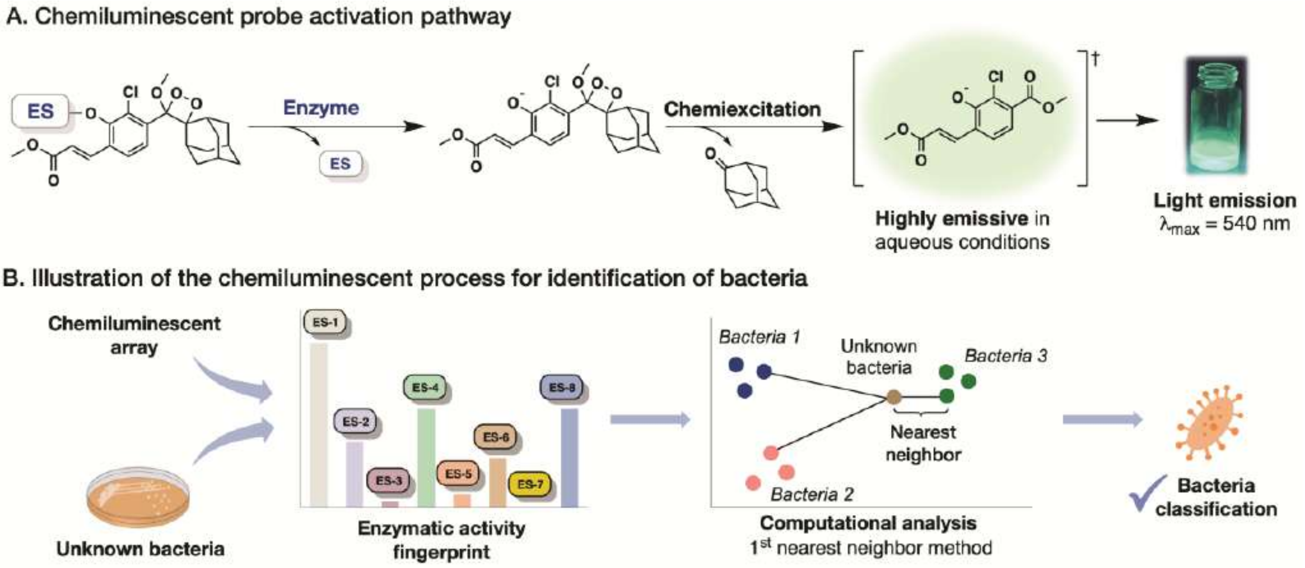
Shabat, Doron [a*] and Fridman, Micha [a*].

[†]These authors contributed equally to this study.

[a] School of Chemistry, Raymond & Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, 6997801, Israel.

E-mail: Shlomi Reuveni, Email: shlomire@tauex.tau.ac.il; Doron Shabat, Email: chdoron@tauex.tau.ac.il; Micha Fridman, Email: mfridman@tauex.tau.ac.il.

Identification and characterization of bacterial species in clinical and industrial settings necessitate the use of diverse, labor-intensive, and time-consuming protocols, as well as the utilization of expensive and high-maintenance equipment[1-3]. Furthermore, while cutting-edge identification technologies like mass spectrometry and PCR are highly effective in identifying bacterial pathogens, they fall short in providing additional information for identifying bacteria not present in the databases upon which these methods rely[4,5]. In response to these challenges, we present a robust and general approach to bacterial identification, based on their unique enzymatic activity profiles. This method delivers results within 90 minutes, utilizing an array of highly sensitive and enzyme-selective chemiluminescent probes. Leveraging on our recently developed technology of chemiluminescent luminophores, which emit light under physiological conditions, we have composed an array of probes designed to rapidly detect various bacterial hydrolytic enzymatic activities[6-8]. The array includes probes for detecting resistance to the important and large class of β-lactam antibiotics. The analysis of chemiluminescent fingerprints from a diverse range of bacterial pathogens has unveiled distinct enzymatic activity profiles for each strain. The reported universally applicable identification procedure offers a highly sensitive and rapid means to depict bacterial enzymatic activity profiles. When applying this method to our bacteria panel unexpected discoveries emerged. Such as, a significantly higher value of β-glucuronidase activity which was observed across all *E. coli* strains in the panel, compared to other bacteria in the panel. This study opens new approaches for characterizing and identifying pathogens in research, clinical, and industrial applications.


A. Chemiluminescent probe activation pathway

B. Illustration of the chemiluminescent process for identification of bacteria

Figure 1: A. Structures and chemiexcitation pathways of ortho-substituted a phenoxy 1,2-dioxetane probe. **B.** Schematic representation depicting the bacterial identification process. ES; enzymatic substrate for the following enzymes: β-glucosidase, β-glucuronidase, β-galactosidase, Pyroglutamyl-peptidase, Phosphatase, Leucine aminopeptidase, Nitroreductase, NQO1, β-Lactamase, Penicillin-G amidase, Periodite oxidative-cleavage, N-acetyl hydrolase.

Poster no. P_BCB_21

Total synthesis of Seleno-Pro-Insulin

Tasneem Ras, Orit Ktorza Weil, Norman Metanis

Corresponding: Metanis@mail.huji.ac.il

Institute of Chemistry, Faculty of Mathematics and Natural Science, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

Proinsulin is single-chained 86 amino acid residues, composed of the A and B chain of insulin linked together by the 35-amino acid, C domain. It contains six cysteine residues, and the folded protein contains three intramolecular disulfide bons .

Dominant mutations in the human insulin gene can lead to pancreatic β-cell dysfunction and diabetes mellitus due to toxic folding of a mutant proinsulin; such mutations can impair the folding of insulin, cause the produced mutants to be retained in the endoplasmic reticulum (ER), triggering an ER stress and β-cell death, as well as impair insulin-IR interaction. These include neonatal-onset diabetes mellitus (NDM), Mutant Insulin-gene Induced Diabetes of Youth (MIDY), and Maturity Onset Diabetes of the Young (MODY). A hot spot for such clinical mutations is found at position B8, which is a conserved glycine within the vertebrate insulin superfamily. One of these mutations is GlyB8Ser, although the exact mechanism of misfolding due to these mutations still unknown.

Recently, several studies reported the use of selenocysteine as a tool to enhance the oxidative folding of proteins including in insulin. The unique chemical properties of selenocysteine contributed to the folding of proteins, where diselenide or selenylsulfide bond formation is favored over a disulfide. For example, the substitution of two selenocysteine residues instead of cysteine at positions A6 and A11 in insulin chain A provided a more stable diselenide bond (Se-Se) instead of disulfide bond (S-S).[1] Therefore, we suggested that insertion of Sec at position 71 and 76 (equivalent to position A6 and A11 in insulin hormone) will rescue the folding of proinsulin mutants, making it more stable despite the mutation SerB8.

The synthesis of the full-length WT-proinsulin (WT-ProIns) and Se-proinsulin (Se-ProIns) was divided into three segments. These segments were then connected to each other using two native chemical ligation reactions (NCL). In this poster we will discuss the our results of the total synthesis of WT- and Se-ProIns.

Poster no. P_BCB_22

Stable Protein 1 Hemin Complex as Peroxidase Mimicking Artificial Enzyme

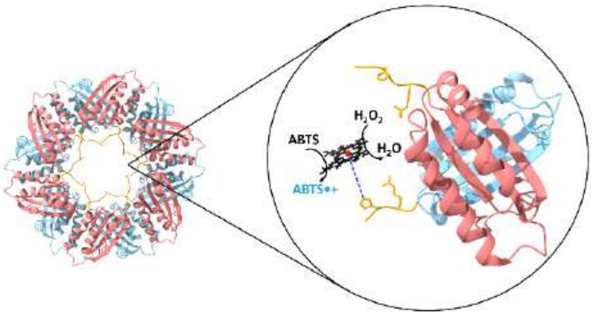
Yara Zeibaq,[a] Oren Bachar,[a] Jenia Skylar,[b] Noam Adir,[b] and Omer Yehezkeli*[a]

[a] Faculty of Biotechnology and Food Engineering, Technion – Israel Institute of Technology Haifa 3200003, Israel. [b] Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 3200003, Israel.

E-mail: y.omer@bfe.technion.ac.il

Enzymes are amazing biocatalysts that gained their unique properties through billions of years of evolution. These biocatalysts allow a high reaction rate with low activation barriers that enable life on earth as we know them today. While enzymes are designed for specific reactions in vitro or ex Vitro, in some industrial processes, unnatural reactions or conditions are required. Enzyme activation requires specific conditions, which are not always available at the industrial level, and therefore, alternatives should be explored. Horseradish peroxidase, (HRP) is a ubiquitous heme-containing enzyme purified from the roots of Armoracia rusticana. The HRP facilitates the oxidation of aromatic molecules while reducing hydrogen peroxide. HRP has been broadly used in medical diagnosis, environmental treatments, and chemical synthesis. However, it doesn't reach its full potential due to its instability in industrial condition and its high-cost purification processes.

Here, we present stable protein 1 (SP1) as a new protein scaffold to design artificial enzymes. The SP1 is an extremely stable ring-shaped protein[1], and its inner cavity can be easily bioengineered to enable the formation of cofactor-protein interactions that in turn mimic the enzyme's active site. Inspired by nature, we engineered the protein cavity to form an activated complex with hemin that mimics the activity of the peroxidase enzyme **(Scheme 1)**. The characterization of this artificial enzyme, and its ability to drive reactions in harsh conditions in addition to its utilization for biosensing will be presented.



Scheme 1: A SP1@hemin complex model based on the 1TR0 structure deposited in the PDB. Left, the dodecameric, double ring SP1 crystal structure. Right, the hybrid active site where pink and blue represent two monomers, respectively. The engineered N-termini presented in orange. The figure was prepared using ChimeraX.[2]

References:

[1] O. Dgany, A. Gonzalez, O. Sofer, W. Wang, G. Zolotnitsky, A. Wolf, Y. Shoham, A. Altman, S. G. Wolf, O. Shoseyov, O. Almog, *Journal of Biological Chemistry* **2004**, *279*, 51516.
[2] E. F. Pettersen, T. D. Goddard, C. C. Huang, E. C. Meng, G. S. Couch, T. I. Croll, J. H. Morris, T. E. Ferrin, *Protein Sci* **2021**, *30*, 70.

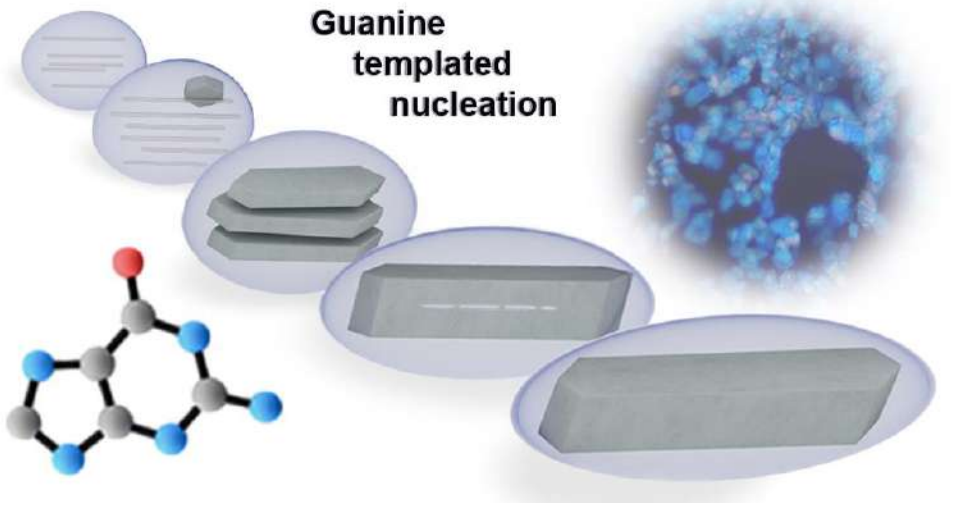
Poster no. P_BCB_23

Plate-like Guanine Biocrystals Form via Templated Nucleation of Crystal Leaflets on Preassembled Scaffolds

[1]Department of Molecular Genetics, Weizmann Institute of Science, Rehovot 76100, Israel.
[2] Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel.

*E-mail: dvir.gur@weizmann.ac.il

The nanoscale morphologies of crystalline materials determine their optical, electrical and mechanical properties and, thus, their potential applications. However, producing crystals with particular shapes requires overriding their strong tendency to adopt thermodynamically stable structures. Nevertheless, many organisms form crystals with distinct morphologies, such as the plate-like guanine crystals formed by a large variety of terrestrial and aquatic species for vision, camouflage, body temperature regulation, and kin recognition. The control over crystal morphogenesis was hypothesized to involve physical growth restriction by the delimiting crystal chamber membrane, combined with fine-tuned interactions between organic molecules and the growing crystals. Using cryo-electron tomography, we followed crystal formation in developing zebrafish larvae in three dimensions. We find that initially, crystals form in the lumen of the crystal forming organelle, with no contact with the delimiting membrane. Only later in development, the elongating crystals reach the membrane and eventually push against it, deforming the organelle shape. We further show that crystals form via templated nucleation of multiple thin leaflets on preassembled, 20 nm thick, amyloid protein scaffolds. The initial thin leaflets then merge and coalesce into a single platelet crystal, with no obvious reminiscence of the initial leaflets. Our findings provide new insights into how organisms control the morphology and, thereby, optical properties of crystals, setting the stage for studying the interaction between proteins and molecular crystals.



References:

Eyal, Z., Deis, R., Varsano, N., Dezorella, N., Rechav, K., Houben, L., & Gur, D. "Plate-like Guanine Biocrystals Form via Templated Nucleation of Crystal Leaflets on Preassembled Scaffolds." *Journal of the American Chemical Society* (2022).

Bridging Chemistry and Medicine

Poster no. P_BCM_01

New Generation of FIT-PNAs : Cyclopentane backbone modifications of surrogate base for improved RNA sensing

Amer Fadila[a], Hongchao Zheng[b], Daniel H. Appella[b], Eylon Yavin[a]

[a]The Institute for Drug Research, The School of Pharmacy, The Hebrew University of Jerusalem, Hadassah Ein-Kerem, Jerusalem 91120, Israel.
[b]Synthetic Bioactive Molecules Section, Laboratory of Bioorganic Chemistry (LBC), National Institute of Diabetes and Digestive and Kidney Diseases (NIDDK), National Institutes of Health, 8 Center Drive, Room 404, Bethesda, Maryland 20892, United States.
E-mail: Amer.fadila@mail.huji.ac.il

FIT-PNA (forced-intercalation-peptide nucleic acid) is a highly sensitive RNA/DNA sensor developed by the Seitz group in the early 2000s. (1) FIT-PNAs are “light-up” probes that are based on the replacement of one of the PNA monomers with a surrogate base. The surrogate base is a monomethine cyanine dye (*e.g.,* thiazole orange (TO), Bis-quinoline (BisQ)). Cyclopentane modified PNAs (cpPNA), developed at the Appella lab (2), are PNA monomers with a cyclopentane backbone that increase the affinity to complementary DNA and RNA.

Our lab has developed cpPNA-FIT probes designed with cyclopentane PNA monomers flanking the BisQ surrogate base. (3) cpPNA affects the close environment of BisQ thereby resulting in brighter and more sequence-specific FIT-PNAs.

Inspired by these findings, we hypothesized that direct introduction of cyclopentane backbone on the surrogate base (e.g., TO or BisQ), should augment the fluorescence intensity of the fluorophores thereby advancing their potential as superior RNA diagnostic molecules. After successfully synthesizing these new cp-modified surrogate bases, we synthesized 11-mer FIT-PNAs as model sequences and introduced these cp-modified surrogate bases in combination with or without cp neighboring PNA monomers. Hybridization assays validates the successful synthesis of the modified fluorophores, demonstrating amplified brightness compared to their unmodified counterparts.

In conclusion, the synergy between cpPNA monomers and cpTO culminates in the creation of the brightest RNA sensor. This optimized combination harnesses the enhanced stability and binding affinity conferred by cyclopentane modifications, alongside the robust fluorescence properties of Thiazole Orange, resulting in a molecular entity with unparalleled brightness.

References:

1. Kçhler, O. et al., (2005) ‘Forced Intercalation Probes (FIT Probes): Thiazole Orange as a Fluorescent Base in Peptide Nucleic Acids for Homogeneous Single-Nucleotide-Polymorphism Detection’, ChemBioChem, 6, pp. 69-77.
2. Tepper, O. et al. (2021) ‘Cyclopentane FIT-PNAs: bright RNA sensors’, Chemical Communications, 57(4), pp. 540–543.
3. Pokorski, J.K. et al. (2005) ‘Cyclopentane-modified PNA improves the sensitivity of nanoparticle based scanometric DNA detection’, Chemical Communications, (16), pp. 2101–2103.

Poster no. P_BCM_02

Peptoids-Chelators Cocktail for Alzheimer's Disease Therapy

Anastasia E. Behar,[a] and Galia Maayan*[a]

[a] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Technion City, 3200008 Haifa, Israel*

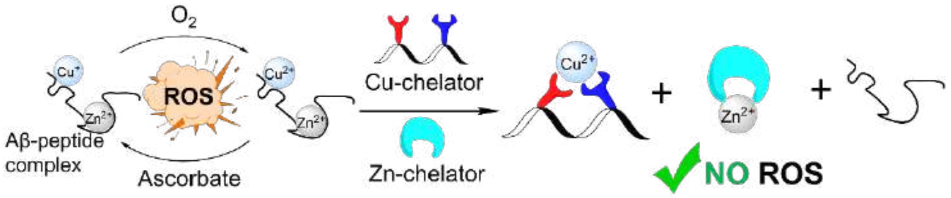
E-mail: gm92@technion.ac.il

Copper(Cu)-targeting chelation is one of the therapeutic approaches in the context of Alzheimer's Disease (AD).[1] Selective extraction of Cu ions bound to amyloid-β (Aβ) peptides by external chelator can affect the formation of reactive oxygen species (ROS) by this CuAβ complex, preventing neuropathologic degradation associated with AD. This chelator should possess high selectivity for Cu over zinc (Zn), that is also present within the synaptic cleft. However, achieving such selectivity in one molecule is generally challenging due to the similarities in the binding preferences of these two metal ions.

As an alternative to small molecules or peptide-based ligands, we consider peptoids an excellent platform for the development of metal chelators for potential AD therapeutics. Peptoids[2] are N-substituted glycine oligomers that can be efficiently synthesized on a solid support and are also biocompatible; thus, they are considered promising drug candidates. Indeed, we recently reported the first peptoid-based chelator, which can inhibit ROS formation in the context of AD.[3] However, it had two major drawbacks: limited solubility in buffered solutions at biological pH and it's selectivity for Cu over Zn being a thermodynamic process, thus limiting it's ability to inhibit ROS formation by Aβ peptide-Cu complex when Zn is co-present.

To overcome these limitations, we present here a new peptoid chelator for Cu with improved solubility under physiological conditions. It is a helical peptoid bearing hydroxyquinoline and terpyridine ligands such that they face the same side of the helix for strong chelation, and can extract Cu ions from Aβ peptide. Moreover, as an alternative to monotherapy (where the active agent is a single molecule), we propose here a different chelation approach in which the new Cu chelator is mixed with a peptoid-based selective chelator to Zn in a cocktail solution, aiming to target both metal ions simultaneously but independently from each other.[4]

Based on rigorous spectroscopic experiments, we demonstrate that proposed peptidomimetic cocktail allows full arrest of ROS production by CuAβ complex. Additionally, we further evaluate the metabolic and proteolytic stability, and initially assess the BBB permeability of the proposed chelators.



Scheme 1: Schematic representation of a cocktail of two structurally different peptoid-based chelators, designed to selectively bind Cu or Zn ions from the Aβ-peptide complex, by this stopping production of ROS species in the context of AD.

Acknowledgements: We thank the ICS for financial support

References:

1. Esmieu, C.; Guettas, D.; Conte-daban, A.; Sabater, L.; Faller, P.; Hureau, C. Copper-Targeting Approaches in Alzheimer's Disease: How To Improve the Fallouts Obtained from in Vitro Studies**.** *Inorg. Chem.,* **2019**, *58 (20)*, 13509-13527.
2. Seo, J.; Lee, B. C.; Zuckermann, R. N. in Comprehensive Biomaterials: Peptoids: Synthesis, Characterization, and Nanostructures. Ducheyne, P.; Healy, K. E.; Hutmacher, D. W.; Grainger, D. W.; Kirkpatrick, C. J. (Eds.), Elsevier, Waltham, MA, USA, **2011**, Vol. 2, 53–76.
3. **Behar, A. E.;** Sabater, L.; Baskin, M.; Hureau, C.; Maayan, G. A Water-Soluble Peptoid Chelator that Can Remove Cu^{2+} from Amyloid-β Peptides and Stop the Formation of Reactive Oxygen Species Associated with Alzheimer's Disease**.** *Angew. Chem. Int. Ed.*, **2021**, *60*, 24588.
4. **Behar, A. E.;** Maayan, G. A Cocktail of Cu^{2+}- and Zn^{2+}-Targeting Peptoid-Based Chelators Towards Potential Application in the Context of Alzheimer's Disease, *in preparation*

Poster no. P_BCM_03

Machine learning-assisted hit-to-lead optimization: prediction, synthesis, and biochemical validation

Barak Akabayov

Department of Chemistry, Ben-Gurion University of the Negev

E-mail: akabayov@bgu.ac.il

Data-driven algorithms have emerged as powerful platforms to consolidate bioisosteric rules for preferential modifications on small molecules with a common molecular scaffold.

I will present complementary data-driven models to optimize the size, structure, and binding properties of molecules targeting an RNA hairpin within the bacterial ribosome. The models' training data set was based on NMR fragment screening followed by virtual screening. Visual, geometrical, and chemical features were extracted to enhance the targeted RNA's binding. Functional validation was conducted after synthesizing 3rd generation of new small molecules pinpointed computationally and revealed specific inhibitors that target bacterial translation and, as a result, kill bacteria.

References:

1. Tam, B.; Sherf, D.; Cohen, S.; Eisdorfer, S.D.; Peretz, M.; Soffer, A.; Vilenchik, D.; Akabayov, S.R.; Wagner, G.; Akabayov, B. Discovery of small-molecule inhibitors targeting the ribosomal peptidyl transferase center (PTC) of *M. tuberculosis*. **2019**. *Chemical Science*, **2019**, 10, 8764-8767.
2. Grimberg, H.; Tiwari, V.S.; Tam, B.; Gur-Arie, L.; Gingold, D.; Polachek, L.; Akabayov, B. Machine learning approaches to optimize small-molecule inhibitors for RNA targeting. **2022**. *Journal of Cheminformatics*, 14 (4).
3. Soffer, A.; Viswas, S.J.; Alon, S.; Rozenberg, N.; Peled, A.; Piro, D.; Vilenchik, D.; Akabayov, B. MolOptimizer: a molecular optimization toolkit for fragment-based drug design. **2024**. *Molecules*, 29(1), 276.

Poster no. P_BCM_04

Enhancing the Gastrointestinal Stability of Salmon Calcitonin through Peptide Stapling

Hiba Ghareeb[1] and Norman Metanis[1,2,3,*]

[1]Institute of Chemistry, [2]The Center for Nanoscience and Nanotechnology, [3]Casali Center for Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.

Salmon calcitonin (sCT) has been in the clinic for over 40 years for the treatment of postmenopausal osteoporosis, Paget's disease and hypercalcemia. Because it is a polypeptide, sCT is unstable and is degraded in the gastrointestinal tract within minutes. While it is currently only available as injection or nasal spray, improving the gastrointestinal stability of sCT may expand its therapeutic applications. In this work, we designed and synthesized several sCT analogues with enhanced gastrointestinal stability while retaining their ability to bind and activate the calcitonin receptor. One of the analogues, KaY-1, in which stapling Lys11 and Tyr22 with a methylene group led to a five-fold improved stability in simulated gastric fluid. Further, we found that modifying this stapled peptide with R24Q substitution showed an additional improved six-fold stability in simulated intestinal fluid. Finally, this novel synthetic analogue (KaY-1(R24Q)) was able to activate the calcitonin receptor in nanomolar range. This work will serve as a starting point for the development of an oral sCT drug.

Poster no. P_BCM_05

NMR investigation of WIP/WASP complexes suggests a structure-based therapeutic approach to Wiskott Aldrich syndrome

I. Sasson, A. Halle-Bikovski, I.Sher, J. Chill

Department of Chemistry, Bar-Ilan University Ramat Gan

E-mail: jordan.chill@biu.ac.il, inna.sasson@biu.ac.il

Wiskott-Aldrich syndrome (WAS) is an X-linked primary immunodeficiency caused by mutations in the Wiskott-Aldrich syndrome protein (WASP), leading to symptoms including eczema, thrombocytopenia, and immunosuppressive neutropenia. An important regulator of WASP is WASP-Interacting Protein (WIP), a 503-residue intrinsically disordered protein (IDP). The interaction between the WIP C-terminal domain and WASP N-terminal EVH1 domain is essential for the immune response because WIP localizes WASP and protects it from degradation [1]. In our group, co-expression of WASP (20-158) and WIP (442-492) fragments allowed structural determination of a natively folded complex [2].

Here we present a final structure of the complex deciphered using NMR methods based on NOESY- and RDC-derived constraints. The WIP-derived peptide wraps around the WASP pleckstrin homology domain and interacts with it via four short structural elements, including a newly identified segment that protects WASP from degradation. We then hypothesized that molecular factors causing WAS could be determined by structural characterization of complexes containing a WAS-causing mutation. We have produced and characterized an array of complexes with pathogenic and benign single-residue mutations spanning different regions of WASP. Based upon our new structure, and placing an emphasis on the WIP/WASP interface (Figure 1), we find a direct relationship between the observed spectral changes (reflecting structural changes) and patterns of disease severity. Our results demonstrate the power of NMR to follow the biological consequences of protein-protein interactions in health and disease and lay the groundwork for ongoing efforts in personalized therapeutic approaches to WAS.

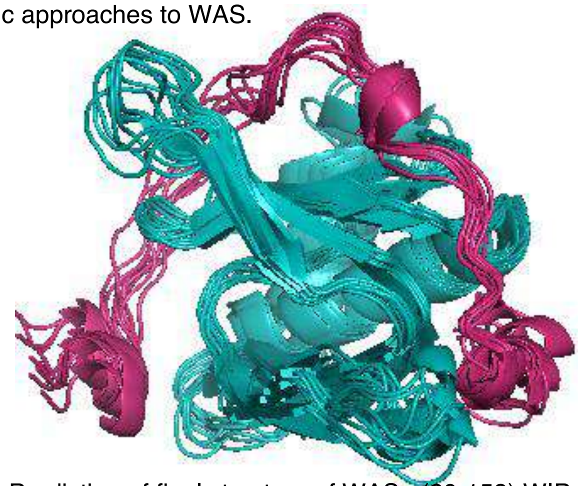


Figure 1. Prediction of final structure of WASp (20-158) WIP (440-492)

Acknowledgements: We thank Drs. Keren Keinan-Adamsky, Hugo Gottlieb and Michal Afri for spectrometer maintenance support, and the ISF (964/2019) for funding this project.

References:

1. Sasahara, Y. et al, Mechanism of recruitment of Wasp to the immunological synapse and of its activation following TCR ligation, Mol Cell 10, 1269-1281 (2002).
2. Halle-Bikovski, Fried et al., New structural insights into formation of the key actin regulating WIP-Wasp complex determined by NMR and molecular imaging. ACS Chem Biol 13, 100-109 (2018)

Poster no. P_BCM_06

Topical hemostatic agents aiming hemorrhage control synthesized from inorganic (chicken eggshells) and organic biomass(pectin biopolymer) feedstocks: An in vitro study case of the transition metal nanoparticles

Guilherme de Paula Guarnieri[a], Guilherme Molinari Sacco[a], Jose. E.F.Souza[a], Arthur L. Barbosa[b], Margarete T.G. Almeida[b] and José Geraldo Nery*[a]

[a] Physics Department, São Paulo State University - UNESP, São José do Rio Preto-SP, CEP 15054-000, Brazil. [b] Dept. of Dermatological, Infectious, and Parasitic Diseases, São José do Rio Preto School of Medicine (FAMERP), São José do Rio Preto, CEP 15090-000, Brazil

E-mail: geraldo.nery@unesp.br

Hemorrhage, or uncontrolled bleeding, remains the leading cause of preventable death for 30–40% of six million trauma victims annually, half of whom die before reaching the hospital. Without intervention, trauma-associated hemorrhage induces systemic responses and manifests as acute trauma of coagulopathy associated with fibrinolysis, platelet dysfunction, and hemostatic dysregulation. Consequently, both military and civilian health care providers face the challenge of providing rapid and effective hemorrhage control [1]. In this study several topical hemostatic agents based on pectin biopolymer and microporous zeolites derived from chicken eggshells were synthesized and characterized by X-ray diffraction (XRD), Scanning Electronic Microscopy (SEM), Phase Contrast Microscopy, Infrared spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) and Solid State ^{13}C MAS NMR. The hemostatic action of the prepared pectin biofilms and the calcium enriched zeolites were analyzed by Thromboelastography (TEG) and both materials were able to promote a shorter clot formation time and superior maximum clot strength higher to the similar commercial ones available in the market. The experimental values obtained for the enriched calcium zeolites concerning the clot formation time (R) and a higher maximum clot strength (MA) were R=1,8 min and MA = 52,1 mm which were comparable to the QuikClot (R = 2,7min, MA = 47,5mm), a commercial hemostatic based on zeolitic structure[2]. Hemostatic action of the biofilms is as effective as that of the pectin hybrid materials reported in the literature [3]. Antimicrobial of the as the made hemostatic agents were studied by incorporating into the pectin biofilms and the zeolites structures with both oxide and metal inorganic nanoparticles such as bismuth, nickel, copper, cobalt, zinc, silver and cerium. Experimental results have showed that the hemostatic agents modified with these nanoparticles were very effective in controlling *Streptococcus mutans* (*S. mutans*). *E. coli* and *P. aeruginosa, S. aureus and Bacillus subtilis (B. subtilis).* These preliminary results indicate a synergistic correlation between the hemostatic action and the antimicrobial activities of materials prepared with abundant and cheap biomass feedstocks with both concomitant capacity of stopping severe bleeding and inhibit microbial growth.

Acknowledgements: We thank The São Paulo Research Foundation (FAPESP), and he National Council for Scientific and Technological Development (CNPq) have supported this work.

References:

1. Santisteban, O. A., Sacco, G. M., Guarnieri, G. D. P., de Godoy, M. F., de Azevedo, E. R., & **Nery, J. G**. (2022). Syntheses of novel topical hemostatic agents based on pectin biopolymer aiming hemorrhage control: Thromboelastographic studies and non-homogeneous swelling effect. *Materials Today Communications*, *33*, 104989.
2. Laurenti, J. B., Zazeri, G., Povinelli, A. P. R., de Godoy, M. F., Braile, D. M., da Rocha, T. R. F., ... & **Nery, J. G**. (2017). Enhanced pro-coagulant hemostatic agents based on nanometric zeolites. *Microporous and Mesoporous Materials*, *239*, 263-271.

3.Chang, L., Chang, R., Liu, X., Ma, X., Chen, D., Wang, Y., ... & Qin, J. (2022). Self-healing hydrogel based on polyphosphate-conjugated pectin with hemostatic property for wound healing applications. *Biomaterials Advances*, *139*, 212974.3. Chang, L., Chang, R., Liu, X., Ma, X., Chen, D., Wang, Y., ... & Qin, J. (2022). Self-healing hydrogel based on polyphosphate-conjugated pectin with hemostatic property for wound healing applications. *Biomaterials Advances*, *139*, 212974.

Poster no. P_BCM_07

Protein-Driven Hydrogel Lenses: Transparent, Biocompatible, and pHResponsive Optical Actuators with Autonomous Focusing Capabilities

Maria Kaeek, [a] and *Luai R. Khoury* *[a]

[a] *Department of Materials Science and Engineering, Technion Institute of Technology, Haifa, Israel.*

E-mail: maria.kaeek@campus.technion.ac.il, and luaikh@technion.ac.il.

The human eye lens, an adaptable and transparent structure primarily constituted of crystalline proteins, can adjust its focal length for vision. In our study, we introduced an innovative method to emulate the biomechanics of the human lens. In the fundamental design, we utilized the aza-Michael addition reaction, which occurs between the lysine residues on the surface of bovine serum albumin (BSA) and the acrylate groups in polyethyleneglycol diacrylate (PEGDA). This reaction resulted in the formation of a lysine-functionalized BSA-PEGDA solution. Subsequent steps involved adding Lithium phenyl-2,4,6-trimethyl-benzoyl phosphinate (LAP) to the BSA-PEGDA mixture. The mixture was then exposed to UV light to initiate radical polymerization among the unbound acrylates, forming transparent BSA-PEGDA hydrogels. The resulting hydrogel samples exhibited exceptional properties, maintaining BSA's structural conformation and functionality, enhancing light transmittance, and enabling actuating capabilities. Utilizing the unique structural folding transitions of BSA and PEGDA hydrogel's transparency, we introduced a novel bilayer hydrogel actuator to explore shape-morphing behavior in response to pH variations. This actuator comprised an active BSA-PEGDA layer and a passive PEGDA layer. The bilayer hydrogel actuator demonstrated bending in acidic environments and recovery in neutral pH, attributed to swelling and stiffness behavior changes between the two layers resulting from protein folding transitions[1].

The remarkable ability of bilayer protein-polymer hydrogels to alter shape in response to external triggers, such as pH, coupled with their outstanding optical transparency, has paved the way for developing protein-driven hydrogel lenses with adjustable focal lengths. We initially used the bilayer actuator concept to create a plano-convex bilayer hydrogel lens. Immersing the lens in an acidic solution triggered a transformation into a convex-concave lens, resulting from uneven swelling caused by protein unfolding, reducing curvature radii, and altering the lens's focal length. Subsequently, immersing the lens again in the TRIS solution resulted in reduced curvature and an increase in focal length. This process demonstrated the lens's reversibility and successful recovery after each cycle and enabled us to fine-tune the lens's focal length, simulating the range of a human lens[2].

The presented biocompatible lenses offer a unique combination of transparency and shape-memory behavior, paving the way for the design of autonomous and responsive optical systems. Integrating protein-diverse biochemistry, folding nanomechanics, and polymer engineering creates novel opportunities to leverage a broad spectrum of proteins. This could lead to improvements in diagnostics, lab-on-chip tech, and bio-optics for deep-tissue applications, expanding our knowledge of using biomaterials in optics.

References:

1. KHOURY, Luai R.; POPA, Ionel. Chemical unfolding of protein domains induces shape change in programmed protein hydrogels. *Nature communications*, **2019**, 10.1: 5439..
2. KAEEK, Maria; KHOURY, Luai R. Toward Tunable Protein-Driven Hydrogel Lens. *Advanced Science*, **2023**, 10.36: 2306862.

Poster no. P_BCM_08

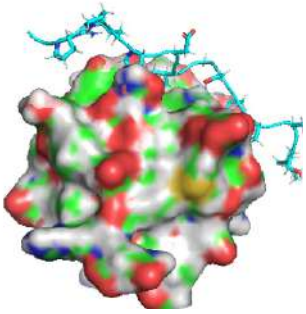
Stopping metastasis through Cortactin-SH3 inhibitors

Miriam Gulman, Jordan Chill, Dan T Major

Bar-Ilan University, Ramat Gan, Israel
E-mail: drorimi2@biu.ac.il

Cortactin is located in the cytoplasm of cells and is important for the polymerization and rearrangement of the actin cytoskeleton. When activated, it stabilizes nucleation sites for actin branching and is important for lamellipodia formation, invadopodia formation, cell migration, and endocytosis. Cortactin SH3 domains are .activated by the binding of proline-rich peptides or protein segments with a trademark “PXXP” motif

Our goal in this project is to discover peptides with high affinity to the cortactin SH3 domain capable of out-competing native binding segments, thus blocking cortactin activation. To achieve this we employ a combination of NMR-based and computational approaches. Initially, 2D-HSQC spectra are acquired along a titration curve to determine peptide affinities, and 3D ^{13}C-edited NOESY spectra provide proton-proton proximities translated into structural restraints for computational docking tools. These restraints form the input for the High Ambiguity Driven DOCKing (HADDOCK) program, which uses these to run a restrained molecular dynamics protocol and find the optimal orientation of a given peptide in the SH3 binding groove. HADDOCK is also used for screening peptides *in silico* to guide us in our choice of peptides for experimental testing. Our work is expected to lead to promising peptides that will be able to inhibit the binding interaction between .cortactin and SH3 and thus stop metastasis in breast cancer cells



S. Das, M. Shimshi, K. Raz, N. Nitoker Eliaz, A. Mhashal, T. Ansbacher, & D. T. Major. *J. Chem. Theory Com- [1] .put.*, **(2019)**, *15*(9), 5116–5134

S. Twafra, C. Sokolik, T. Sneh, K. Srikanth, T. Meirson, A. Genna, J.H Chill, & H. Gil-Henn. **2022**, *Oncogene*. [2] .2023;42(4):278-292

.K. Saksela, P. Permi. *FEBS Lett.*, **2012,** 586(17):2609-2614 [3]

Poster no. P_BCM_09

Positively charged purines: A novel and facile route for PNA delivery

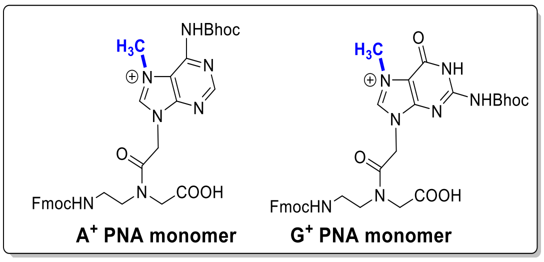
Salam Maree, Eylon Yavin*

The Institute for Drug Research, The School of Pharmacy, The Hebrew University of Jerusalem, Hadassah Ein-Kerem, Jerusalem 91120, Israel.
E-mail: Salam.Maree@mail.huji.ac.il
* E-mail: eylony@ekmd.huji.ac.il

Oligonucleotides have caught much attention in recent years due to their great contribution in molecular biology procedures, genetic diagnostics, and antisense therapies. Peptide Nucleic Acid (PNA) is a synthetic oligonucleotide with a neutral pseudo-peptide backbone and high structure resemblance to DNA and RNA. PNA binds DNA and especially RNA with affinity greater than that of the native nucleic acid and highly discriminates between targeted and non-targeted DNA/RNA sequences.[1]

PNA has several advantages over other DNA analogs such as resistance to nucleases/peptidases (due to its uncharged backbone) and high affinity to complementary RNA. However, PNAs suffer from poor cellular uptake into cells and tissues. Currently, PNA delivery relies on either backbone modification of the PNA to introduce a positive charge (GPNA and γGPNA) or using a cell penetrating peptide (CPP).

N-7 Methylation of guanine and adenine PNA monomers produces a positively charged nucleobase which suppresses the formation of self-duplexes whilst improving DNA affinity through electrostatic interactions.[2] In this work we have designed and synthesized PNA sequences with multiple charged purines (G+ and A+). We also synthesized the same PNA sequence with a short CPP consisting of either 4 or 6 D-lysines to serve as control. Premilitary studies showed that introducing 6 positively charged purines into a PNA sequence resulted in efficient cellular uptake in OVCAR8 cells. In summary, this approach provides cell permeable PNAs in a very simple and straightforward manner.



Scheme 1 Chemical structures of G^+ and A^+ PNA monomers.

References:

1. Nielsen, P.E., Egholm, M., Berg, R.H. and Buchardt, O., 1991. Sequence-selective recognition of DNA by strand displacement with a thymine-substituted polyamide. *Science*, *254*(5037), pp.1497-1500.
2. Hibino, M., Aiba, Y. and Shoji, O., 2020. Cationic guanine: Positively charged nucleobase with improved DNA affinity inhibits self-

Poster no. P_BCM_10

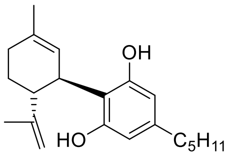
Design, synthesis, and characterization of novel hybrid cannabidiol: highly potent agents toward AAPH and Cu^{2+} -induced LDL oxidation

Eliav Peretz [a] and Sanaa Musa*[a]

[a] *Natural Compounds and Analytical Chemistry Laboratory, Migal- Galilee Research Institute and Tel-Hai academic college, Qiryat Shmona, Israel.*

E-mail: sanaa@migal.org.il

Natural product-based medicine plays a pivotal role in medicinal aspects, emphasizing the exploration of natural components found in medicinal plants as a fundamental basis for creating innovative bioactive compounds. In our research, we focus on a natural source of cannabidiol (**CBD**), a well-studied non-psychotropic component of plant-derived cannabinoids that has shown significant therapeutic potential for various diseases and disorders, including antioxidants and anti-inflammatory effects [1, 2].



(-)- Cannabidiol (CBD)

CBD's antioxidant capacity depends on the presence of the resorcinol group, responsible for transferring hydrogen atoms or electrons to the oxidants. Additionally, the limonene ring and the n-pentyl moiety contribute to the stability of the cation free radical or its semiquinone forms [2]. The antioxidant properties of the phytocannabinoids, including their ability to prevent Low-density lipoprotein (LDL) – oxidation, have been previously reported [3]. Studies have indicated that **CBD** can prevent the formation of conjugated dienes during LDL oxidation by extending the lag phase of the initial stages, albeit with moderate activity [4].

Herein, we describe the design and synthesis of novel hybrid derivatives based on the cannabidiol framework. These derivatives have demonstrated strong antioxidant properties against AAPH and Cu^{2+}-induced LDL oxidation.

References:

[1] Atalay, S., Jarocka-Karpowicz, I., and Skrzydlewska, E. (2020) Antioxidative and Anti-Inflammatory Properties of Cannabidiol, *Antioxidants 9*, 21.
[2] Borges, R. S., and da Silva, A. B. F. (2017) Chapter e12 - Cannabidiol as an Antioxidant, In *Handbook of Cannabis and Related Pathologies* (Preedy, V. R., Ed.), pp e122-e130, Academic Press, San Diego.
[3] Singla, S., Sachdeva, R., and Mehta, J. L. (2012) Cannabinoids and atherosclerotic coronary heart disease, *Clinical Cardiology 35*, 329-335.
[4] Musetti, B., González-Ramos, H., González, M., Bahnson, E. M., Varela, J., and Thomson, L. (2020) Cannabis sativa extracts protect LDL from Cu2+-mediated oxidation, *Journal of Cannabis Research 2*, 37.

Poster no. **P_BCM_11**

Leveraging Emulsification in Porous Media for Hydrogel Microparticle Synthesis

Tina Khairallah, [a] and Luai R. Khoury *[a]

[a] *Department of Material Sciences and Engineering, Technion Israel Institute of Technology, Haifa, 32000, Israel.*

E-mail: luaikh@technion.ac.il, Tinak@campus.technion.ac.il

The field of hydrogel microparticle (HMP) materials is rich and diverse. Various methods exist for HMP fabrication, including batch emulsion, microfluidics, fragmentation, spraying, lithography, and centrifugation-based techniques. However, these approaches often encounter size control, precision, and scalability limitations, and challenges can arise regarding assembly, cost-effectiveness, and compatibility with sensitive biomolecules [1]. Emulsification through a porous medium to synthesize functional hybrid protein-polymer HMPs has yet to be addressed. Here, we introduce an innovative approach capitalizing on mixing phases using centrifugation as the driving force to emulsify two immiscible fluids within 3D heterogeneous porous media for optimal droplet production. The resulting emulsion droplets can be subjected to various crosslinking mechanisms, forming HMPs.

We successfully synthesized responsive hybrid protein-polymer HMPs in various sizes, ranging from small and monodisperse to large and polydisperse droplets (5.97 ± 0.05 to 19.37 ± 0.33 μm), by modifying lysine residues of bovine serum albumin with polyethylene glycol diacrylate (PEGDA) via an aza-Michael addition reaction [2]. These HMPs demonstrate dynamic behavior responding to pH variations and denaturing chemicals through (un)folding mechanisms. Preserving protein structural integrity and functionality enabled the formation of cytochrome c (cyt c) - PEGDA HMPs, which are suitable for biosensing applications. When these HMPs encounter oxidizing agents like hydrogen peroxide (H_2O_2), the heme group of cyt c undergoes oxidation, resulting in observable differences in the absorption spectra. To assess the reversibility of electron transfer, the HMPs were exposed to H_2O_2, followed by reduction by ascorbic acid, showcasing cyt's efficacy in reversible electron transfer across oxidation and reduction states within the HMPs. This unique attribute makes cyt c highly useful in biomedical applications, where changes in its absorption spectrum can serve as a sensing signal for H_2O_2.

The flexibility of our system is demonstrated by its ability to efficiently synthesize HMPs using low volumes (~50 μL) and concentrations (100 mM) of proteins, achieving results within minutes while preserving proteins' structural and functional properties. Additionally, the capability of our method to produce a diverse array of HMP types, such as synthesizing alginate-based HMPs through physical crosslinking, enriches the palette of HMP fabrication techniques, presenting it as a cost-effective, biocompatible, and scalable alternative for various biomedical applications, such as controlled drug delivery, 3D printing bio-inks, biosensing devices, with potential implications even in culinary applications.

References:

1. DALY, Andrew C., et al. Hydrogel microparticles for biomedical applications. Nature Reviews Materials, 2020, 5.1: 20-43.
2. KAEEK, Maria; KHOURY, Luai R. Toward Tunable Protein-Driven Hydrogel Lens. Advanced Science, 2023, 10.36: 2306862.

Poster no. P_BCM_12

Toward metal-free catalytic antibiotics

Tomasz Pieńko*[a], Moshe N. Goldmeier [a], Alina Khononov [a], Valery Belakhov [a], Timor Baasov [a]

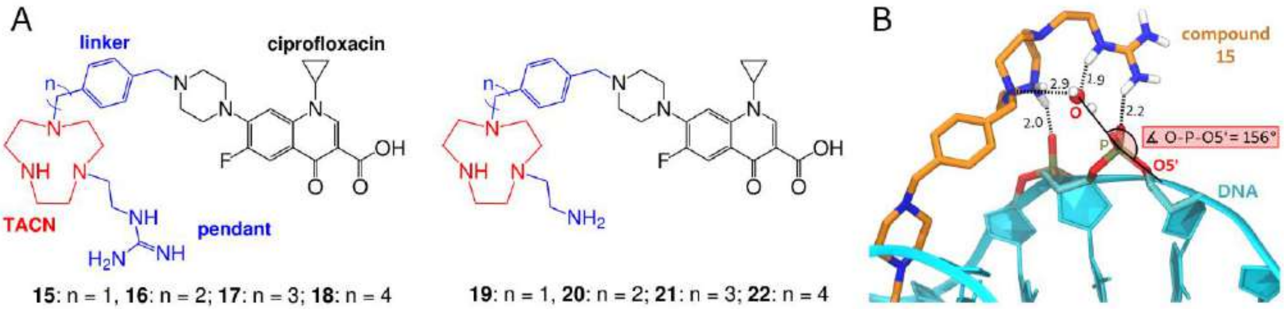
[a] *Edith and Joseph Fischer Enzyme Inhibitors Laboratory, Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel*

E-mail : tomaszp@campus.technion.ac.il

The increasing resistance of bacteria to conventional antibiotics has prompted innovative approaches to combat pathogenic bacteria. One promising strategy is the development of catalytic antibiotics, which not only bind to their target molecules but also deactivate them through catalytic breakdown. This allows each catalytic drug molecule to impact on multiple target macromolecules over time, potentially reducing the drug's therapeutic doses, minimizing its side effects, and mitigating the emergence of resistance.

We applied the concept of catalytic antibiotics to fluoroquinolones, which inhibit bacterial DNA topoisomerases. Ciprofloxacin was modified with a catalytic warhead designed to cleave DNA phosphodiester bond at the binding site within the DNA-topoisomerase complex. Initially, we utilized complexes of cyclen with Cu(II) and Co(III) as the warheads in the first two generations of conjugates. While the first generation of Cu(II) complexes exhibited promising DNase activity *in vitro*, they were vulnerable to various endogenous nucleophiles under physiological conditions[1]. Therefore, in the second generation, we introduced amine and guanidine pendants on the cyclen moiety to protect the metal center. While for the Cu(II) complexes, they were ineffective due to their high pK_a, for the Co(III) complexes, an amine arm protected the metal ion under cellular conditions and enhanced their DNase activity[2]. However, the high positive charge of the Co(III) complexes made them strongly bound to DNA, hindering their catalytic performance.

To potentially improve catalytic activity and address the vulnerability of Cu(II) complexes by reducing the pK_a of the pendants, we synthesized the third generation of ciprofloxacin conjugates with TACN armed with guanidine (compounds **15**-**18**) or amine (**19**-**22**) pendants (Figure 1A). Among these, the amine derivatives, notably **20**-Cu(II), demonstrated excellent DNase activity *in vitro* but lost efficacy under cellular conditions. However, we were pleased to discover that compound **15**, in its metal-free form, exhibited robust DNase activity unaffected by experimental conditions and significant antibacterial activity. We verified that the mechanism of DNA cleavage by **15** does not rely on metal ions, and we suggested its molecular pathway by employing docking, molecular dynamics, and quantum mechanics-molecular mechanics (QM-MM) simulations (Figure 1B). We discuss the structure-activity relationship of the compounds studied and provide mechanistic insights to guide the rational design of catalytic antibiotics with DNase activity with no metal involvement.



15: n = 1, **16**: n = 2; **17**: n = 3; **18**: n = 4

19: n = 1, **20**: n = 2; **21**: n = 3; **22**: n = 4

Figure 1: A) Third-generation ciprofloxacin conjugates with TACN armed with guanidine (**15**-**18**) and amine (**19**-**22**) pendants. B) In-line nucleophilic attack of water coordinated by compound **15** at the DNA phosphodiester bond, represented by the O-P-O5' angle.

References:

1. Goldmeier, M. N.; Katz, S.; Glaser, F.; Belakhov, V.; Khononov, A.; Baasov, T. Toward Catalytic Antibiotics: Redesign of Fluoroquinolones to Catalytically Fragment Chromosomal DNA. *ACS Infect. Dis.* **2021**, *7(3)*, 608–623.
2. Goldmeier, M. N.; Khononov, A.; Belakhov, V.; Pieńko, T.; Orbach, N.; Gilad Barzilay, Y.; Baasov, T. Dynamic Intramolecular Cap for Preserving Metallodrug Integrity—A Case of Catalytic Fluoroquinolones. *J. Med. Chem.* **2022**, *65(20)*, 14049-14065.

Poster no. P_BCM_13

Trypsin-induced BSA-PEGDA Hydrogels for Actuation and Drug Delivery

Yuchen LIU [a], Luai R Khoury* [a]

[a] *Department of Materials Science and Engineering, Technion-Israel Institute of Technology, Haifa, Israel.*

E-mail: (yuchen.liu@campus.technion.ac.il, luaikh@technion.ac.il.)

Developing smart, responsive, shape-morphing protein-polymer hybrid hydrogel drug delivery systems is fascinating. They can release drugs precisely under specific stimuli and influence the drug release process through shape change, ultimately achieving an active, advanced soft robotic drug carrier. However, these remain a challenge. Our approach involves functionalizing the free amino groups of lysine amino acids on the surface of bovine serum albumin (BSA) to react with the vinyl groups of poly(ethylene glycol) diacrylate (PEGDA) via a Michael addition reaction forming covalent bonds [1]. This mixture is mixed with APS and TEMED, creating a hydrogel via free radical polymerization [2]. We found that these hydrogels exhibit tailored behavior in their mechanical and physical properties and microstructure by adjusting the concentrations of the hydrogel components and their reaction with trypsin. The swelling and mechanical behavior alterations upon trypsin digestion (0.01% and 0.25% w/v) have enabled us to engineer hydrogels that automatically untie knots and induce shape-morphing behavior in arc-shaped bilayer actuators, demonstrating their outstanding shape transformation capabilities. In addition, leveraging the biochemical structural diversity of BSA allowed us to load fluorescein isothiocyanate (FITC), a model drug, on its surface and use it as a carrier for small molecule drugs, significantly enhancing the hydrogel's functionality as a dynamic drug delivery system. By forming a FITC-BSA-PEGDA hydrogel, we discovered that the hydrogels efficiently regulate the release of FITC, showcasing their capability for highly targeted drug delivery, especially in the gastrointestinal tract. Furthermore, we revealed that the drug release rate can be precisely adjusted by modifying trypsin concentrations and altering the hydrogel's cross-linking density. Our findings indicated that erosion and diffusion are the primary mechanisms driving drug delivery from our hydrogel, as indicated by the Korsmeyer-Peppas model analysis [3]. These changes are primarily due to the enzymatic degradation of BSA in the hydrogel matrix. More interestingly, integrating shape-morphing behaviors with drug release capabilities to develop a soft robotic drug carrier demonstrated a significant influence of shape transformation on drug release rates at physiological trypsin concentrations. In conclusion, our research provides a novel perspective on developing advanced soft robotic drug carriers and opens new avenues for responsive biomedical engineering devices.

References:

1. Kaeek M, Khoury L R. Toward Tunable Protein-Driven Hydrogel Lens[J]. Advanced Science, 2023, 10(36): 2306862.
2. Orakdogen N, Okay O. Influence of the initiator system on the spatial inhomogeneity in acrylamide-based hydrogels[J]. Journal of applied polymer science, 2007, 103(5): 3228-3237.
3. Rabeh M E, Vora L K, Moore J V, et al. Dual stimuli-responsive delivery system for self-regulated colon-targeted delivery of poorly water-soluble drugs[J]. Biomaterials Advances, 2024, 157: 213735
.

Chemical Education

Poster no. P_CE_01

From Glass to Gold: Grasping Abstract Concepts of Self-Assembly Methodologies in a Laboratory Experiment

Noach Treitel, [a] Einat Kohn[b] and Ruthy Sfez*[a]

[a] Materials Engineering department, Azrielli College of Engineering, Jerusalem, Israel, 9103501. [b] Department of Neurology, Brain Division, Shaare Zedek Medical Center, Jerusalem 9103102.

E-mail: ruti@jce.ac.il

Nanothecnology plays a pivotal role in contemporary engineering, finding expression in diverse applications that leverage surface-chemistry modifications to create tailored 2D-nanolayers. It is crucial for today's engineering student to not only grasp but also appreciate the construction and characterization of these monolayers through hands-on experiences in the laboratory. In this context, we propose an experiment designed for third year materials engieering students, focusing on the fabrication of Self-Assembled Monolayers (SAM) using two methodologies: Self assembly (SA) and Electrostatic Self Assembly (ESA). Additionally, the studnts are introduced to the distinctive optical properties of gold nanoparticles (AuNP) and to electroless deposition principles. During the lab session students are engaged in the SA process on two distinct substrates: hydroxyl-terminated glass and an electrolessly deposited gold film. Each substrate undergoes a surface modification with a specific coupling agent featuring a relevant head group, such as alkoxysilane on glass and thiols on the gold layer. Between these two steps, the ESA methodology, involving the sequential deposition of negatively charged Au-NP and positively charged polyethyleneimine (PEI) bilayers is systematically demonstrated (**Figure 1**). All synthetic steps are characterized through contact angle and UV-Vis measurments. In the spectroscopic analysis, the results clearly depict the aggregation process that occurs with each added bilayer. As anticipated, absorbance in the visible range is directly correlated to the number of the AuNP/PEI bilayers, accompanied by a distinct red shift and broadening upon each bilayer addition due to size dependence properties of the AuNP. The contact angle measuremnts give some insight on the wettability and homogenity of the layers, resulting in a major change of the contact angle especially upon the introduction of the coupling agents, both on glass and gold substartes.

This experiment offers several key advantages. It not only familiarizes the students with SA and ESA methods, showcasing the relative ease with which these techniques yield SAMs, but also highlights the immediate applicative potentials of the obtained layers. The immediate analyses conducted after each synthetic step enables the students to witness and evaluate the practical outcome. The use of Au-NP in the ESA process give the great advantage of naked eye vizualisation of layers construction and monitoring due to the visible color changes which is correlated to number of bilayers, broadening and red shift which occurs in the nanometric regime. Together with the contact angle trends which are easily discerned, the student learning outcome after the lab session consists of a comprehensive underdtanding of SA and ESA concepts across different substrates and technologies, along with size dependence properties of the adsorbed nano-layers.

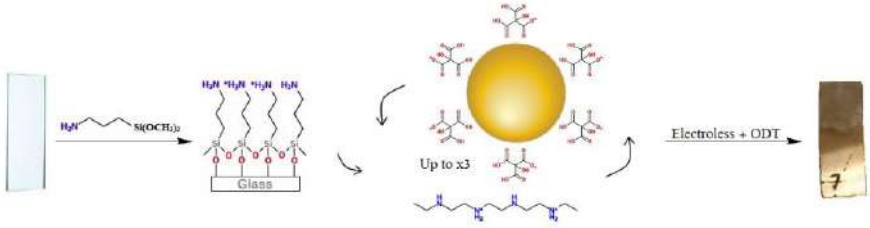


Figure 1: Schematic synthetic multi assembly steps of the experiment.

Referentes: 1. Treitel, N.; Kohn, E.; Sfez, R. From Glass to Gold: Visualization of Electrostatic Self-Assembly of Au-NPs. *J. Chem. Educ.* **2023**, *100*, 835–843.

Electrochemistry

Poster no. P_EC_01

An approach to Electrochemical Ammonia synthesis using Concentrated Electrolytes

M.C. Achyuth[a], H. Teller[a} and A. Schechter*[a,b]

[a] *Department of Chemical Sciences, Ariel University, Israel*

[b]*Research and Development Centre for Renewable Energy, New Technology Centre, University of West Bohemia, Czech Republic.*

E-mail: (salex@ariel.ac.il)

The Haber-Bosch process (HBP) is undoubtedly one of the most important inventions of the 20th century. An industrial-level ammonia production has helped to sustain global population growth. Yet, its drawbacks, notably the substantial energy demand and carbon footprint, loom large in the contemporary context of climate change and global warming. Consequently, there's a pressing demand for an energy-efficient and carbon-neutral alternative for ammonia synthesis. Two primary avenues of exploration have emerged: electrochemical nitrogen reduction (ENRR) to ammonia and photocatalytic ammonia synthesis. Additionally, efforts are underway to develop a "green" variant of the HBP, where ammonia is synthesized using green hydrogen at lower temperatures and pressures. Our research primarily focuses on electrochemical nitrogen reduction to ammonia at ambient conditions. Although the reaction (Equation 1) is sluggish and poorly selective towards ammonia, many catalysts have been developed and tested for ENRR to improve the rate of ammonia formation and efficiency. However, there's a noticeable gap in research concerning electrolytes. This research narrows down on electrochemical nitrogen reduction to ammonia with Water in salt-type electrolytes of $CaBr_2$ and $MgBr_2$. Their high solubility for nitrogen gas, which was tested and shown higher value compared to aqueous electrolytes, and low water concentration due to the formation of solvated ions is expected to show improved ammonia formation rate and Faradaic Efficiency. Also, at the anode, the oxidation of bromide to bromine, which occurs at a lower potential than that of water oxidation, helps to reduce the anodic potential. Preliminary results with Pt: Ru (1:1)[1] alloy as the catalyst have shown improved rate and efficiency compared to the catalytic activity in aqueous electrolytes with a maximum rate of 80.52 μg $h^{-1}cm^{-2}$ at -0.35 V vs RHE and a maximum Faradaic Efficiency of 13.72% at -0.15 V vs RHE. Further optimization and expanding studies into other concentrated electrolytes and better catalysts will pave the way for a better rate of ammonia formation and Faradaic Efficiency.

$$N_{2(g)} + 6H^+ + 6e^- \xrightarrow{\hspace{2cm}} 2NH_{3(aq)} \qquad E^0 = 0.092 \text{ V vs RHE} \qquad (1)$$

Acknowledgements: I thank Ariel University and the ICS.

References:

1. Manjunatha, R.; Schechter, A., Electrochemical synthesis of ammonia using ruthenium–platinum alloy at ambient pressure and low temperature. *Electrochemistry Communications* **2018,** *90*, 96-100.

Poster no. P_EC_02

Hydroxylamine Oxidation on Carbon and Fe-doped carbon Electrocatalysts

Amit Hadar *[a], Inbal Offen Polak [a] and David Eisenberg [a]

a Schulich Faculty of Chemistry, the Resnick Sustainability Center for Catalysis, and the Grand Technion Energy Program,

Technion – Israel Institute of Technology, Haifa 3230003, Israel

E-mail: Amit.hadar@campus.technion.ac.il

Hydroxylamine (NH_2OH) plays an important role in the semiconductor, chemical, and pharmaceutical industries. It is used as a solvent in microchip production to remove organic and inorganic impurities from wafers and as an important feedstock for dyes, rust inhibitors, and products such as painkillers, antibiotics, and tranquillizers [1]. Additionally, hydroxylamine is a possible intermediate in ammonia electro-oxidation reaction. Thus, studying its oxidation reactions is crucial in the alternative fuel industry [2]. However, hydroxylamine is unstable in room temperature with respect to a disproportionation reaction, which complicates any investigation of its oxidation reaction.

Herein we used a single-layered graphene (SLG) and an Fe-N doped SLG based on phthalocyanine (Fe-Pc-SLG) as catalysts for the hydroxylamine oxidation. When studied by cyclic voltammetry, both catalysts presented oxidation peaks with onset potential of 0.6 V vs. RHE at pH=14, 100mV advance in the onset potential of Platinum. Moreover, we found SLG needs to be activated by a reduction process before the addition of hydroxylamine, while the Fe-based catalyst can oxidize the Hydroxylamine without being activated. The mechanism of the hydroxylamine oxidation will be discussed, considering its chemical degradation.

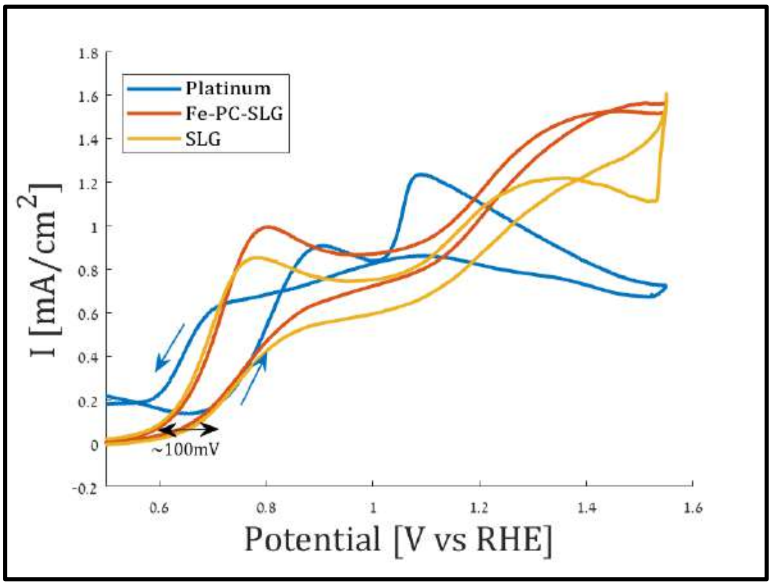


Figure 1: voltammograms of hydroxylamine (5mM) oxidation on Platinum, Fe-N doped SLG and SLG as catalysts, at 20 mV s^{-1} scan rate in Ar-purged KOH (1 M).

References:

1. Wang, Qingsheng, et al. "Thermal decomposition pathways of hydroxylamine: theoretical investigation on the initial steps." *The Journal of Physical Chemistry A* 114.34 (2010): 9262-9269.
2. Pacheco, A. Andrew, et al. "Techniques for investigating hydroxylamine disproportionation by hydroxylamine oxidoreductases." *Methods in enzymology*. Vol. 486. Academic Press, 2011. 447-463.
3. Bengtsson, Gösta, Sture Fronaeus, and Lars Bengtsson-Kloo. "The kinetics and mechanism of oxidation of hydroxylamine by iron (III)." *Journal of the Chemical Society, Dalton Transactions* 12 (2002): 2548-2552.

Poster no. P_EC_03

Co-Cu Spinel Catalysts as Electrocatalysts for Ammonia Oxidation

Annie Cleetus, Hanan Teller, Alex Schechter
Department of Chemical Sciences, Ariel University

E-mail: anniecleetus2@gmail.com

In the field of electrochemical oxidation of ammonia(AOR) using fuel cells, a major drawback is the development of an electro-catalyst that efficiently oxidizes ammonia at low temperatures with a high selectivity to nitrogen, and high durability in ammoniacal solutions, to meet the emerging clean energy demands. The electrochemical activity, stability and selectivity towards ammonia oxidation (AOR) of Cu-Co based spinels prepared by co-precipitation method from their nitrate precursors have been explored in their different stochiometric ratio's. Spherical particles of varying diameter from 10-70nm in diameter with the purity of the spinel phases decreasing with the increase in Cu content was observed with further characterization using ICP, HR-SEM, PXRD and XRF. While no significant AOR activity was seen in the case of CO_3O_4; $CuCo_2O_4$ and Cu_2CoO_4 was found to show improved peak current densities (7.1mA/mg and 7.5mA/mg) towards AOR relative in a solution of 0.1M KOH and 0.1M NH_4OH. CuO even though was found to show initially high peak current density (8.4mA/mg) its stability was found to decrease gradually with time. Though less active; $CuCo_2O_4$ was found to be more stable towards AOR over 16hrs of oxidation in the same solution at AOR potential (1.1V vs RHE) [Figure 1]. Pre-oxidising the catalyst in 0.1M KOH prior to the addition of NH_4OH was found to double the initial current density but this effect was found to diminish over time. XRD of the electrodes oxidised in 0.1M KOH and in the presence of 0.1M NH_4OH shows the formation of CuO(111) phase which is found to coexist under alkaline and ammoniacal environments unlike other phases which contributes to the improved activity and stability of $CuCo_2O_4$ spinels. N_2 and nitrite were found as by-products of the process using online mass spectroscopy, UV-Vis spectroscopy and insitu-SERS techniques.

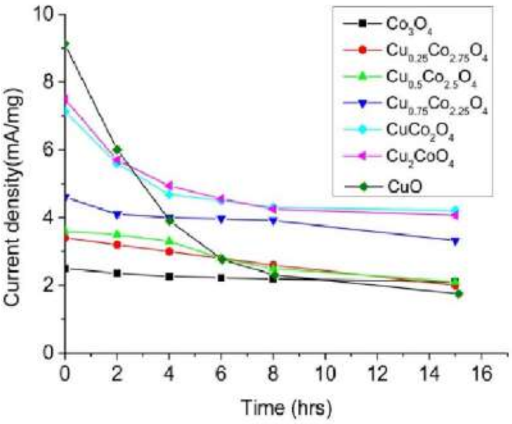


Figure 1: Variation of peak current density with time in solution of 0.1M KOH+0.1M NH_4OH over time with oxidation at 1.1V vs RHE, current density was measured at intervals using LSV (scan rate =20mV/s)

Acknowledgements: We thank Ariel University for financial support

References:

1. Shaheen, W. M., and A. A. Ali. "Characterization of solid–solid interactions and physico-chemical properties of copper–cobalt mixed oxides and CuxCo3− xO4 spinels." *Materials Research Bulletin* 36.9 (2001): 1703-1716.

Poster no. P_EC_04

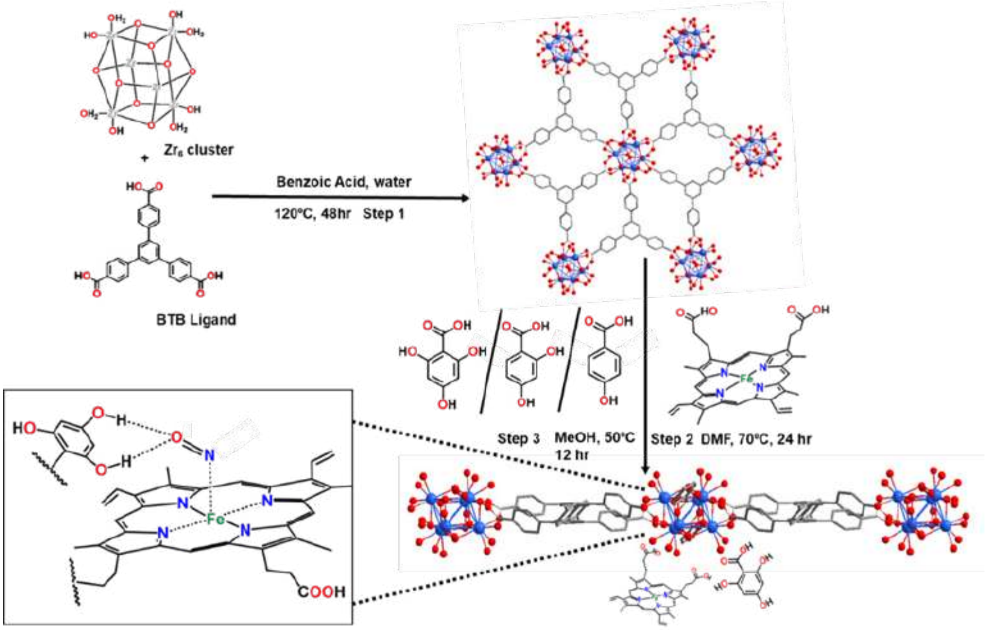
Electrocatalytic Nitrite Reduction by Fe-Porphyrin Based Metal-Organic Framework with High Rate and Selectivity in Presence of Pendant Proton Relays

Arnab Ghatak, Idan Hod*

Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel

E-mail: (ghatak@post.bgu.ac.il, hodi@bgu.ac.il)

The The challenge with six electron nitrite reduction process is selectivity as well as slow kinetics in presence of competitive hydrogen evolution reaction owing to low Faradaic efficiency (FE), and hence proper design of suitable catalyst is the need of the hour. Heme (Fe-porphyrin) embedded Zr_6-oxo based 2D MOF(Zr-BTB)[1], has been used as an efficient selective nitrite reduction catalyst, taking advantage of the chemical robustness and mass transport properties of the MOF, where for the first time in MOF system post synthetic tethering with hydroxy benzoic acid is done to mimic the H-bond donor ability and proton translocation of the Tyr residue present in the native enzyme. Generating second sphere H-bonding and proton relay interaction with the iron porphyrin in presence of MOF's inherent properties enables to achieve more than 90% selectivity in terms of FE of NH_3 from nitrite in aqueous solution under heterogeneous electrochemical condition. Spectroelectrochemical analysis shows the formation of reactive intermediate Fe bound NO during the course of the reaction, which gets stabilized in presence of hydroxy groups to increase the rate (~5 times) and selectivity (>30%). This depicts an alternative NH_3 synthesis method with clean reagent from wastewater nitrite having high selectivity and reactivity.



Scheme 1: Schematic illustration of the synthesis of Zr-BTB MOf with the post synthetic modification by Heme and hydroxybenzoic acids. The second sphere -OH interaction with potential intermediate is shown in the zoomed in figure.

Acknowledgements: We thank Ben-Gurion University and ERC grant for funding and instrument facilities

References:

1. Shimoni, R.; Shi, Z.; Binyamin, S.; Yang, Y.; Liberman, I.; Ifraemov, R.; Mukhopadhyaya, S.; Zhang, L.; Hod, I. Electrostatic Secondary-Sphere Interactions That Facilitate Rapid and Selective Electrocatalytic CO_2 Reduction in a Fe-Porphyrin-Based Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2022**, *61* (32) e202206085.

Poster no. P_EC_05

A Simple Laser Exfoliation Boosts 2D MXene Supercapacitor Performances

Asmita Dutta [a], Arie Borenstein [a]*

[a] - Department of Chemical Sciences, Ariel University, Ariel, Israel

* Corresponding author. Email: arieb@ariel.ac.il

MXenes-based compounds, particularly $Ti_3C_2T_x$, have been studied intensively as electrodes for supercapacitors due to their layered structure and high conductivity, enabling facile ion diffusion and charge transfer. However, tight restacking of the 2D layers in these materials limits their practical, accessible surface area, impeding their capacity and rate capability performance. To mitigate this phenomenon, we present a new approach using a processing method based on laser beam irradiation to modify $Ti_3C_2T_x$ films. We found that the laser treatment induces chemical and morphological changes, ultimately optimizing the stacking arrangement of the MXene electrodes and consequently enhancing their capacity in both neutral and acidic electrolytes. Furthermore, the laser-modified MXene electrodes demonstrate excellent rate capabilities, showing 84% retention at extreme rates of 0.5 V compared to only 33% of the original $Ti_3C_2T_x$ electrodes. Finally, we discuss the chemical and physical changes induced by the laser treatments and their influence on the electrochemical behavior of the lasered MXene described briefly in Figure 1. The principles of laser exfoliation discovered in this study can be implemented in broader 2D materials for various applications.

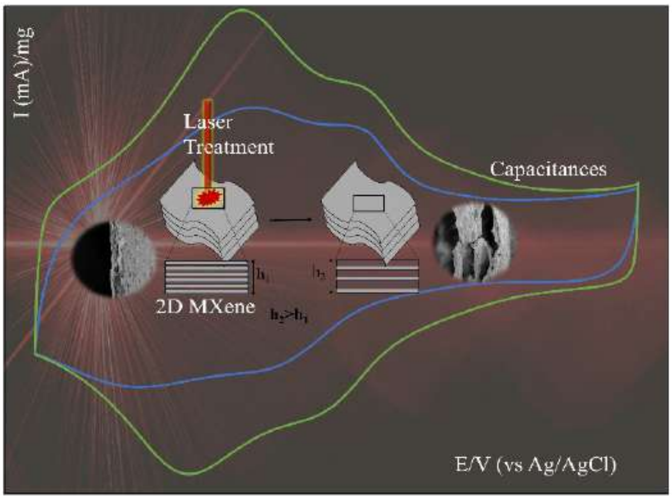


Figure 1: Illustration of Laser treatment on 2D $Ti_3C_2T_X$ MXene for exfoliation and their influence on the electrochemical behavior.

Acknowledgments: We thank ICS for financial support and for organizing such scientific meetings to expand knowledge by presenting our work.

Poster no. P_EC_06

Real-Time Surface Study of Ni as Catalyst during Oxygen Evolution Reaction (OER) via Ambient Pressure X-Ray Photoelectron Spectroscopy (AP-XPS)

Bat-Or Shalom,[a] Miguel A. Andrés,[a] Ashley R. Head,[b] Olga Brontvein,[c] Alex S.Walton,[d] Kacper Polus,[d] Boruch Z. Epstein,[d] Robert S. Weatherup,[e], Baran Eren,*[a]

[a] Department of Chemical and Biological Physics, Weizmann Institute of Science, 234 Herzl Street, 76100 Rehovot, Israel. [b] Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton 11973, New York, United States. [c] Chemical Research Support, Weizmann Institute of Science, 234 Herzl Street, 76100 Rehovot, Israel. [d] Photon Science Institute, and the Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom. [e] Department of Materials, University of Oxford, Parks Road, Oxford, Oxfordshire, OX1 3PH, United Kingdom.

E-mail: baran.eren@weizmann.ac.il

Oxygen Evolution Reaction (OER) has significant importance in the fields of electrochemistry and energy conversion, being a crucial step in electrochemical water splitting, a process that is central to the development of green hydrogen as a sustainable fuel source. However, a major challenge arises in the form of sluggish kinetics during the OER process [1], preventing the realization of the technology's full potential for producing hydrogen efficiently. Nowadays, only as little as 4% is produced by water electrolysis, with the rest of its production being largely covered by the conversion of fossil fuels that concomitantly pollute [2]. Therefore, investigating OER mechanisms and catalysts is instrumental in enhancing the efficiency of water electrolysis, a key technology for hydrogen production, and subsequently, for advancing the utilization of hydrogen in fuel cells for clean energy generation. In fact, this topic appears in the list of high-priority interests of the Ministry of Energy in Israel.

In our group, we employ operando Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) to elucidate the dynamic evolution of the chemical state of nickel nanoparticles (NPs) in OER conditions. For this purpose, our group has designed a microelectrochemical cell that can be easily placed in nearly any AP-XPS system.

Our studies using an alkaline bicarbonate-carbonate buffer solution show that at the OER onset potential, $Ni2^+$ and Ni^{3+} species are observed, displacing the metallic Ni entirely. Notably, the identified species include NiO, which undergoes transformation into other Ni^{2+} and Ni^{3+} states as the potential goes above the OER onset potential. In contrast, using 20 nm thick film results in surface oxidation only, with metallic Ni being preserved within the inner layers.

Besides chemical changes, the Ni NPs undergo substantial morphological and structural changes during the OER, as confirmed by ex-situ Transmission Electron Microscopy (TEM) measurements. The amorphization of the NPs is attributed to the substantial incorporation of H_2O, evident in the considerable increase in oxygen intensity in both operando AP-XPS and ex-situ Energy Dispersive Spectroscopy (EDS) measurements.

Overall, these findings offer valuable insights into the oxidation behavior of Ni anode during OER in alkaline conditions. Our results can help in the advancement of electrocatalytic processes.

Acknowledgements: We thank the Ministry of Energy of Israel for the doctoral fellowship. Authors also acknowledge financial support from the following institutions and programs: U.S.–Israel Binational Science Foundation (BSF), the Weizmann-UK making Connections Program, the European Research Council (ERC). This research used the AP-XPS facility at Brookhaven National Laboratory (U.S.).

References:

1. Chen, D. J.; Chen, C.; Baiyee, Z. M.; Shao, Z. P.; Ciucci, F. Nonstoichiometric Oxides as Low-Cost and Highly-Efficient Oxygen Reduction/Evolution Catalysts for Low-Temperature Electrochemical Devices, *Chem. Rev.* **2015**, *115*(18), 9869-9921.
2. Stančin, H.; Mikulčić, H.; Wang, X.; Duić, N. A Review on Alternative Fuels in Future Energy System, *Renew. Sust. Energ. Rev.* **2020**, *128*, 109927.

Poster no. P_EC_07

Operando Spectroscopic Characterization of the Electrocatalytic Nitrogen Reduction Reaction

Verma Deepraj, [a] Vogt Charlotte, *[a]

[a] *Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa.*

E-mail: (c.vogt@technion.ac.il)

Ammonia (NH_3) stands as a crucial chemical compound and a carbon-free energy reservoir, extensively employed in industrial processes and agricultural applications. The prevalent method for NH_3 production, the Haber-Bosch process which needs harsh condition (*i.e.,* high temperaure, and high pressure) to overcome the energy barrier as mentioned in the equation 1, currently accounts for approximately 2% of total energy production and contributes 1.3% to global CO_2 emissions.

$$N_{2\,(g)} + 3H_{2(g)} \xrightarrow[P\,=\,100-200atm]{T\,=\,400-600℃} 2NH_{3(g)} \qquad \Delta G_{0}{}^{T\,=\,298.15K}_{P\,=\,1atm} = -\frac{16.4kJ}{mol} \qquad \text{eq. 1}$$

In pursuit of an environmentally sustainable alternative, the electrochemical nitrogen reduction reaction (NRR) has emerged as a promising solution due to its lower energy demands, as mentioned in the equation 2. However, persistent challenges arise, notably the limited Faradaic efficiency and selectivity in NH_3 production due to the inert characteristics of nitrogen molecules with triple bonds and the competing hydrogen evolution reactions.

$$N_2 + 6H_2O + 6e^- \quad \leftrightarrow \quad 2NH_{3(g)} + 6OH^- \qquad E_0 = -0.736V\ vs\ SHE \qquad \text{eq. 2}$$

Recent studies have unveiled the potential of iron (Fe) metal, being one of the most cost-effective and abundant transition metals extensively used in the Haber-Bosch process, to exhibit high performance in electrochemical NRR. Our study focuses on the electrochemical synthesis of ammonia using two distinct types of electrocatalysts: the first involves a metal iron layer deposited via the vapor phase deposition method, while the second utilizes iron nanoparticles generated through the spark ablation method. Additionally, we are in the process of fabricating internal reflective elements from polycrystalline silicon wafers to investigate reaction mechanisms. This involves depositing electrocatalysts and employing ENRR coupled with FTIR analysis. Complementing these experiments, we are developing a data analysis tool to track the time behaviour of the ENRR reaction and the phase changes in the electrocatalysts.

Acknowledgements: We thank Technion graduate school for financial support.

References:

1. IEA (2021), Ammonia Technology Roadmap, IEA, Paris https://www.iea.org/reports/ammonia-technology-roadmap, Accessed: December, 2023.
2. Yang, H. *et al.* Achieving high activity and selectivity of nitrogen reduction via Fe-N_3 coordination on iron single-atom electrocatalysts at ambient conditions. *ACS Sustain Chem Eng* **8**, 12809–12816 (2020)
3. Andersen, S. Z. *et al.* A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements. *Nature* **570**, 504–508 (2019).

Poster no. P_EC_08

Polymer-based LFP cathode/current collector microfiber-meshes with biand interlayered architectures for Li-ion battery.

Edi Mados, Diana Golodnitsky, and Amit Sitt

School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, Israel
E-mail: ednamados@mail.tau.ac.il

Lithium Iron Phosphate (LFP) has gained considerable attention as a cathode material for lithium-ion batteries due to its high energy density, low cost, and stable electrochemical performance. However, the performance of LFP cathodes is often limited by poor electron conductivity and low-rate capability. This study presents the development of a free-standing fiber-based mesh cathode composed of electrospun composite microfibers containing a high content of LFP and conductive microfibers containing carbon nano-fillers acting as the current collector (CC). Both CC and LFP microfibers can be directly utilized without requiring additional post-treatment.

Two cathode architectures of LFP/polymer-based CC meshes were explored: bilayered and interlayered. Both are characterized by a high surface-to-volume ratio. The interlayered structure showed superior electrochemical performance due to enhanced LFP-CC fiber-to-fiber contacts and reduced resistance. Comparative analysis with electrospun LFP on aluminum foil revealed comparable specific capacity but higher polarization in the electrospun LFP/PBCC meshes, attributed to increased internal resistance and limited fiber-to-fiber contacts. However, the electrospun interlayered LFP/CC mesh exhibited significantly higher gravimetric energy density (197 Wh/kg (LFP+PBCC) and 94 Wh/kg (LFP+Al), respectively), offering lightweight and higher-energy-density electrode materials, thus guiding the design of high-performance flexible lithium-ion batteries.

Poster no. P_EC_09

Investigating Biomimetic Polyoxometalate Electrocatalysts in Redox Reactions Through In-Situ Spectroscopy

Elias Haddad[1], Emiliano Sánshez-Navarro[2], Dima Azaiza Dabbah[3], Ronny Neumann[3], Marteen Nachtegaal[4], Mario U.Delgado-Jaime[2] and Charlotte Vogt[1]*

*[1]*Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Israel*

[2]Department of Chemistry, University of Guadalajara, Mexico

[3]Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Israel

[4]Paul Scherrer Institute (PSI), Villigen, Switzerland

E-mail: *C.Vogt@technion.ac.il*

Carbon monoxide dehydrogenase enzymes (CODHase) are highly active biological catalysts to reversibly oxidize CO (or reduce CO_2), the enzymatic active site contains a metallocluster of di-transition metal (TM) nature; [Ni-Fe] or [Cu-Mo][1]. In order to mimic the activity of these unique structures for applied purposes, numerous attempts were made to mimic (parts of) the structure but with limited success[2].

Polyoxometalates (POMs) are inorganic, metal oxide nanoscale structures which have proven to be interesting platforms for biomimetic catalysis. POM structures consist of oxometal polyhedra of MOx (with X = 5, 6), where M can be early transition metals (TM) in a high oxidation state, e.g., W, Mo, V, Nb, etc[3]. Some polyanions have centered heteroatoms of main group elements, including Si, P, S Ge, or even late TM's, consequently strongly affecting their catalytic properties. Studying these highly active biomimetic catalysts can potentially both elevate our understanding of the nature of various highly active enzymatic reaction mechanisms, and give insight to further optimize rational catalyst design, for example, by studying the effect of substitution of mono, di, or tri-TM metal atoms (Fe, Cu, Ir, Rh, Pt, etc.) in the various POM structures[4]. In this work we will study the reaction mechanism of CO_2 electroreduction by a highly active {CuFeGa}-POM through the use, and development of a variety of different operando spectroelectrochemical techniques e.g., modulated-excitation surface-enhanced infrared reflection absorption spectroscopy (SEIRAS) & quick-X-ray absorption spectroscopy (QXAS).

Acknowledgements: The authors thank the Emanuel Gottesmann Fellowship Fund and the German-Israeli Foundation for financial support.

References:

1. Wittenborn, Elizabeth C., et al. "Redox-dependent rearrangements of the NiFeS cluster of carbon monoxide dehydrogenase." Elife 7 (2018): e39451.
2. Azaiza-Dabbah, Dima, et al. "Molecular transition metal oxide electrocatalysts for the reversible carbon dioxide–carbon monoxide transformation." Angewandte Chemie International Edition 61.5 (2022): e202112915.
3. Veríssimo, Marta IS, Dmitry V. Evtuguin, and M. T. S. R. Gomes. "Polyoxometalate functionalized sensors: a review." Frontiers in Chemistry 10 (2022): 840657.
4. Li, Ning, et al. "Polyoxometalate-based compounds for photo-and electrocatalytic applications." Angewandte Chemie International Edition 59.47 (2020): 20779-20793.

Poster no. P_EC_10

Outstanding Hydrazine Oxidation Electrocatalysis on an Accessible FeN_4 Site

Inbal Offen-Polak,*[a,b] Tomer Y. Burshtein,[a,b] Mushrifa Syeda[b,d] Nagaprasad Reddy Samala,[c] Ilya Grinberg,[c]
Charlotte Vogt,[a,b] Dario Dekel[b,d] and David Eisenberg[a,b]

[a] *Schulich Department of Chemistry and the Resnick Sustainability Center for Catalysis, Technion – Israel Institute of Technology, Haifa 3230003, Israel.* [b] *Grand Technion Energy Program, Technion* [c] *Department of Chemistry, Bar Ilan University.* [d] *Department of Chemical Engineering, Technion*

E-mail: inbaloffen@campus.technion.ac.il

Hydrazine hydrate has been considered as a fuel in direct hydrazine fuel cells (DHFC) since 1960, due to its high energy density. Yet, it has not become commercial, so far. The hindrance stems from the need of an electrocatalyst for the hydrazine oxidation reaction (HzOR). The leading options, beside the scarce platinum group metals, are based on Ni and Co.Unfortunately, both Ni and Co are quickly deactivated during potential sweeps, due to rapid formation of hydroxide layers.[1,2]

Iron and nitrogen doped carbon (Fe-N-C) electrocatalysts, based on earth abundant materials, show promise as electrocatalysts for a variety of reactions, including HzOR; they are stable, conductive, have tunable structures and porosity, and a low-cost preparation. The atomically dispersed Fe sites, in the form of FeN_4, are the most active sites in Fe-N-C materials, with HzOR onset potential of 0.25-0.3 V vs. RHE at pH=14.[3] Yet, the structure and electrocatalytic mechanism of the FeN_4 active site, remains unsolved.

Herein we designed an Fe-N-C catalyst with an open and accesible FeN_4 site. Different organometallic complex were used is Fe precursor on a graphene substrate.The HzOR electrocatalytic ability of the pyrolyzed products was compared, with the open site demonstrating a remarkable advance of about 100mV in the onset potential compared to any other Fe-N-C tested. The catalyst structure, composition and morphology were thoroughly examined by XPS, ICP-MS, XRD, HAADF-STEM, HRSEM and RAMAN spectroscopy, while XAS and DFT feeting were used to elucidate the nature of the active sites. We will share our results describing the ultra-active FeNx active site, beating the record of all Fe-N-C-based HzOR electrocatalysts

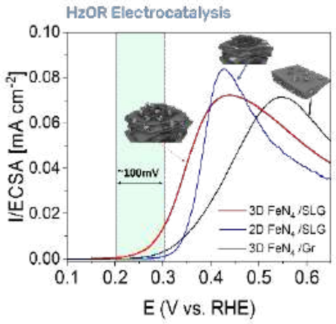


Figure 1: Hydrazine oxidation voltammograms of some of the Fe-N-C catalysts in Ar-purged KOH (1 M) with hydrazine (20 mM). Scan rates 10 mV s−1. Current densities are normalized by electrochemical surface area (ECSA)

Acknowledgements: We thank the ICS for financial support.

References:

1. Finkelstein, D. A., Imbeault, R., Garbarino, S., Roué, L. & Guay, D. Trends in Catalysis and Catalyst Cost Effectiveness for N2H4 Fuel Cells and Sensors: A Rotating Disk Electrode (RDE) Study. Journal of Physical Chemistry C 120, 4717–4738 (2016).
2. Khalafallah, D., Zhi, M. & Hong, Z. Development Trends on Nickel-Based Electrocatalysts for Direct Hydrazine Fuel Cells. ChemCatChem 13, 81–110 (2021).
3. Burshtein, T. Y. et al. Fe-N-C electrocatalysts in the oxygen and nitrogen cycles in alkaline media: The role of iron carbide. Physical Chemistry Chemical Physics 23, 26674–26679 (2021).

Poster no. P_EC_11

Cerium Ferrite Composites: A New Frontier in Electrochemical Reduction of Nitrates to Ammonia

James Ebenezer,[a] Parthiban Velayudham,[a] and Alex Schechter *[a,b]

[a] Department of Chemical Sciences, Ariel University, Ariel 40700, Israel. [b] Research and Development Centre for Renewable Energy, New Technology Centre, University of West Bohemia, 301 00 Pilsen, Czech Republic.

*E-mail: salex@ariel.ac.il; Tel.: +972 39371470; Fax: +972 547740254

In pursuit of sustainable ammonia synthesis and nitrate remediation, the electrochemical reduction of nitrate to ammonia (eNO_3RR) was explored as an alternative to the carbon-intensive Haber-Bosch process (HBP). The conventional HBP emits 1.6 to 2.0 tons of CO_2 per ton of ammonia,[1] whereas eNO_3RR, primarily when powered by renewable energy, offers a potential reduction in emissions and energy consumption. However, due to its complex reaction mechanism, eNO_3RR is facing challenges in product selectivity. Addressing these challenges, we synthesized $CeO_2/CeFeO_3$ composites using a microwave polyol method with varying Ce:Fe atomic ratios and conducted comprehensive characterizations and kinetic investigations. Our electrochemical analysis indicated that pure CeO_2 catalysts provide a high ammonia yield rate of 4040.5 µg h^{-1} cm^{-2} with lower Faradaic Efficiencies (FE) of 50.6 % at -0.45 V vs. RHE 0.1 M KOH electrolyte containing 0.1 M NO_3^-. Significant improvement in the FE was observed with the formation of the $CeFeO_3$ phase in the $CeO_2/CeFeO_3$ composite catalyst. The maximum FE of 88.1 % was observed in catalysts containing 75 % $CeFeO_3$ with an ammonia yield rate of 3223.9 µg h^{-1} cm^{-2}. Furthermore, only 3.1 % of the FE contributed to parasitic hydrogen evolution, with the remainder being distributed to 8.0 % hydroxylamine and 0.8 % nitrite, both intermediates in the ammonia synthesis pathway. This composite catalyst maintained stability over 25 cycles of eNO_3RR at -0.45 V vs. RHE (a total of 25 hours), with electrolyte exchange in each cycle. The improved catalytic performance is attributed to the intrinsic perovskite structure of $CeFeO_3$, which utilizes oxygen vacancies[2] for oxygen exchange with the NO_x intermediates. This study highlights the potential of rare earth orthoferrites, particularly cerium ferrite composites, to facilitate eNO_3RR. These materials present a promising avenue for sustainable ammonia production and environmental remediation, showcasing a viable alternative to traditional methods.

Keywords: Sustainable Ammonia Synthesis, Cerium Ferrite Composites ($CeO_2/CeFeO_3$), Efficiency and Selectivity, Environmental Remediation

Acknowledgements: We thank Ariel University, Samaria & Israel Chemical Society

References:

1. Soloveichik, G., Electrochemical synthesis of ammonia as a potential alternative to the Haber–Bosch process. Nat Catal., **2019,** 2, 377–380.

2. Jabbarzare, S. et al., A study on the synthesis and magnetic properties of the cerium ferrite ceramic, J Alloys Compd., **2017,** 694, 800–807.

Poster no. P_EC_12

Sodium Metal Deposition and Stripping in Carbonate Electrolytes

L. Faktorovich*, R. Marrache, T. Assa, and E. Peled

School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, Israel, 6997801

E-mail: faktorovich.lina@gmail.com; peled@tauex.tau.ac.il

There is a growing interest in sodium metal batteries as a potential next-generation rechargeable battery technology, thanks to its abundance, low cost, and high theoretical specific capacity. However, despite these advantages, sodium metal anodes suffer from uneven metal plating/stripping, dendrite formation, and continuous side reactions between sodium and an electrolyte. These concerns lead to low coulombic efficiency (CE) and poor cycle life. Here, we present a study on sodium metal cells in a carbonate-based electrolyte. We propose the addition to the electrolyte VC as well as oxide nanoparticles such as Al_2O_3 and TiO_2. That to improve the Solid Electrolyte Interphase (SEI) and the CE of sodium metal cells at different current rates. Additionally, we conducted a study on the capacity losses in these cells during cycling. We found that the highest CE value, 90.1%, was achieved in cells with VC addition. The addition of 2% Al_2O_3 increased the CE from 77.8% to 79.3% at current density of 30μA/cm^2 and from 83.4% to 84.1% at a current density of 55μA/cm^2. When the current density was reduced from 30μA/cm^2 to 6μA/cm^2, the CE of cells with 0.5% Al_2O_3 and 2% Al_2O_3 increased from 72.4% to 85.4% and 85.9%, respectively. Energy-Dispersive X-ray Spectroscopy (EDS) analysis of the SEI showed that sodium and oxygen are found at the same locations. The highest content of oxygen was observed in the reference cell, suggesting the presence the highest amount of sodium oxide and carbonate compounds. The highest carbon and fluoride content were detected in the cell with VC, suggesting an SEI richest in NaF and in organic compounds. From the Open Circuit Voltage (OCV) at the end of a 20-minute rest, it can be concluded that the temporarily connected dead sodium can be more efficiently stripped in the initial stage of cycling. After about 43/50 cycles, dead sodium remains at the current collector even after 19 dissolution attempts in most cells. It was also revealed that more than 99% of the total capacity losses were due to the formation of dead sodium isolated from the current collector.

Poster no. P_EC_13

Synthesis of copper based nanomaterials for CO_2 electroreduction into commodity chemicals

Manish Yadav Kumar[1], Arie Borenstein[1,*]

1- Department of Chemical Sciences, Ariel University, Ariel, Israel

Email- arieb@ariel.ac.il

Abstract:

The electrochemical carbon dioxide reduction process (CO_2RR) using copper-based catalysts has garnered a lot of interest because of production to commodity chemicals. One potential strategy for managing the CO_2RR performance at the electrode interface is the alteration of catalysts with various copper concentrations in graphitic carbon supports. The influence of laser irradiation of copper-induced carbon nanodot on the CO_2RR activity and selectivity over Cu-based catalysts is not well understood. In this project we report a unique laser irradiated nanoparticles (NPs) consisting of Cu supported on reduced carbon nanodots (Cu-rCND) with a high catalytic activity for CO2 reduction, it displays the electrochemical measurements for CO_2RR of Cu-based catalysts to investigate the impacts of particle size, graphitic carbon support, and varied concentrations of copper doped nanomaterials. The best optimized nanomaterials Cu-rCND4 effectively reduce CO_2 to CO, HCOOH at potential −1.20 Ewe/V vs Ag/AgCl at -10mA CO_2 saturated 0.5 M $NaHCO_3$ solution. This Cu-rCND nanocomposite is promising for the electrochemical reduction of CO2 to value-added products to solve the urgent environmental and energy issues because of its outstanding catalytic activity and excellent stability.

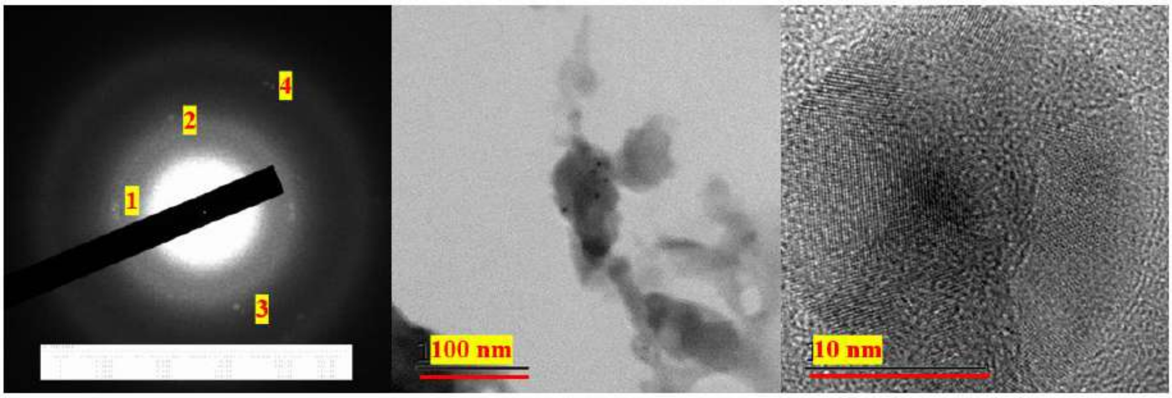


Figure: Transmission electron microscopy (TEM) Characterization of the Cu-rCND 4.1% and selected area diffraction pattern for the Cu nanoparticle.

Poster no. P_EC_14

Ion Transport in Plasticized LAGP-Based Electrolytes

Moran Lifshitz,[a] Anna Greenbaum[b,c], Kaito Sasaki[d], Alex Gladkich[e], Yuri Feldman[b], and Diana Golodnitsky[a*]
E-mail: golod@tauex.tau.ac.il

a) School of Chemistry and Applied Materials Research Center, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, 6997801, Tel Aviv, Israel;
b) Department of Applied Physics, The Hebrew University of Jerusalem, Jerusalem, 9190401, Israel
c) Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem, 9190401, Israel
d) Department of Physics, Tokai University Hiratsuka, Kanagawa, 259-1292, Japan
e) Applied Materials Research Center, Tel Aviv University, 6997801, Tel Aviv, Israel

The development of an efficient devices for energy storage, conversion, and transmission is one of the key priority areas today. At the center of these activities is the development of all-solid-state high-energy and high-power lithium-ion batteries.

Our research is focused on the study of ion transport in a plasticized-by-ionic-liquid composite membrane formed by electrophoretic deposition (EPD). The EPD membrane comprises above 85% of high-ion-conductivity ceramic matrix $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) and less than 15% polyethyleneimine (PEI). The EPD rate and morphology of the membrane were characterized by SEM, TOFSIMS and DSC methods. 0.3M LiTFSI–PYR14TFSI was infused in the membrane to form a quasi-solid electrolyte. The complex, non-Debye dielectric response of the quasi-solid electrolyte, tested over the temperature and frequency ranges of (-140ºC) to (+100ºC) and 10^{-2} – 10^{6} Hz, has been described in terms of several distributed relaxation processes separated by different frequency and temperature ranges. While at low temperatures, the main contribution is from LAGP, in the middle- and high-temperature regions, the superposition of a few non-Arrhenius processes is observed. Relaxation is perturbed by clear phase transition related to melting of the ionic liquid. Different scales of the ionic transport and corresponding relaxation of the apparent dipole moment in the materials are discussed.

Poster no. P_EC_15

Heterogeneous Electrochemical CO_2 Reduction to Multi-Carbon Products Using a Metal-Free Redox Catalysts Within a Metal-Organic Framework

N.Cohen[a] and I.Hod*[a]

[a] *Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel*

E-mail: Naorcohe@post.bgu.ac.il

The growing energy demand has resulted in increased greenhouse gas emissions, leading to severe environmental consequences like global warming. Carbon dioxide (CO_2) is a critical greenhouse gas responsible for global warming and climate change. Electrochemical reduction of CO_2 offers a promising approach to mitigate carbon emissions by converting CO_2 into useful products while simultaneously utilizing renewable energy sources such as solar or wind power. In this regard, Metal-Organic Frameworks (MOFs) and MOF-converted materials have emerged as promising electrocatalysts for those reactions. MOFs are crystalline materials consisting of metal ions/clusters and organic ligands, possessing unique properties such as high surface area, porosity, and chemical stability, making them suitable for various applications like gas storage, drug delivery, and catalysis. Among MOFs, UIO-type has gained significant attention due to its exceptional mechanical and chemical durability, making it ideal for catalysis.

Although transition metals serve as prevalent catalysts for CO_2 electroreduction due to their significant catalytic activity, researchers are actively exploring alternative molecular catalysts. This pursuit aims to bolster selectivity, efficiency, and stability in the realm of sustainable chemistry. In our investigation, we seamlessly integrated molecular catalysts into the UIO-type framework, resulting in a notable enhancement in catalytic performance. This strategic approach capitalizes on the inherent stability of the MOF while leveraging the efficiency and exceptional selectivity provided by the molecular catalyst. Utilizing a UIO-66-gel matrix and employing post-modification techniques, we were able to introduce several organic redox catalysts which showed an impressive level of activity and selectivity toward a multi-carbon (C_2) reaction product.

Acknowledgements: We thank the ICS for financial support.

References:

1. Armando Gennaro, Abdirisak A. Isse, Jean-Michel SaveÂant,*, Maria-Gabriella Severin, and Elio Vianello* J.Am.Chem.Soc.**1996**,118,7190-7196
2. Shimoni, R., He, W., Liberman, I., & Hod, I. Tuning of Redox Conductivity and Electrocatalytic Activity in Metal–Organic Framework Films Via Control of Defect Site Density. The Journal of Physical Chemistry C, **2019**, 123(9), 5531-5539.

Poster no. P_EC_16

Bubble release from tunable porous carbons

Nicola M. Seraphim, Noa Soffer-Lugassy, David Eisenberg [a]

[a] *Schulich Faculty of Chemistry, the Resnick Sustainability Center for Catalysis, and the Grand Technion Energy Program, Technion – Israel Institute of Technology, Haifa 3230003, Israel*

E-mail: nmser245@campus.technion.ac.il

Fuel cells and electrolyzers are considered a promising alterantive for energy storage. Through a redox reation occuring on an anode and a cathode, we can extract an electric current to extract energy. However, fuel cells are not yet commercial due to many obstacles. Catalysts alrentatives and low power density isuues are usually discussed, but another major problem of FC (or electrolyzer) is bubble poisining, which occurs when gas is generated through an electrochemical reaction, leading to bubble formation and adhesion to the electrode. This continues adhesion lowers the surface area, decreases mass transfer, reduces exposure of active material.

One of the methods to tackle bubble poisining is by porous structures. Different types of porous strucures can help with mitigating bubbles, each with its own unique pore size distribuation, surface area, tortuosity etc. Nevertheless, cracking the link between porous structure and bubble mitigation is not simple, as many variables come to play at the bubble release and dynamics.

In order to understand better the relationship between mitigating bubbles and pore size, we synthesized 4 different materials with spherical pores, through hard template method, using acrylonitrile as a precursor and silica spheres as template, changing only the pore size (40, 80, 120, 200 nm). Decoupling pore size from the porous structure parameters, we can understand the relation between bubble release and pore size.

The materials were characterized with scanning electron microscopy, N_2 adsorption, and Raman spectroscopy. Hydrazine oxidation and hydrogen evolution were used for electrochemical making of bubbles, using voltammetry and amperometry methods, measuring different parameters to study this link. Different setups of 3 electrode cell was also used to study the bubble formation and adhesion using photography, showing a trend as pore size increases.

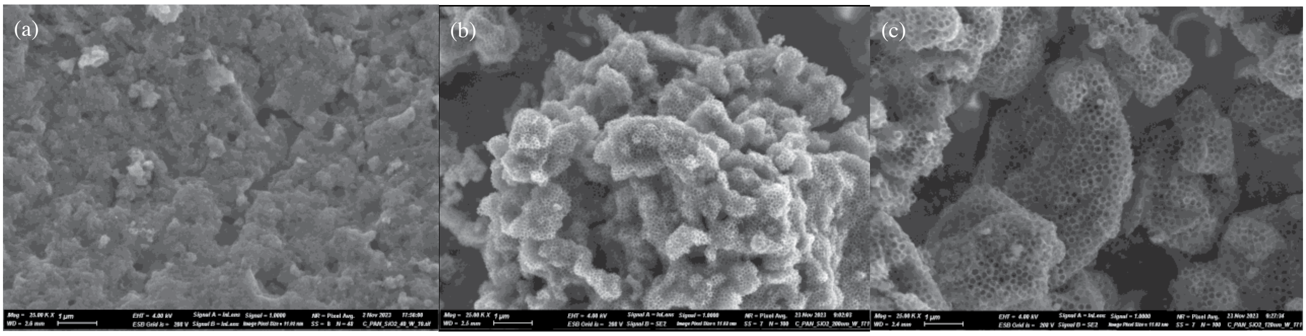


Figure 1: Hard templated carbons using PAN as a precursor and SiO_2 spheres a) 40 nm b) 120 nm c) 200 nm

Poster no. P_EC_17

Templating Macroporous Channels in Carbon by Custom-Designed ZnO Rods: A Gateway to New Applications

Noa Soffer Lugassy, Nicola M. Seraphim, David Eisenberg [a]

[a] Schulich Faculty of Chemistry, the Resnick Sustainability Center for Catalysis, and the Grand Technion Energy Program, Technion Israel Institute of Technology, Haifa 3230003, Israel

E-mail: noa.soffer@campus.technion.ac.il

The world is amidst a technological transition into sustainable and clean energy sources. Electrochemistry and electrochemical devices play a critical role in clean energy conversion technologies. One of the biggest challenges of these technologies is energy storage.

There are several energy storage tools such as fuel cells, batteries, supercapacitors etc. all of which require electrodes, usually depending on expensive metals. The requirement is for an electrode with high surface area, good flow, and mass transport, hosts active material and releases bubbles.

For these properties we introduce porosity using ZnO rods crystals into our carbon electrodes. This porous structure is theoretically favorable for electrocatalysis for several reasons, namely the crystal structure's ability to create better connectivity compared to spheres (ZnO, silica). In addition, the ZnO performs a carbothermal reaction and reduces the carbon, creating micro-pores in it.

In this work we synthesized ZnO crystals in two different lengths and widths through a hydrothermal reaction, in a custom-made reactor. Afterwards, we used the ZnO rods as a template to create N-doped porous carbons (PAN) via hard templating. Receiving porous carbon which were characterized in a variety of methods such as N_2 sorption, scanning electron microscopy, XRD and Raman spectroscopy. Finally, we tested these carbons two electrochemical applications, water remediation and PEMFC. Showing great promise in their activity, especially regarding mass transfer effects. This research empathizes the importance of macro-pore templating with its regard to electrochemistry.

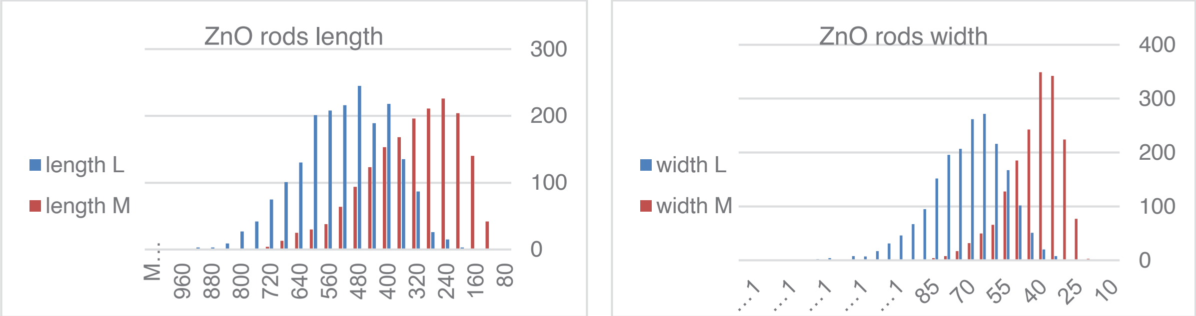


Figure 1: ZnO rods crystals histograms

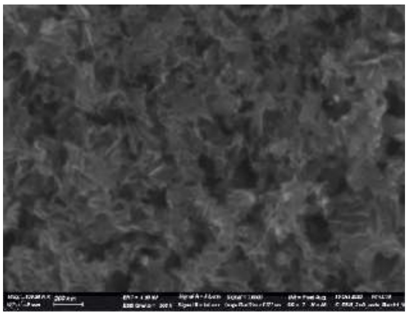


Figure 3: SEM porous carbon

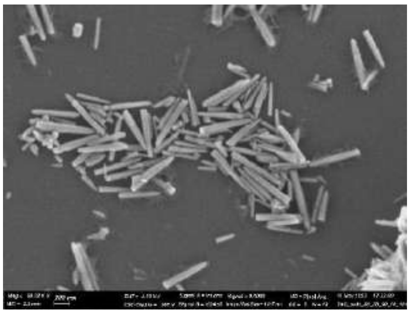


Figure 2: SEM of ZnO rods

Poster no. P_EC_18

Towards All-Extruded Custom-Shape Batteries

Olga Guchok[1], Gilat Ardel[1], Tommer Kidar[1], Hadar Nakar[1], Elay D. Kindler[1],Heftsi Ragones[2]
Igor Shulman[3], Naum Naveh[3], Allen Zheng[4], Steve G. Greenbaum[4] and Diana Golodnitsky [1*]

[1]School of Chemistry, Tel Aviv University, Tel Aviv 6997801, Israel
[2]Faculty of Engineering, Holon Institute of Technology, Holon 5810201, Israel
[3]The Department of Polymer Materials Engineering, Pernick Faculty of Engineering, Shenkar - Engineering. Design. Art, Raman-Gan, Israel
[4]Department of Physics, Hunter College of City University of New York, New York, New York 10065, USA

**golod@tauex.tau.ac.il*

The rapid growth of flexible electronics for wearable devices, on-skin or environmental sensors, and flexible displays have resulted in intensive research in the field of free form-factor energy-storage systems. Since batteries must withstand bending, folding, or stretching while maintaining their electrochemical performance, the design and processing of battery components, must be reconsidered. Moreover, there is a clear tendency to shift battery technology to clean and cost-effective dry methods with no toxic solvents. Dry fabrication methods are environmentally friendly, involve lower energy consumption, shorter time and are cost-effective. Hot-pressing and melting-extrusion strategies are appropriate for the fabrication of flexible, solid-polymer electrolytes and electrodes with high contents of active materials and high mass loading.

Here we present the progress towards the simple, one-step extrusion of a solid-state battery with a multi-shell and layered architecture. Such structures fundamentally minimize the ionic pathway for Li^+. As in the conventional battery, high ionic conductivity of extruded electrolyte and compatibility with electrode materials, are the essential properties for enabling high performance of the battery. The electrolytes are composed of LiTFSI, mix of polyethylene oxide (PEO), which is a known lithium-ion conductor, and thermoplastic recyclable and biodegradable polymer polyurethane (TPU) for enhanced mechanical properties and high-temperature durability. The extruded electrolytes of different polymers ratios and salt content were characterized by means of ESEM imaging, mass spectroscopy, differential-scanning calorimetry (DSC), electrochemical-impedance spectroscopy (EIS) and solid-state nuclear magnetic resonance (NMR) diffusion measurements. The structure and electrochemical properties of extruded electrolytes were compared with cast films. It was found that TPU, having in its structure, both soft segments from polyol regions and hard segments from isocyanate not only improves the mechanical properties of neat PEO-based polymer electrolyte, but also forms complexes with lithium salt and serves as a conducting medium. Bulk conductivity vs. temperature dependencies obey Arrhenius behavior. The highest conductivity values varying from 0.3 to 1mS/cm over a temperature range from RT to 90 C were achieved for the extruded 1:15 (Li:EO) solid polymer electrolyte. The NMR tests show that lithium self-diffusion coefficients in extruded PE with alumina filler are close to that in cast PE, but the anion diffusion coefficients (accessible through ^{19}F NMR) are lower in extruded filaments, indicating a correspondingly higher Li^+ transference number induced by the extrusion. Lithium cells with extruded LFP cathode and solid extruded polymer electrolyte demonstrated 40 reversible cycles with close to 96% coulombic efficiency. The electrochemical performance of half-cells composed of extruded LFP-based anode and all extruded solid state full also will be presented.

Poster no. P_EC_19

Nitrate Reduction to Ammonia: Assessing the Electrocatalytic Behavior of Cu3N

Paz Stein,[a], Ronen Bar-Ziv[b] and Maya Bar-Sadan*[a],

[1]*Department of Chemistry, Ben Gurion University, Beer-Sheva, 8410501 Israel.*
[2] *Department of Chemistry, Nuclear Research Center Negev, P.O. Box 9001, Beer-Sheva 84190, Israel*

E-mail: barsadan@bgu.ac.il, bronen@post.bgu.ac.il

This research project explores the electrocatalytic activity of Cu_3N nanocubes in the reduction process of nitrate ions (NO_3^-) to ammonia (NH_3/NH_4^+). The nanocubes were synthesized using a colloidal route, and were characterized using transmission electron microscopy (TEM), x-ray diffraction (XRD) patterns, and x-ray photoelectron spectroscopy (XPS). The linear sweep voltammetry (LSV) curve was used to demonstrate that the addition of nitrates considerably improved the activity of Cu_3N. To evaluate the selectivity towards ammonia production, the researchers conducted a series of chronoamperometric experiments at varying potentials. The two main possible products, NH_4^+ and NO_2^-, were colorimetrically quantified. The highest faradaic efficiency and NH_3 formation rate were produced at a potential of -0.9 V vs. RHE. Furthermore, Cu_3N demonstrated the ability to maintain its activity through 10 cycles of catalysis with 5 coulombs applied in each cycle.

Acknowledgements:

References:

Poster no. P_EC_20

Tuning Electrocatalytic CO_2RR Product Selectivity of an FeTCPP-Based 2D MOF via Secondary Sphere Interactions

Ran Shimoni,[a] and Idan Hod*[a]

[a] Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel

E-mail: hodi@bgu.ac.il, ranshi@post.bgu.ac.il

Electrochemical reduction of CO2 to valuable chemical fuels provides a promising pathway for reducing the continuously growing global carbon footprint. One of the critical components of an efficient electrochemical CO_2 reduction system is the catalyst which accelerates the reaction's kinetics.

Metal-Organic Frameworks (MOFs) are a class of crystalline coordination polymers with high surface area, consisting of metal clusters and organic multi-topic linkers. MOFs were highly useful in chemical catalysis because of their unique physical properties, such as high surface area and porosity. These unique properties allow us to use MOFs for integrating the fundamental functional elements needed for the efficient electrocatalytic system: 1) immobilization of high concentration of the molecular catalysts, 2) installation of the redox shuttles for charge transport to and from the catalytic sites, 3) optimization of the mass transport channels through the MOFs pores, and 4) modulation of the catalyst's secondary chemical environment. The notion of using MOF to immobilize high concentrations of molecular electrocatalysts to drive electrochemical reactions was demonstrated. Yet, the modulation of the active-site's immediate chemical environment to boost electrocatalysis rate and selectivity has rarely been shown..

Herein we demonstrate that in a FeTCPP-Based 2D MOF, using an heterogeneous incorporation of ligands bearing a fixed cationic charge, one can electrostatically-stabilize FeTCPP-bound COO- intermediate, and thus systematically tune its CO_2-to-CO selectivity up to practically 100%. As such, we believe that these results will widen our understanding of MOF-based electrocatalytic systems and accelerate their implementation is energy-conversion schemes.

References:

1 Liberman, I+., Shimoni, R.+, Ifraemov, R., Rozenberg, I., Singh, C., & Hod, I. (2020). Active-site modulation in an Fe-porphyrin-based metal–organic framework through ligand axial coordination: accelerating electrocatalysis and charge-transport kinetics. Journal of the American Chemical Society, 142(4), 1933-1940.Link to article (IF 16.38 Rank 16/179 Q1)

Shimoni, R., He, W., Liberman, I., & Hod, I. (2019). Tuning of redox conductivity and electrocatalytic activity in metal–organic framework films via control of defect site density. The Journal of Physical Chemistry C, 123(9), 5531-5539. Link to article (IF 4.17 Rank 78/165 Q2)

Shimoni, R., Shi, Z., Binyamin, S., Yang, Y., Liberman, I., Ifraemov, R., ... & Hod, I. (2022). Electrostatic Secondary-Sphere Interactions That Facilitate Rapid and Selective Electrocatalytic CO2 Reduction in a Fe-Porphyrin-Based Metal–Organic Framework. Angewandte Chemie, 134(32), e202206085. Link to article (IF 16.82 Rank 15/179 Q1)

Poster no. P_EC_21

Design of Electroactive Metal-Organic Framework Thin Films Via a Gel Precursor Method

Rotem Balilty, Idan Hod*

Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel.

E-mail: balilty@post.bgu.ac.il

Metal-organic frameworks (MOFs) are a class of porous crystalline materials, that consist of metal ions or cluster based nodes and multitopic organic linkers. Their unique properties make MOFs attractive candidate materials to be used in a wide variety of applications such as gas separation, chemical catalysis, drug delivery, and sensing. As MOFs are typically electrically insulating, there are three approaches to render MOFs redox-active. The first method involves incorporating redox-active units, while the second approach is doping with conductive materials, and also post-synthetic modifications can be employed to add electroactive functionalities directly to the MOF surfaces. [1]. To develop an electro-active surface, several methods can be applied, among them: EPD (Electrophoretic Deposition), drop-casting of a binder-containing ink and electrodeposition.

In our research, we used UIO-66 MOF which is a prototype of Zr-based MOFs with a $Zr_6O_4(OH)_4$ cluster coupled to 12 terephthalic acids (H_2BDC) molecules to form a 3D framework. Ferrocene is a well-known electrochemical redox-probe and therefore, can be used as a model system to study MOF's charge-transport properties by incorporating FcCOOH (Ferrocene carboxylic acid) molecules in post-synthetic modification. Recently, MOF gels were explored, and shown that the capacity of MOFs to gel under specific synthetic conditions offers up new possibilities for the synthesis and structuring of hierarchically porous MOF monoliths, which might be used directly for catalytic and adsorptive applications [2]. Based on this knowledge, post-synthetic modification of UIO-66 gel with ferrocene carboxylic acid was performed [4], and thus electroactive MOFs thin films were constructed via drop-casting of a gel precursor. This film deposition technique has many advantages, as: 1. Fine Control over film thickness 2. No need to use a binder, thus allowing for easier analysis of film structure and composition 3. Allows the creation of a high defect concentration, which Enables immobilization of high ferrocene loadings via post-synthetic modification.

Our findings demonstrate that the gel precursor method provides a versatile platform for the controlled synthesis of electroactive MOF thin films, understanding the correlation between the amount of gel that we put on the electrode, the electrode thickness, and the charge-transfer properties [3], and enabling the customization of their properties for specific applications. These MOF thin films hold great promise for the development of advanced electronic devices, energy storage systems, and catalytic processes. This research contributes to the expanding field of MOF-based materials and opens new avenues for the design and utilization of MOF thin films in various technological applications.

References:

1. Hod, I., Sampson, M. D., Deria, P., Kubiak, C. P., Farha, O. K., & Hupp, J. T. (2015). Fe-porphyrin-based metal–organic framework films as high-surface concentration, heterogeneous catalysts for electrochemical reduction of CO2. Acs Catalysis, 5(11), 6302-6309.
2.Deng Z, Peng X, Zeng Y. Ferrocenecarboxylic acid: a functional modulator for UiO-66 synthesis and incorporation of Pd nanoparticles. CrystEngComm 2019;21:1772-9.
3.Bueken, B., Van Velthoven, N., Willhammar, T., Stassin, T., Stassen, I., Keen, D. A., Baron., G. V., Denayer, J. F. M., Ameloot, R., Bals, S., De Vos, D., and Bennett, T. (2017), 'Gel-based morphological design of zirconium metal–organic frameworks. Chem. Sci. 8, 3939–3948
4.Palmer, RH, Liu, J, Kung, CW, Hod, I, Farha, OK & Hupp, JT (2018), 'Electroactive Ferrocene at or near the surface of Metal-Organic Framework UiO-66'. 4707-4714.
2. Lewis, W. G.; Green, L. G.; Grynszpan, F.; Radic, Z.; Carlier, P.R.; Taylor, P.; Finn, M. G.; Sharpless, K. B. Click chemistry in situ: acetylcholinesterase as a reaction vessel for the selective assembly of a femtomolar inhibitor from an array of building blocks. *Angew. Chem., Int. Ed.* 2002, *41*, 1053-57.

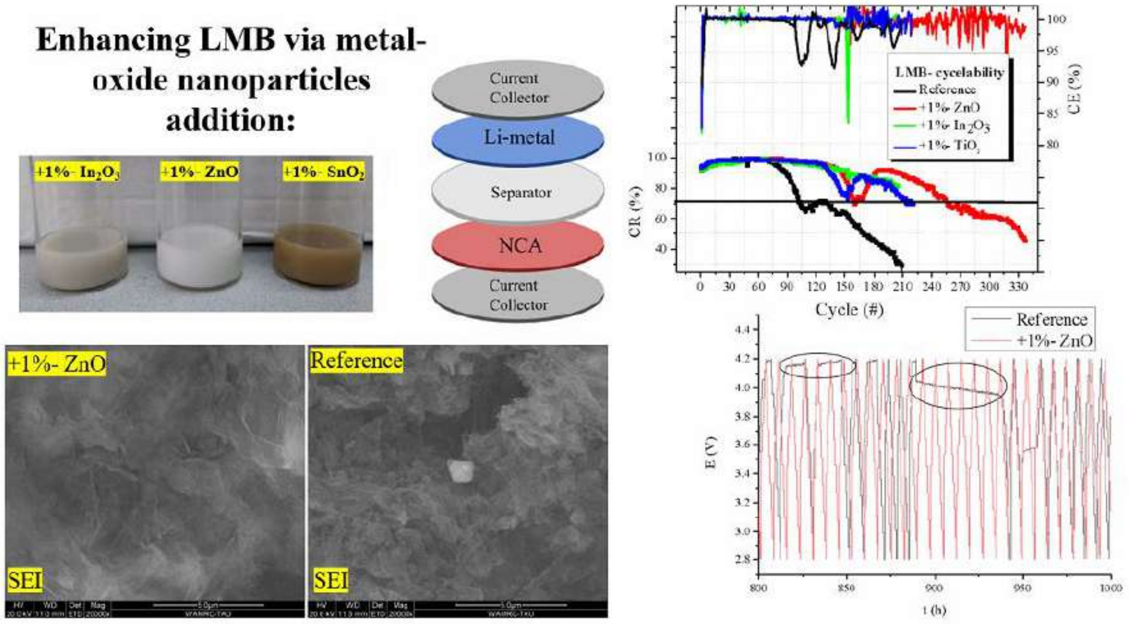
Poster no. P_EC_22

Understanding and Minimizing Capacity Losses in Li-Metal Batteries

Roy Marrache

Humans have started dramatic atmospheric changes since the industrial evolution, mainly by the emissions of CO_2 caused by burning fossil fuels. Many options are being and have been used to create a cleaner atmosphere. Green electricity is already a present solution, using photovoltaic panels which harvest energy from the sun or turbine that harvest energy from the wind and other solutions. In order to complete these solutions, energy accumulation is needed. Several solutions were emerged and proposed over the years, including green H_2, and lithium and sodium batteries.

Li-ion batteries (LIB) have been the main energy storage solution for most applications since 1991. Now adays their capacity is pushed to its limits and new higher energy systems emerge such as Li-metal and anode-free systems with liquid and in the future with solid electrolytes. This work reveals a new method to characterize capacity losses in Li-metal batteries (LMB) as well as an approach to increase the cycle-life and safety of LMB and anode-free LMB via addition of small amounts of metal oxides nanoparticles to liquid electrolytes.



Enhancing LMB via metal-oxide nanoparticles addition:

Poster no. P_EC_23

Regulation of Catalyst Immediate Environment Enables Acidic Electrochemical Benzyl Alcohol Oxidation to Benzaldehyde

G. Shiva Shanker, Arnab Ghatak, Rotem Balilty, Shahar Binyamin, Ran Shimoni, Itamar Liberman and Idan Hod*

Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology,
Ben-Gurion University of the Negev,
Beer-Sheva, 8410501, Israel.
E-mail: shivasha@post.bgu.ac.il

Abstract:

Electrocatalytic alcohol oxidation in acid offers a promising alternative to the kinetically sluggish water oxidation reaction, toward low-energy H_2 generation.[1-2] However, electrocatalysts driving active and selective acidic alcohol electrochemical transformation are still scarce. In this poster presentation, I demonstrate efficient alcohol-to-aldehyde conversion, achieved by reticular chemistry-based modification of the catalyst's immediate environment. Specifically, coating a Bi-based electrocatalyst with a thin layer of Metal-Organic Framework (MOF), substantially improves its performance toward benzyl alcohol electrooxidation to benzaldehyde in 0.1 M H_2SO_4 electrolyte. Detailed analysis reveals that the MOF adlayer influence catalysis by increasing the reactivity of surface hydroxides, as well as weakening of catalyst-benzaldehyde binding strength. In turn, low-potential (0.65V) cathodic H_2 evolution was obtained through coupling it with anodic benzyl alcohol electrooxidation. Consequently, the presented approach could be implemented in a wide range of electrocatalytic oxidation reactions for energy-conversion applications. I will discuss more details of these aspects in the presentation.

References:

1. Sheldon, R. A.; Arends, I. W. C. E.; ten Brink, G. J.; Dijksman, A., Green, Catalytic Oxidations of Alcohols. *Acc. Chem. Res.* **2002,** *35*, 774-781.
2. Wang, T.; Cao, X.; Jiao, L., Progress in Hydrogen Production Coupled with Electrochemical Oxidation of Small Molecules. *Angew. Chem. Int. Ed.* **2022,** *61*, e202213328.

Poster no. P_EC_24

Cs^+ Ions Detection Using Immobilized Hexacyanoferrate into ElectroReduced or Electro-Polymerized Graphene Oxide Coatings

Shuli Halevy,*[a] Yacov Iflah,[a] and Armand Bettelheim[b]

[a] Chemistry Department, Nuclear Research Center NEGEV, POB 9003 Beer-Sheva [b] Chemical Engineering Department, Ben Gurion University of the Negev

E-mail: (shulih8@gmail.com)

Selective sensing of cesium radionuclide in contaminated water is a challenging issue. In the present study, the adsorption and cation exchange properties of hexacyanoferrates (HCFs) are exploited for the detection of Cs^+ ions using potassium-nickel hexacyanoferrate, $K_2Ni[Fe(CN)_6]$. However, the reported immobilization methods of HCF nanoparticles onto electrodes suffer from major disadvantages such as poor conductivity, and low stability mainly due to agglomeration. These issues are dealt with in the present study using the well documented electrochemically reduced graphene oxide (erGO) coatings, or alternatively using ones we recently reported and which can be obtained by direct electro-polymerization of graphene oxide sheets (epGO). The epGO films have been shown to be highly electron conducting, as well as much thinner than the erGO ones (~30nm and ~1μm, respectively), which is essential for fast response when being used in electrochemical sensors.

Potassium-nickel HCF nanoparticles were synthesized and incorporated onto glassy carbon (GC) electrodes via one step electrodeposition of erGO or epGO. According to TEM observations, the HCF nanoparticles with sizes within the 2-20 nm range were uniformly distributed in the two types of coatings. The erGO-HCF and epGO-HCF coated GC electrodes were used to probe Cs^+ ions in a 1M NaCl solution by applying a potential of 0.5V vs. Ag/AgCl. A linear correlation was found between current densities and $\log[Cs^+]$ and a detection limit of 0.1 ppb Cs^+ was determined for both types of electrodes.

Poster no. P_EC_25

From NO_x Waste to Ammonia Fuel: NO_x Reduction on Single Atom Catalysts

Yair Shahaf, Davis Eisenberg*

Schulich Faculty of Chemistry, the Resnick Sustainability Center for Catalysis, and the Grand Technion Energy Program, Technion−Israel Institute of Technology, Haifa 3230003, Israel.

E-mail: *yair.shahaf@campus.technion.ac.il , david.eisen2@gmail.com*

Ammonia is one of the most important chemicals to human existence on the planet. As of today, ammonia is produced by the Haber-Bosch process. The harsh conditions of the process it a very polluting and energy consuming process, currently responsible for about 1% of the annual energy consumption worldwide, with 1.673 ton of CO_2 emission per ton of ammonia produced.[1]

Recent advances opened possibilities to improve ammonia synthesis *via* electrochemical methods. To overcome the large energy barrier needed to break the triple bond of dinitrogen, focus has shifted to electrochemically reducing NO_x compounds which are abundant and need less energy to reduce, particularly NO_3^-.

Nitrogen-coordinated iron ions, such as FeN_4 moieties, are commonly found in enzymes,[2,3] such as nitrogenase, an enzyme responsible for N_2 fixation. FeN_4 active sites are efficient at the electrocatalysis of oxygen reduction, CO_2 reduction and hydrazine oxidation[4]. The unoccupied *d* orbital of Fe ion sites, like in enzymes, is a promising electron acceptor and donor, suitable to facilitate nitrate reduction. The catalytic properties of enzymes are co-determined by the active site and its highly adapted protein-chain surroundings.

Recently, NO_3^- and NO_2^- electroreduction on single atom metal-nitrogen sites was demonstrated. While substantial breakthroughs were achieved, current catalysts do not offer sufficient activity for the reduction of NO_x^- and are not selective for the production of high value ammonia. We believe that careful manipulation of the active site's immediate environment, e.g., the first and second coordination sphere, could improve activity by regulating the supply of protons to the adsorbed NO_x molecule and boost selectivity by stabilizing reactive intermediates. We successfully prepared a novel graphene based single iron site catalyst, active toward nitrate and nitrite reduction (figure 1). We would further develop the catalyst and reaction conditions to address activity, selectivity, and stability by functionalizing the surface.

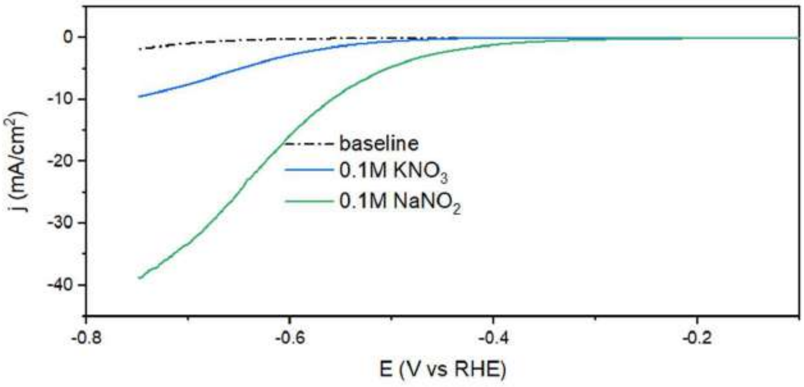


Figure 1: ***Cyclic voltammogram of FeN_4@graphene catalyst. baseline 0.5 M K_2SO_4, blue: 0.5 M K_2SO_4 + 0.1M KNO3, green: 0.5 M K_2SO_4 + 0.1M $NaNO_2$, scan rate 10 mV/s***

References:

[1] J. N. Galloway, J. D. Aber, J. W. Erisman, S. P. Seitzinger, R. W. Howarth, E. B. Cowling, B. J. Cosby, *BioScience* 2003, *53*, 341–356.
[2] V. Rosca, M. Duca, M. T. de Groot, M. T. M. Koper, *Chem. Rev.* 2009, *109*, 2209–2244.
[3] J. Ji, J. Woo, Y. Chung, S. H. Joo, Y. Kwon, *Chem. Eng. J.* 2020, *381*, 122679.
[4] T. Y. Burshtein, D. Aias, J. Wang, M. Sananis, E. M. Farber, O. M. Gazit, I. Grinberg, D. Eisenberg, *Phys. Chem. Chem. Phys.* 2021.

Poster no. P_EC_26

The effect of polydentate ethers on the structure and electrochemistry of bridge Magnesium phenyl Aluminates. The novel approach for synthesis of the $MgCl^+$ and Mg^{2+} cationic electrolytes:

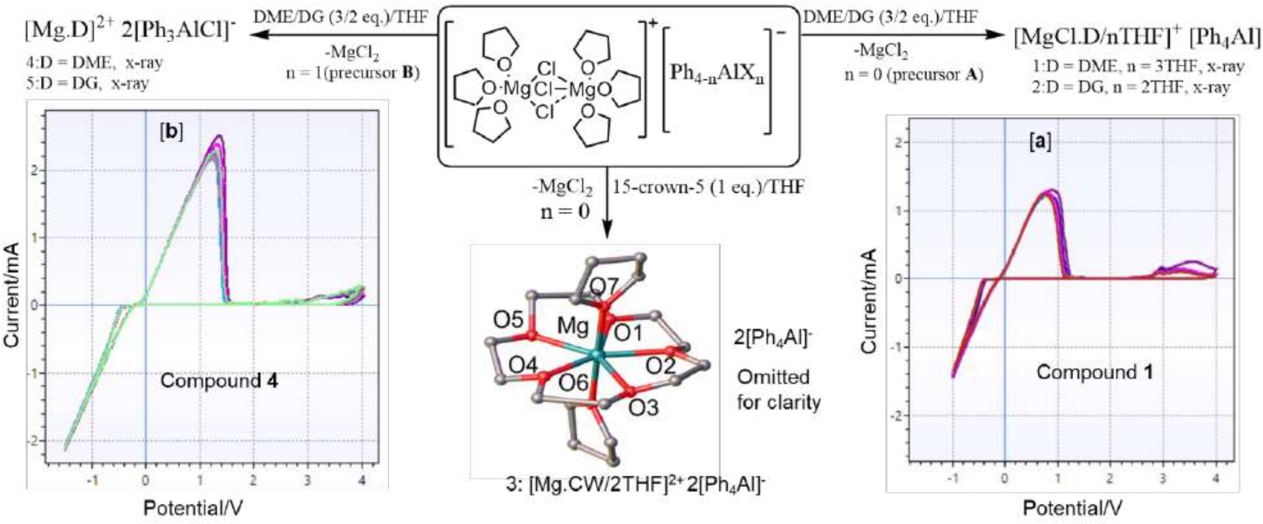
Dr. Yogendra Kumar, [a, b] Ananya Maddegalla, [b] Yuri Glagovsky, [a] Natalia Fridman,[a] Dmitry Bravo-Zhivotovskii,*[a] and Prof. Malachi Noked* [b]

[a] Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel
[b] Department of Chemistry Nanotechnology Center, Building: 206, Room B736, Bar-Ilan University, Ramat Gan, 5290002

E-mail: chrbrzh@technion.ac.il; mnoked@gmail.com

Here, we report the synthesis of novel electrolytes by addition of polydentate ligands to known precursor[1] $[Mg_2(\mu\text{-}Cl)_3{\bullet}6THF]+$ $[Ph_4Al]^-$, **A,** and $[Mg_2(\mu\text{-}Cl)_3{\bullet}6THF]^+$ $[Ph_3AlCl]^-$, **B**. Reaction of **A** with dimethoxyethane (DME), diglyme (DG) and 15-Crown -5 (CW) produces compounds $[DME{\bullet}MgCl{\bullet}3THF]^+$ $[Ph_4Al]^-$ **1,** $[DG{\bullet}MgCl{\bullet}2THF]^+$ $[Ph_4Al]^-$ **2** , **and** $[CW{\bullet}Mg{\bullet}2THF]^{2+}2[Ph_4Al]^-$ **3.** Reaction of precursor **B** with DME and DG leads to formation of $[Mg{\bullet}3DME]^{2+}$ $[Ph_3AlCl^-]_2$ **4** and $[Mg{\bullet}2DG]^{2+}$ $[Ph_3AlCl^-]_2$ **5,** respectively. All obtained compounds were isolated and fully described by NMR spectroscopy and X-ray crystallography.

We have found that the counter anion plays an important role in dictating the final product. In all cases addition of polydentate ligands leads to dissociation of the bridged $[Mg_2(\mu\text{-}Cl)_3{\bullet}6THF]^+$ cation: in case of precursor **A** with $[Ph_4Al]^-$ counter anion formation of $[MgCl]^+$ monocation species was observed, but in case precursor **B** with $[Ph_3AlCl]^-$ counter anion addition of polydentate ligands leads to formation of $[Mg]^{2+}$ dication. Reaction of precursor **A** with 15- crown-5 formed dication also. We found that the second product of dissociation of the bridged cation, i.e. $MgCl_2$, provides better solubility, wider electrochemical windows, and cyclic stability for the obtained electrolytes. All novel Mg electrolytes (**1**, **2**, **4** and **5**) have shown better electrochemical performance than previously reported precursors **A** and **B**.



Scheme. Synthesis of novel compounds (1, 2, 3, 4 and 5) and CV of novel electrolytes **1** (fig. a) and **4** (fig. b).

References:

1 J. A. Blázquez, R. R. Maça, O. Leonet, E. Azaceta, A. Mukherjee, Z. Zhao-Karger, Z. Li, A. Kovalevsky, A. Fernández-Barquín, A. R. Mainar, P. Jankowski, L. Rademacher, S. Dey, S. E. Dutton, C. P. Grey, J. Drews, J. Häcker, T. Danner, A. Latz, D. Sotta, M. R. Palacin, J. F. Martin, J. M. G. Lastra, M. Fichtner, S. Kundu, A. Kraytsberg, Y. Ein-Eli, M. Noked, D. Aurbach, *Energy Environ Sci* **2023**, 16, 1964.

Poster no. P_EC_27

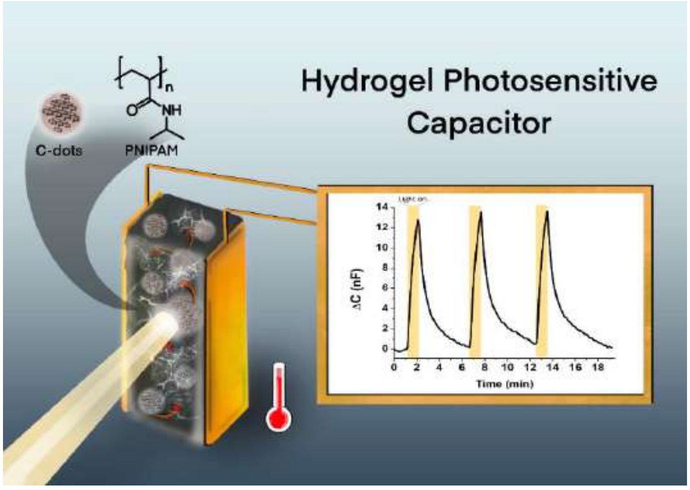
Mixed carbon-dot / thermo-responsive polymer capacitive wavelength-specific photodetector

1 Department of Chemistry, Ben Gurion University of the Negev, 84105, Beer Sheva, Israel 2 Ilse Katz Institute for Nanotechnology, Ben Gurion University of the Negev, 84105, Beer Sheva, Israel

Noa Prishkolnik‡,1Nitzan Shauloff,‡,1Seema Singh,1Rajendran Manikandan,1Uri Ben Nun,1 Raz Jelinek.*, 1, 2
‡ These authors are equally contributors.

E-mail: (noapri@post.bgu.ac.il)

Organic photodetectors are considered attractive alternatives to inorganic, semiconductor-based devices. We constructed a wavelength-specific capacitive photodetector, comprising carbon dots (C-dots) and poly-(N-isopropylacrylamide) (PNIPAM), a thermo-responsive polymer. Upon illuminating the C-dot/PNIPAM composite, light absorbed by the C-dots is released as heat; the photothermal effect gives rise to a rapid temperature increase con-sequently affecting structural transformation of the PNIPAM host and concomitant change in the recorded capacitance. Importantly, wavelength sensitivity of the photodetector is determined by the excitation wavelength of the embedded C-dots; we show that tuning the wavelength response of the system can be readily achieved through selection of the C-dot species incorporated within the PNIPAM matrix. The C-dot/PNIPAM photodetector ex-hibits reversibility and rapid light response, is synthesized from inexpensive and recyclable building blocks. The technology may be employed for photo-switching, photoinduced ca-pacitors, smart windows, and other photo-electronic applications.



Scheme 1: Schematic illustration of the capacitive photodetector prepared via
embedding the C-dot/PNIPAM hydrogel in a plastic cuvette plated on two sides with thin copper sheets.

Energy

Poster no. P_E_01

The correlation between the photoactivity of photocatalysts and the tensorial properties of the effective mass of their charge carriers

Eitay Shtayinberg, Professor Yaron Paz

Chemical engineering, Technion-Israel Institute for Technology, Haifa 3200003.

E-mail: Shtayinberg@campus.technion.ac.il , Paz@technion.ac.il

The potential of photocatalysis is well known and has been studied intensively[1]. photocatalysts may be used for water splitting, conversion of solar energy to electricity, conversion of CO2 to fuel, and decontamination of water, air, and surfaces[2]. When a photocatalyst absorbs a photon, generation of charge carriers occurs. The excited electron and the hole diffuse to the surface to perform redox reactions, or might recombine and annihilated[3]. The photoactivity of a photocatalyst depends on many coupled parameters. Consequently, the large diversity in terms of efficiency among the many types of photocatalysts is far from being understood[4-8]. In this study we suggest a correlation between the tensorial properties of the effective masses of the charge carriers and the photoactivity of photocatalysts. The BiOX (X= F, Cl, Br, and I) family of materials was chosen as a first model system. Micrometric single crystals of these materials were synthesized by microwave assisted synthesis. The crystals were fixed on self-manufactured micro-electrodes made by us under clean room conditions. Two measurement modes were developed in the clean rooms, the first one is based on two parts: one functions as a fixing device and the second as the measuring electrode and as an optical window that allows the crystal to be illuminated only through a 5 µm hole. The other setup is made of one integrated device, which functions as both the measuring electrode and the fixing device. In this setup, the whole crystal is illuminated. Integrating the measuring of photoinduced electrical currents at different conditions (different electrodes, different bias voltage) with the characterization of the directions in the crystals, and the calculated effective masses' tensors for the BiOX materials will, hopefully, allow us to construct a general parameter which will enable to confirm or to negate our hypothesis.

References:

1.Melchionna, M. & Fornasiero, P. Updates on the Roadmap for Photocatalysis. ACS Catal 10, 5493–5501 (2020).

2. Wang, S., Yun, J. H. & Wang, L. Nanostructured Semiconductors for Bifunctional Photocatalytic and Photoelectrochemical Energy Conversion. in Semiconductors and Semimetals vol. 97 315–347 (Elsevier Inc., 2017).

3. Emeline, V., A., Ryabchuk, K. V., Kuzenetsov, N., V. & Serpone, N. Interplay Between Physical and Chemmical Events in Photoprocesses in Hetrogeneous Systems. in Photocatalysis: Fundamentals and Perspectives. 218–244 (The Royal Society of Chemistry, 2016).

4. Hesari, M., Mao, X. & Chen, P. Charge Carrier Activity on Single-Particle Photo(electro)catalysts: Toward Function in Solar Energy Conversion. J Am Chem Soc 140, 6729–6740 (2018).

5. Meng, J. et al. Cubic-like BaZrO3 nanocrystals with exposed {001}/{011} facets and tuned electronic band structure for enhanced photocatalytic hydrogen production. J Mater Sci 54, 1967–1976 (2019).

6. Ohno, T., Sarukawa, K. & Matsumura, M. Crystal facets of rutile and anatase TiO2 particles and their roles in photocatalytic reactions. New Journal of Chemistry 26, 1167–1170 (2002).

7. Padmanabhan, N. T., Jayaraj, M. K. & John, H. Mechanistic insights into CTAB assisted TiO 2 crystal growth with largely exposed high energy crystal facets. J Environ Chem Eng 6, 5510–5519 (2018).

8. Wang, H. et al. Anisotropy of Photocatalytic Properties in Nanostructured Photocatalysts. Soft Nanoscience Letters 06, 11–30 (2016).

Poster no. P_E_02

Metal-Organic Framework-Based Photoelectrochemical cells for Selective Oxygen Reduction Reaction to Hydrogen Peroxide

E. Slavsky, I. Hod*

* *Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel*
E-mail: hodi@bgu.ac.il

Photo-electrochemical cells (PECs), which convert sunlight directly into chemical fuels, are considered to be one of the most promising and economically feasible future technologies for production of alternative energy sources. The main challenge in PECs currently revolves around designing appropriate photo-active materials that possess essential properties, such as broad range of visible light absorption, efficient charge carrier separation, and durability.

Metal-organic frameworks (MOFs) are class of porous crystalline materials consisting of metal ions or clusters linked by organic ligands to form a 3D/2D network structure. In recent years, MOFs have shown great potential to be utilized in photo/electro-catalytic energy-related schemes, due to their large surface area, tunable pore size and structure, chemical stability etc. Photo-active MOFs can potentially be used as a porous platform for the assembly of extremely high density of catalytically active sites (molecular catalysts) while providing mass-transport conduits accessible for diffusion of ions and catalytic-substrates towards the active sites. This study presents a novel approach for the photoelectrochemical reduction of oxygen to hydrogen peroxide by incorporating a cobalt porphyrin catalyst and a ruthenium N3 dye into a PEC based on a UIO-66 MOF. The Co-porphyrin functions as an efficient oxygen reduction reaction (ORR) catalyst, while the Ru N3 dye acts as a sensitizer to facilitate light absorption and electron injection into the PEC. The synergistic combination of these components aims to enhance the efficiency of the PEC system for the selective two electron reduction of oxygen to hydrogen peroxide as a promising avenue for sustainable energy storage and generation.

References:

1. Ifraemov, R., Mukhopadhyay, S., Rozenberg, I., & Hod, I. Metal–Organic-Framework-Based Photo-electrochemical Cells for Solar Fuel Generation. *The Journal of Physical Chemistry C*. **2022**, *126*(11), 5079-5091.
2. Chou, C. C., Wu, K. L., Chi, Y., Hu, W. P., Yu, S. J., Lee, G. H., ... & Chou, P. T. Ruthenium (II) sensitizers with heteroleptic tridentate chelates for dye-sensitized solar cells. *Angewandte Chemie*. **2022**, *123*(9), 2102-2106.
3. Ifraemov, R., Binyamin, S., Pearlmutter, Y., Liberman, I., Shimoni, R., & Hod, I. Photo-electrochemical O2 Reduction to H_2O_2 Using a Co-Porphyrin Based Metal-Organic Framework. *ChemElectroChem*, **2024**.

Poster no. **P_E_03**

Enhancing Brightness of Microelements through Plasmonic Nanostructure Coupling with Fluorescent Molecular Systems

Inbal Atzmon[1], Amit Krener[2] , Haleli Ben-Shushan[3], Ilya Olevsko[4] , Adi Salomon[4]*✉

1. Yehud Mekif High School, Mevo Natan Yonatan 1, Yehud. Israel
2. Ben Zvi High School , Shlomo ha-Melekh St 31, Kiryat Ono. Israel
3. Bar Ilan Ulpan, Olei HaGardom St 10, Netanya. Israel
4. Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52900 Israel;

Inbal Atzmon, Amit Krener , Haleli Ben-Shushan are equally contributed to this work.

E-mail: adi.salomon@biu.ac.il

Recent advancements in surface plasmon (SP) structures have led to the utilization of metallic hole arrays for color generation and filtering, offering reliability and color tunability. These structures, which can be manufactured in sub-micron sizes, are instrumental in achieving high pixel densities crucial for enhancing the clarity, sharpness, and overall quality of displayed images. However, conventional SP-based pixels suffer from limitations such as low brightness and only transmitting light rather than emitting it, thereby restricting the dynamic range and contrast of the technology.

In this study conducted as part of the Alpha program, we aimed to address the brightness issue of hole array-based structures by coupling SP with a molecular system. By introducing fluorescent molecules in close proximity to the plasmonic structures through the deposition of ultrathin layers, we sought to enhance the brightness. These layers were created utilizing a novel thin film platform known as Nano-Bead Emitters (NBE), developed in Prof. Adi Salomon's laboratory at Bar Ilan University. NBE facilitates the fabrication of thin, highly homogeneous fluorescent layers on various surfaces using a wide range of molecules, including those typically unable to form emitting thin films.

We developed three different colored NBEs based on bright emitting molecules emitting at RGB colors. Hole arrays with varying periodicities were fabricated to be coupled with the electronic transitions of these emitting molecules. The functional hybrid structures demonstrated increased transmittance and significantly higher emission, indicating potential applications as brighter optoelectric elements and platforms for energy transfer studies.

Poster no. P_E_04

Enhanced photocatalytic activity of Cs_4PbBr_6/WS_2 hybrid nanocomposite

Philip Nathaniel Immanuel[a] and Lena Yadgarov*[a]

[a] *Department of Chemical Engineering, Ariel University, Ariel, 4076414, Israel*..

E-mail: lenay@ariel.ac.il

Photocatalytic processes are among the prime means for mitigating the pollution caused by toxic effluents. In this context, photocatalysis presents a promising path and is undergoing rapid evolution. Halide perovskite-nanocrystals (HP-NCs) are excellent candidates due to their negative conduction band minimum and low work function, essential for photocatalysis. Yet, HP-NCs face limitations within this domain because they are prone to chemical degradation when exposed to external factors like high temperature, polar solvents, oxygen, and light. A practical approach toward stabilizing HP-NCs involves hybridizing them with a chemically inert material that can provide steric stabilization and act as a co-catalyst. Transition-metal dichalcogenides emerge as outstanding candidates to sterically stabilize the HPs as they are stable, chemically inert, and can serve as co-catalysts, enabling suppressed charge recombination. Here, we investigate the photocatalytic performance of Cs_4PbBr_6/WS_2-nanocomposites towards organic dye degradation in polar solvents under visible light illumination. We found that the presence of WS_2 nanostructures significantly stabilizes the HP-NCs and promotes dye degradation rate compared to pristine Cs_4PbBr_6-NCs. Using transient absorption measurements, we found that the WS_2-nanostructures act as an electron transport channel, effectively reducing charge recombination in the NCs. Our findings pave the way for implementing Cs_4PbBr_6/WS_2-nanocomposites as stable and superior photocatalysts.

Poster no. P_E_05

High-performance organic supercapacitors utilizing anthraquinonefunctionalized polydiacetylene and functionalized anthracene

Sudipta Biswas,* [a] Nitzan Shauloff,[a] Rajesh Bisht,[a] Rajendran Manikandan,[a] Shubhra Kanti Bhaumik,[a] and Raz Jelinek[a],[b]

[a] Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 8410501, Israel. [b] Ilse Katz Institute for Nanotechnology, Ben Gurion University of the Negev, Beer Sheva 8410501, Israel.

E-mail: sudiptab@post.bgu.ac.il

Organic supercapacitors are considered an attractive alternative to traditional inorganic-based charge storage devices due to their synthetic versatility, low cost, and environment-friendly features. Over the last decade, the surge in application-based research and miniaturization of devices created a demand for alternative small-scale but high-performance devices and so, organic electrodes are gaining attraction in the energy industry. Here, we present supercapacitor electrodes comprising organic derivatives as the core component of the electrode and tune them to have the best performance from them.

In the first set of electrodes, photopolymerized anthraquinone-polydiacetylene is employed as a core component in high-performance asymmetric supercapacitors (ASCs). Specifically, interspersed polydiacetylene-anthraquinone/polyaniline (PANI) electrodes are prepared via drop-casting and used as cathodes in devices employing polypyrrole/reduced graphene oxide anodes using aqueous or ionic liquid electrolytes. The excellent electrochemical properties of the polydiacetylene-anthraquinone/PANI electrodes, specifically high capacitance (specific capacitance ≈720 F g^{-1} at 1 A g^{-1}), long discharge time, and cycling stability, are ascribed to the superior redox profile of the anthraquinone and ambipolar charge transport associated with the polydiacetylene framework. The asymmetric supercapacitor can display a high energy density of 36 Wh kg^{-1} at a power density of 995 W kg^{-1}, underscoring the possible utilization of the anthraquinone-polydiacetylene derivative in practical energy storage devices.

In the second set of electrodes, anthracene derivatives were used as the core component. Specifically, anthracene linked to functionalized ethylene displaying different electron acceptors endows the electrodes with tunable energy gaps and concomitant redox potentials. The conjugated anthracene units in such systems both furnished the structural framework via adopting crystalline nanorod organization via π-π stacking, while the delocalized electrons likely participated in the reversible redox reactions contributing to electrode pseudo-capacitance. Asymmetric supercapacitors consisting of tert-butyl-ethylene-ketone-anthracene/polyaniline as the cathode were constructed, featuring excellent electrochemical performance. Specifically, the asymmetric device using an ionic liquid electrolyte displayed a broad voltage window, high cycling stability, and energy density of 30 Wh kg^{-1} at a power density of 620 W kg^{-1}. Overall, we show that organic electrodes with tuning and enhanced conductivity can serve as a probable electrode material for exiting supercapacitor technology.

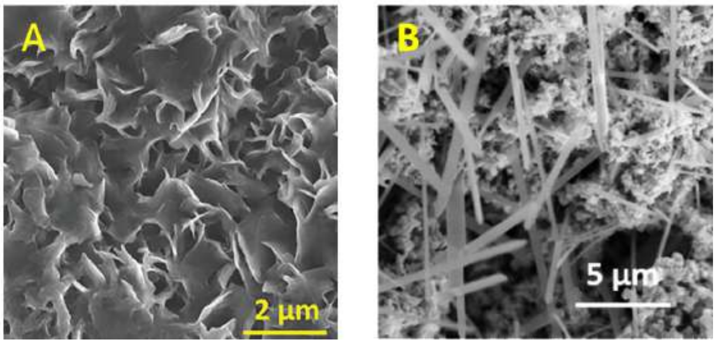


Figure 1: SEM micrographs for **A.** polydiacetylene-anthraquinone and **B.** anthracene/Polyaniline composite.

References:

1. Biswas, S., Shauloff, N., Bisht, R., & Jelinek, R., Anthraquinone‐Functionalized Polydiacetylene Supercapacitors. Advanced Sustainable Systems, **2023**, 2300035.
2. Biswas, S., & Chowdhury, A., Organic Supercapacitors as the Next Generation Energy Storage Device: Emergence, Opportunity, and Challenges. ChemPhysChem, **2023**, 24(3), e202200567.

Poster no. P_E_06

Unraveling the Mechanism of Haber-Bosch Catalysis under Working Conditions

The Haber-Bosch Process (HBP) is an industrial chemical process that converts hydrogen and nitrogen into ammonia at relatively harsh conditions (> 80 bar, > 450 °C). It is the most energy-intensive industrial process, accounting for ~2% of the world's energy consumption. However, the process operates at below 20% ammonia conversion and produces 1-2% of global CO2 emissions.

Our current understanding of the process is primarily based on oversimplified systems that utilize single-crystal facet metals, ultra-high vacuum (UHV) conditions, and apply static, ensemble spectroscopic measurements. In contrast, the HBP utilizes multifaceted and highly promoted nanoparticles that operate under pressures significantly higher than ultra-high vacuum conditions, with a difference of 13-15 orders of magnitude, where the active centers can undergo drastic dynamic alterations. Thus, substantial disparities in terms of materials, pressure, and time scales persist between our present comprehension of the process and its actual functioning.

In this work, we conduct operando modulation excitation FTIR operated at industrially relevant conditions to characterize the reaction under relevant conditions of Haber-Bosch catalysis. An industrial HBP catalyst and a set of well-defined silica-supported iron nanoparticles are synthesized. These catalysts are studied under operando transmission-FTIR (≤60 bar, 430-600 °C, N2/H2 gas flow) in real-time. Reactant gases (H2, N2) are then modulated and the data is processed using adapted phase-sensitive detection to unambiguously determine reaction intermediates. By investigating the reaction under real conditions, we provide the first realistic picture of the surface processes that occur in Haber-Bosch catalysis, which can help us to generate better processes and catalysts.

Energy and Sustainable Materials

Poster no. P_ESM_01

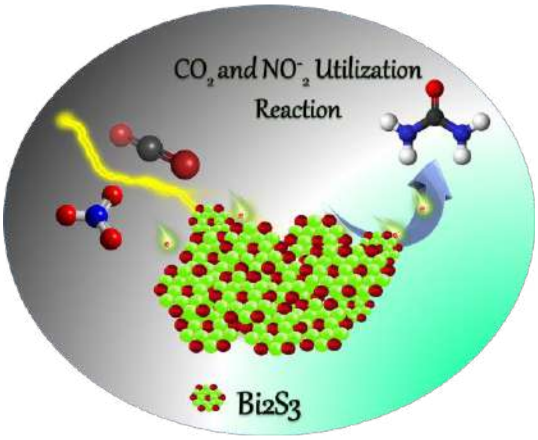
Efficient C-N coupling in the direct synthesis of urea from CO_2 and NO_3 on Bi_2S_3 nanoparticles

Ajay V. Munde [a] and Alex Schechter *[a,b]

[a] Department of Chemical Sciences, Ariel University, Ariel 40700, Israel. b Research and Development Centre for Renewable Energy, New Technology Centre, University of West Bohemia, 301 00 Pilsen, Czech Republic.
*E-mail: salex@ariel.ac.il; Tel.: +972 39371470; Fax: +972 547740254

The effective reduction and utilization reactions of organic small molecules (H_2O, O_2, CO_2, NH_3, N_2, and NO_x) into useful products have recently attracted a lot of attention. The electrochemical coupling of CO_2 and NO_2^- in H_2O to synthesize urea under ambient conditions remains a major challenge. The synthesized noble metal-free Bi_2S_3 NPs have been characterized by various techniques such as The XRD pattern confirming the Face centred cubic (FCC) crystal structure of Bi_2S_3, Raman spectrum and Furrier transform-Infrared (FT-IR) confirmed Bi-S bond. The cyclic voltammetry (CV) demonstrates an ultra-low potential of -0.4 V vs. RHE. The bulk electrolysis on Bi_2S_3 NPs electrocatalyst demonstrated a potential of -0.5 V vs. RHE to reach up to high yield urea formation with a Faradic yield of 56.7%.In this study, Bi centre promotes the absorption and activation of inert CO_2 and NO_3. Electronegative S adjutant to Bi further improves the mass transfer efficiency and stability towards the urea synthesis. Current studies have highlighted the enhancement in activity along with selectivity for product formation could be due to having a capable active interface from electrocatalysts for low-cost and proficient production of fuels and fertilizer.

Keywords: Urea Synthesis, Bi_2S_3 NPs electrocatalyst, fertilizer, sustainable energy and environment



Scheme: Electrochemical urea synthesis. ..

Acknowledgements: We thank Ariel University, Samaria & Israel Chemical Society

References:

1. Mei, Z.; Zhou, Y.; Lv, W.; Tong, S.; Yang, X.; Chen, L.; Zhang, N., Recent Progress in Electrocatalytic Urea Synthesis under Ambient Conditions. ACS Sustainable Chem. Eng. **2022**, 10 (38), 12477-12496.

2. Wu, W.; Yang, Y.; Wang, Y.; Lu, T.; Dong, Q.; Zhao, J.; Niu, J.; Liu, Q.; Hao, Z.; Song, S., Boosting electrosynthesis of urea from N2 and CO2 by defective Cu-Bi. Chem Catalysis. **2022**, 2 (11), 3225-3238.

Poster no. P_ESM_02

Metal-Organic Frameworks (MOFs) for Enhanced Stability of Halide Perovskites in Renewable Energy Applications

Alen Sam Thomas [a], Lena Yadgarov [a]*

[a] *Department of Chemical Engineering, Ariel University, Ariel, Israel*

E-mail: lenay@ariel.ac.il

Perovskite nanocrystals (NCs) have emerged as promising optical materials holding significant potential for diverse optoelectronic applications.[1] However, their inferior stability against moisture, oxygen, light, and heat limits their practical applications. Incorporating metal-organic frameworks (MOFs) with halide perovskites (HP) has emerged as a promising approach for enhancing their stability.[2] Our study uses the hot-injection method to synthesize CsPbBr3 NCs, followed by the composite formation with Zn-based MOFs known as zeolitic imidazolate frameworks (ZIFs). Specifically, we use zeolitic imidazole framework-8 (ZIF-8) as the MOF template for this composite formation. The encapsulation matrix created by these MOFs effectively isolates CsPbBr3 from the surroundings and prevents the perovskite from decomposing or oxidizing in ambient conditions. Structural and optoelectronic studies of these composites indicate the successful formation and extraordinary stability of the CsPbBr3/ZIF-8. Our findings offer a potential avenue for a wide range of applications in renewable energy, offering promising opportunities for further advancements. Moreover, this work will provide valuable insight into stabilizing halide perovskite materials via facile and cost-effective methods.

References:

(1) Chouhan, L.; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites. *Chem. Soc. Rev.* **2020**, *49* (10), 2869–2885. https://doi.org/10.1039/c9cs00848a.

(2) Zhang, C.; Li, W.; Li, L. Metal Halide Perovskite Nanocrystals in Metal–Organic Framework Host: Not Merely Enhanced Stability. *Angew. Chemie* **2021**, *133* (14), 7564–7577. https://doi.org/10.1002/ange.202006169.

Poster no. P_ESM_03

High-Entropy: An Effective Approach to Improve Electrochemical Performance of Ni-rich Zero-Cobalt Layered Cathodes for Li-ion Batteries

Amreen Bano,* Malachi Noked and Dan T Major

Department of Chemistry and Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel

E-mail: (banoamreen.7@gmail.com)

Owing to their high-energy density, Ni-rich, Co-free layered cathodes are potential candidates for next-generation Li-ion batteries. However, such cathode materials face severe capacity fading during electrochemical cycling. As a solution to this drawback, high entropy (HE) materials, which are created by multiple-element doping (**Figure 1**), have been proposed. Although a comprehensive mechanism of action has not yet been presented, recent experimental work[1] has demonstrated that HE Ni-rich cathode materials can offer outstanding capacity retention on cycling. In order to clarify the key characteristics of HE layered oxides as cathode materials in Li-ion batteries, we here provide calculations using first principles and classical methods. We propose that the superior performance of HE Ni-rich layered oxide cathode materials over other Ni-rich cathodes could be attributed to the following five prime factors: (1) low degree of anti-site defect; (2) invariant local crystal field environment; (3) strong metal-oxygen bonding; and (4) low operational voltage.[2]

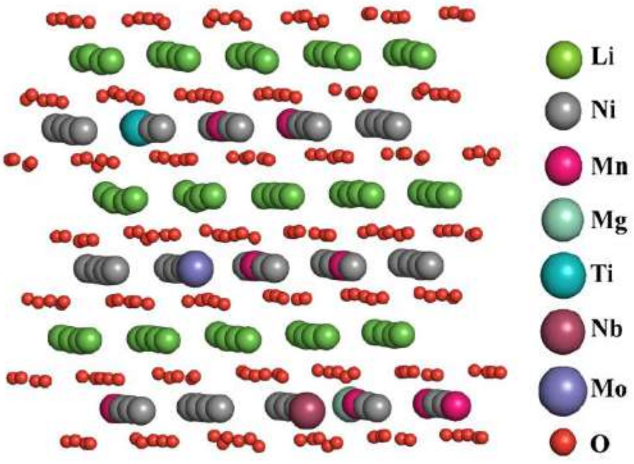


Figure 1: MCSA simulated and geometrically optimized R3m structure of HE-LNMO with layered atomic arrangement.

Acknowledgements: Support for this project was provided by the Israeli Committee for Higher Education within the framework of the INREP project.

References:

1. Zhang, R.; Wang, C.; Zou, P.; Lin, R.; Ma, L.; Yin, L.; Li, T.; Xu, W.; Jia, H.; Li, Q.; Sainio, S.; Kisslinger, K.; Trask, S. E.; Ehrlich, S. N.; Yang, Y.; Kiss, A. M.; Ge, M.; Polzin, B. J.; Lee, S. J.; Xu, W.; Ren, Y.; Xin, H. L., Compositionally complex doping for zero-strain zero-cobalt layered cathodes, Nature 2022, 610 (7930), 67-73.
2. Bano, A.; Noked, M.; Major, D. T., Theoretical Insights into High-Entropy Ni-Rich Layered Oxide Cathodes for Low-Strain Li-Ion Batteries, Chem. Mater. 2023, 35 (20), 8426-8439.

Poster no. P_ESM_04

Understanding the excited state structural dynamics of a phase transformable photoactive metal-organic Framework MIP 177 through Time-Resolved Infrared spectroscopy

Aneek Kuila [a], Yaron Paz*[a]

[a] *Department of Chemical Engineering, Technion- Israel Institute of Technology, Haifa, Israel, 3200003.*

(e-mail: paz@technion.ac.il)

MIP 177 LT and MIP 177 HT are two phase transformable metal organic framework consisting of a $Ti_{12}O_{15}$ oxocluster and a tetracarboxylate ligand that exhibit robust chemical stability and improved photoactivity. The LT differs from the HT through the changes in attachment of its Ti-Oxo subunits. In terms of chemical and photoactivity MIP 177 LT is found to perform better than the MIP 177 HT. Step-scan Fourier transform absorption difference time-resolved spectroscopy has been used to collect mid-IR time-resolved infrared spectra of the transient electronic excited states of a nano-porous metal–organic framework MIP 177 LT and HT with 2.5 ns time resolution. Analyzing the time-resolved vibrational data after 355nm LASER excitation reveals the presence of temporal changes of ν (O-Ti-O) of the Ti-O metal cluster and ν (-COO) of the ligand, concluding the fact that these moieties are the ultimate acceptors of the excited charges which are localized over those regions at the nanosecond timescale (Figure 1). A direct negative correlation between the differential absorbance (Δ Absorbance) reveals the charge transfer relation among these two moieties. A longer-lived transient signal up to 180ns for MIP 177 LT compared to the 100 ns of MIP 177 HT shows the extended lifetime of the reactive charges over the surface that exerts in their effectivity. An ultrafast change of bidentate to monodentate bridging in the -COO-Ti-O ligand-metal coordination environment was observed after the photoexcitation of MIP 177 LT. This change was found to be long-lived. The phenomenon is unique to MIP 177 LT as it was not observed with HT. This in-situ change in the coordination denticity during the photoexcitation, which was not observed previously, may explain the ability of MIP 177 LT to accumulate electrons during continuous photoexcitation leading to a superior photocatalytic activity.

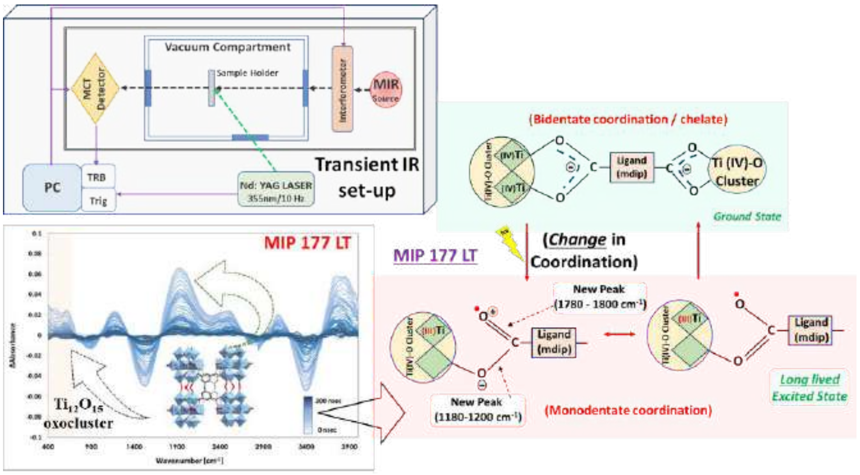


Figure 1: A block diagram of the transient IR set up along with the transient difference spectra of MIP 177 LT HT 355 nm LASER excitation and the corresponding excited state structural dynamics

Acknowledgements: We acknowledge the support received from the European Union Horizon 2020 research and innovation programme (METHASOL project, Grant Agreement N°101022649).

References:

1. García-Baldoví, Alberto, et al. "Active site imprinting on Ti oxocluster metal–organic frameworks for photocatalytic hydrogen release from formic acid." *Energy & Environmental Science* 16.1 (2023): 167-177.
2. Paz, Yaron. "Transient IR spectroscopy as a tool for studying photocatalytic materials." *Journal of Physics: Condensed Matter* 31.50 (2019): 503004.

Poster no. P_ESM_05

Multi-functional MN_4 Macrocycles as Electrocatalysts

Arik Raslin,[a] Zeev Gross*[a]

Schulich Faculty of Chemistry, Technion- Israel Institute of Technology, Haifa 320008, Israel.

raslin.arik@campus.technion.ac.il, chr10zg@technion.ac.il

The preparation and utilization of efficient, affordable, and non-toxic catalysts for the electrochemical reactions could improve the sustainability of our energy supply. Particular interest is in the hydrogen evolution reaction (HER), selective water oxidation to oxygen (OER), and selective reduction of oxygen to water (the oxygen reduction reaction, ORR).[1,2] Platinum group metals (PGM) are outstanding catalysts for all these reactions, but are rare and expensive, which prevents their industrialization. Within the search for catalysts based on earth abundant 1st row transition metals, we now introduce two different molecular catalysts: Co(III) complexes of corroles, with very different in size *meso*-C substituents (C_6F_5 >> CF_3 >> H), as well by newly synthesized and fully characterized Co(II), Cu(II) and Ni(II) monoazaporphyrins (MAzP) with *meso*-CF_3 substituents. All the catalyst were adsorbed on carbon supports with very different porosity and surface area (BP2000 >> Vulcan). The corrole-modified electrodes were studied as ORR catalysts, revealing that the onset potential of the best performing cobalt corrole is approaching that of Pt. That complex was studied as a cathode for an anion exchange membrane fuel cell (AEMFC), revealing high power density relative to other molecular catalysts and high stability over 12 hours.

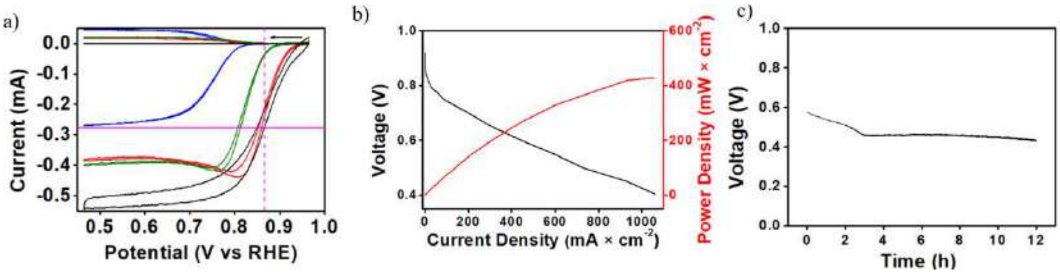


Figure 1: RRDE measurements in 0.1 M KOH solution, at 1000 rpm, of a) *meso*-C_6F_5 substituted complex (blue), *meso*-CF_3 substituted complex (red), and unsubstituted corrole (green), all adsorbed onto Vulcan, compared to 20% Pt/Vulcan (black). b) AEMFC polarization curves of voltage (black) and power density (red) vs current density for the combination of Pt-Ru anode and the best complex cathode, at cell temperature of 60 °C. c) Stability experiment of the studied cathode.

Metal complexes of the novel MAzP with CF_3 on the three *meso*-C positions were accidentally discovered in the attempt to improve the synthesis of minimally substituted corroles. The cobalt, copper, and nickel complexes were studied as catalysts for HER. OER, and ORR in 0.1 M KOH. The cobalt complex performed best in all processes. Compared to cobalt porphyrins with either three or four CF_3 groups on the *meso*-C positions, Co-MAzP was the best catalyst for water oxidation. For HER catalysis, it has the same onset potential and current as the tetra-CF_3 cobalt porphyrin and more current than the tris-CF_3 analogue. In ORR catalysis, Co-MAzP performs with the lowest onset potential, but less H_2O_2 is formed via catalysis by the other porphyrins.

(1) Meng, J.; Lei, H.; Li, X.; Qi, J.; Zhang, W.; Cao, R. Attaching Cobalt Corroles onto Carbon Nanotubes: Verification of Four-Electron Oxygen Reduction by Mononuclear Cobalt Complexes with Significantly Improved Efficiency. *ACS Catal.* **2019**, *9*, 4551–4560.

(2) Fornaciari, J. C.; Weng, L.-C.; Alia, S. M.; Zhan, C.; Pham, T. A.; Bell, A. T.; Ogitsu, T.; Danilovic, N.; Weber, A. Z. Mechanistic Understanding of PH Effects on the Oxygen Evolution Reaction. *Electrochim. Acta* **2022**, *405*, 139810.

Poster no. P_ESM_06

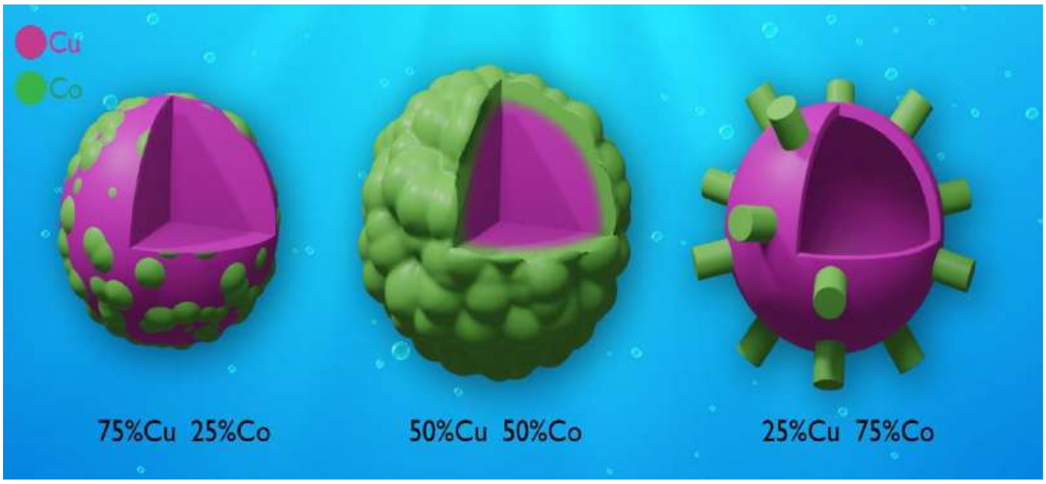
Copper-Cobalt Phosphides as efficient electrocatalysts for overall water splitting and methanol oxidation reaction

Dyuti Bandyopadhyay[1], Maya Bar-Sadan[1,2] *

[1]*Ben-Gurion University of the Negev, Department of Chemistry, Beer-Sheva, Israel.*
[2]*Ilze Katz Institute of Nanoscale Science and Technology, Ben Gurion University, Israel*.

E-mail: ((barsadan@bgu.ac.il))

Forming complex structures of functional materials in a controlled and reproducible fashion is a well-known challenge. Specifically, bimetallic phosphides are of interest for energy-related applications; however, a satisfactory structure-function relationship has not been fully deciphered yet. In this work, we show that a colloidal chemistry approach produces bimetallic phosphides electrocatalysts of Co and Cu, where segregation and phase transformation induce significant changes in morphology compared to solid solutions **(Figure 1)**. Their complexity permits the tuning of the catalytic sites to the hydrogen and oxygen evolution reactions (HER and OER), allowing the bimetallic phosphides to catalyze the full water splitting reaction. [1] The experimental results show that in alkaline medium water cleavage is particularly favorable on Cu_xCo_yP catalysts (and especially when x = 50%), enhancing their HER performance with an overpotential of 184 mV @ 10 mA/cm^2. As for the OER enhancement, the results show that the bimetallic phosphides undergo a surface transformation during the OER, whereby (oxy)hydroxides form at anodic potentials in alkaline solution and serve as the actual electrocatalysts. The best OER performance was displayed by $Cu_{25}Co_{75}P$ having an overpotential of 283 mV @ 10 mA/cm^2. [2,3] Additionally, these Cu_xCo_yP catalysts offer promising functionality towards methanol oxidation reaction (MOR) without fully oxidizing it to CO_2 and rather producing beneficial by product of formate, displaying a lower overpotential by up to 160 mV as compared to OER and a higher mass activity. This kind of selective oxidation of methanol is highly desired in direct alcohol fuel cell applications.[4]



Scheme 1: Scheme showing the predicted morphologies of Cu_xCo_yP catalysts.

Poster no. P_ESM_07

Self-Healing Phenomenon in Antimony Trichalcogenides and Chalcoiodides: Insights into Photoinduced Damage Recovery and SolidState Reactions

Balakrishnan, Subila Kurukkal,[a]

Parambil, Priyakumari Chakkingal,[a] Anchal Vashishtha,[a] Yaniv Dror, [a] and Edri Eran*[a]

[a] *Chemical Engineering, Ben-Gurion University of the Negev, Ben-Gurion Blvd.. 1, Be'er Sheva, Israel*

E-mail: edrier@bgu.ac.il

The prevalence of self-healing semiconductors is limited to a select few cases, impeding a comprehensive understanding of this phenomenon. In this oral presentation, we present our findings on the self-healing process observed after photoinduced damage in antimony trichalcogenides and chalcoiodides. These materials, characterized as quasi-one-dimensional semiconductors, hold great potential for applications in photovoltaics and other electronic devices. Our study establishes a correlation between self-healing and photoinduced phase transition (PIPT), whereby the "damaged" state of the semiconductors recovers through a process of self-healing. Through the use of vibrational spectroscopy, we have successfully identified intermediate species and examined the dynamics of the reaction. By comparing four different materials with similar crystal structures, we have identified a shared structural feature that contributes to self-healing in these materials. Additionally, a thorough analysis of the chemical bonding has allowed us to rationalize the chemical reaction and identify bonding states at the bottom of the conduction band as pivotal factors in driving the hidden phase. Expanding our knowledge of self-healing materials, both in terms of variety and quantity and gaining insights into the underlying solid-state reactions will foster the development of self- healing electronic building blocks, thereby enabling the creation of dynamic electronic devices.

Poster no. P_ESM_08

Localized synthesis and in-situ catalytic characterization of MOF-Based materials using SECM

I. Liberman[1], R. Shimony[1], R. Iframove[1], and I. Hod[1]

[1] *Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel*
Idan Hod e-mail: hodi@bgu.ac.il

Electrocatalysis is considered to be a promising and economical solution for the fossil fuel-free energy market as a part of the solar fuels production cycle[1]. To date, great efforts are being made to find new, efficient, and earth-abundant catalytic materials as a substitute for the currently used noble metal-based electrocatalysts. In this regard, Metal-Organic Frameworks (MOFs) and MOF-converted materials have emerged as promising electrocatalysts for those reactions owing to their intrinsic properties, such as robust porosity and large surface area, crystalline structure, and tuneable chemical composition. Lately, we have shown several strategies for the utilization of MOF-based materials for different energy conversion applications. This was achieved by careful design of the MOF platform, [2] introduction of guest molecules[3], or by electrochemical conversion of the MOF (EC-MOF) into metal sulfide-based catalysts. EC-MOF allows us to carefully control the rate of MOF conversion and, therefore control the structure and chemical composition of the resulting catalyst.[4] Nevertheless, future improvement of electrocatalytic performance must involve the design of new methods for swift, high-throughput electrochemical performance screening.

Scanning electrochemical microscopy (SECM) is a powerful scanning probe technique aimed for rapid electrochemical activity screening of catalytic materials with varying compositions. In addition, SECM was also utilized for micrometric scale deposition of a variety of materials such as metals, polymers, and semiconductors. In my research I am combining the synthetical and analytical capabilities of SECM in order to fabricate MOF-based electrocatalysts and subsequently study their catalytic performance (HER and OER) in a localized fashion. Specifically, using localized EC-MOF,[5] we demonstrate an electrochemical conversion, in a localized fashion, of two types of MOF, ZIF-67 and (Fe, Ni)-MIL-53 into their respective metal sulfides (CoS_x and $FeNiS_x$). Moreover, pristine MOF micropatterns (HKUST-1 and $Al_2(OH)_2$-TCPP) were electro-synthesized using an SECM tip.[6] The electrocatalytic activities of the resulting MOF-converted CoS_x, $FeNiS_x$, and pristine $Al_2(OH)_2$-TCPP MOF micropatterns were studied using SECM mapping. These results may open a new path for high-throughput electrocatalysts characterization toward the development of highly efficient catalysts for a wide range of energy-related reactions

References:

[1] A. Züttel, A. Remhof, A. Borgschulte and O. Friedrichs, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 2010, 368, 3329-3342.
[2] R. Ifraemov, R. Shimoni, W. He, G. Peng and I. Hod, J. Mater. Chem. A, 2019, 7, 3046-3053.
[3] I. Liberman, R. Shimoni, R. Ifraemov, I. Rozenberg, C. Singh and I. Hod, Journal of the American Chemical Society, 2020, 142, 1933-1940
[4] W. He, R. Ifraemov, A. Raslin and I. Hod, Adv. Funct. Mater., 2018, 28, 1707244
[5] I. Liberman, W. He, R. Shimoni, R. Ifraemov and I. Hod, Chem. Sci., 2020, 11, 180-185
[6] I. Liberman, R. Ifraemov, R. Shimoni and I. Hod, Adv. Funct. Mater. 2022, 32, 2112517

Poster no. P_ESM_09

Molecular dynamics simulation of electrode-electrolyte interfaces in aqueous sodium ion batteries

Amey Nimkar[a], Khorsed Alam*[a], Gil Bergman[a], Mikhael D. Levi[a], Dan Thomas Major[a], Netanel Shpigel[a], Doron Aurbach[a]

[a] *Department of Chemistry, Institute of Nanotechnology and Advanced Materials (BINA), Bar-Ilan University, Ramat Gan, Israel, 5290002*

*E-mail: khorsed.dumkal@gmail.com

Designing aqueous sodium ion batteries that work in diluted electrolytes is critical for developing cost-effective batteries for large-scale energy storage applications. We recently demonstrated a stably operated organic perylenetetracarboxylic dianhydride (PTCDA) anode in diluted (1M) sodium electrolyte solutions by regulation of electrolyte anions. Chaotropic anions, such as ClO_4^- and Cl^-, facilitate impressive performance of PTCDA anodes, whereas kosmotropic anions, such as CO_3^{2-} and SO_4^{2-}, cause rapid capacity fading. To better understand the effect of anions on the performance of PTCDA electrodes, in this work we performed classical molecular dynamics (MD) simulations of PTCDA-electrolyte interfaces in the presence of 1M Na_2CO_3 and $NaClO_4$ electrolytes. Analysis of the MD simulation trajectories revealed the distributions of electrolyte ions and water molecules at the interface, radial distribution function of water around anions, and the rate of PTCDA dissolution into the electrolyte.

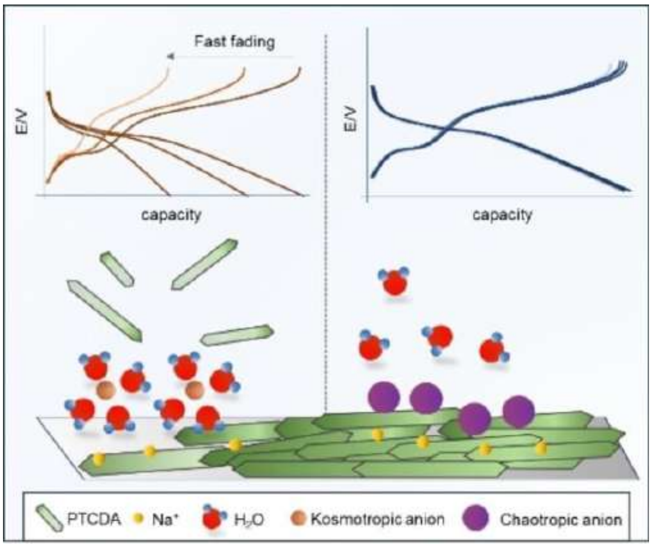


Figure 1: Charge-discharge voltage profiles and PTCDA dissolution in presence of kosmotropic and chaotropic anions.

References:

1. Nimkar, A.; **Alam, K.**; Bergman, G.; Levi, M. D.; Major, D. T.; Shpigel, N.; Aurbach, D. Is “Water in Salt” Electrolytes the Ultimate Solution? Achieving High Stability of Organic Anodes in Diluted Electrolyte Solutions Via a Wise Anions Selection. Angew. Chem., **2023**, 135, 47, 1521-3757.

Poster no. P_ESM_10

Light-driven Microbial Fuel Cell for Direct Conversion of Cellulose to Electrical Power

Mor Shemesh, [a] Yifat Cohen, [a] Matan M. Meirovich, [a] and Omer Yehezkeli*[a]

[a] *Faculty of Biotechnology and Food Engineering, Technion-Israel Institute of Technology, Haifa 320000, Israel.*

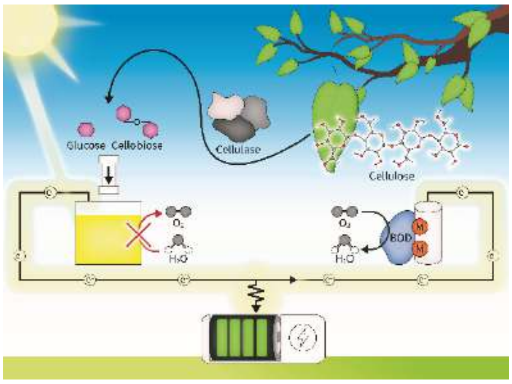
E-mail: morshemesh34@campus.technion.ac.il

Exploiting biomass and other cellulose-based materials as fuel has attracted increasing attention in the last few decades. Lignocellulose biomass is an abundant renewable resource, which is mainly composed of polysaccharides (cellulose and hemicellulose) and lignin. However, approximately 40% of this cellulosic material biomass cannot be exploited as food and ends up as waste. Therefore, many efforts are directed toward biomass utilization for renewable energy generation with the potential to replace conventional fossil fuels.[1,2]

Herein, we develop a modular biotic/abiotic model configuration that facilitates one-pot degradation and light-induced conversion of cellulosic material into electrical power and added valued compounds. To enable high photo-oxidation efficiency, bismuth vanadate functionalized with high cobalt phosphate loading ($BiVO_4$-HL-CoP) photoanode was developed and optimized to fully suppress undesired competing reactions. The suppression limits the water oxidation reaction nevertheless, enables glucose oxidation. The $BiVO_4$-HL-CoP-based photoanode was coupled with bilirubin oxidase (BOD) based biocathode for full photo-bio-electrochemical cell configuration. In this configuration, the ‘cellulase’ enzymatic complex was used to enable the complete breakdown of cellulose into glucose that in turn consumed as fuel at the photoanode for energy generation (**scheme** 1).[3]

We will further show the development of a bias-free microbial fuel cell device that directly utilizes cellulose for electrical energy generation. The insoluble cellulose is degraded by *Clostridium thermocellum* anaerobic cellulolytic bacteria to different saccharides, e.g. cellobiose. In turn, these energy-valued chemicals are further oxidized by the $BiVO_4$-HL-CoP photo-anode to generate photocurrents. The developed photoanode is then coupled with a photo-cathode to establish a photo-microbial-fuel cell apparatus. The photo-driven microbial cell exhibits high performance with great stability.

The designed configuration presents a novel platform that may be utilized for the conversion of other non-environmentally friendly waste sources e.g. bioplastic to electrical energy and added-value chemicals in a pollution-free manner.



Scheme 1: Illustration of the $BiVO_4$-HL-CoP/BOD photo-bio-electrochemical cell converting directly cellulose to electrical power.

References:

1. Kuehnel, M.F., and Reisner, E. (2018). Solar Hydrogen Generation from Lignocellulose. Angewandte Chemie International Edition 57, 3290–3296. 10.1002/anie.201710133.
2 .Turner, J.A. (1999). A Realizable Renewable Energy Future. Science 285, 687–689. 10.1126/science.285.5428.687.
3. Shemesh, M., Cohen, Y., Cohen, R., Meirovich, M.M., Herzallh, N.S., Chmelnik, O., Shoham, Y., and Yehezkeli, O. (2023). Light-driven and bias-free direct conversion of cellulose to electrical power. CR-PHYS-SC 0. 10.1016/j.xcrp.2023.101546.

Poster no. P_ESM_11

Carbon dots and poly-(N-isopropylacrylamide) (PNIPAM) composite for organic photodetectors a

Abstract

Organic photodetectors are considered attractive alternatives to inorganic, semiconductor-based devices. We constructed a wavelength-specific capacitive photodetector, comprising carbon dots (C-dots) and poly-(N-isopropylacrylamide) (PNIPAM), a thermo-responsive polymer. Upon illuminating the C-dot/PNIPAM composite, light absorbed by the C-dots is released as heat; the photothermal effect gives rise to a rapid temperature increase con-sequently affecting structural transformation of the PNIPAM host and concomitant change in the recorded capacitance. Importantly, wavelength sensitivity of the photodetector is determined by the excitation wavelength of the embedded C-dots; we show that tuning the wavelength response of the system can be readily achieved through selection of the C-dot species incorporated within the PNIPAM matrix. The C-dot/PNIPAM photodetector ex-hibits reversibility and rapid light response, is synthesized from inexpensive and recyclable building blocks. The technology may be employed for photo-switching, photoinduced ca-pacitors, smart windows, and other photo-electronic applications.

Poster no. **P_ESM_12**

CO_2 conversion via reverse water gas shift on Ni(111) model catalyst

Roey Ben David,[a] and Baran Eren*[a]

[a] *Department of Chemical and Biological Physics, Weizmann Institute of Science, 234 Herzl Street, 76100 Rehovot, Israel*

E-mail: baran.eren@weizmann.ac.il

Catalytic conversion of CO_2 to useful chemicals or fuels might be the key for dealing with the major problems of global warming and oceans acidifications. Two important CO_2 conversion reactions with H_2 are CO_2 methanation, also known as the Sabatier reaction, and CO_2 reduction to CO via the reverse water gas shift (RWGS) reaction. Ni-based catalysts are known to be active for both reactions, while the selectivity towards methane or CO depends on the reaction conditions and the structure of the catalyst. Recently, extensive experimental and theoretical research has been carried out to elucidate some fundamental mechanistic aspects of the Ni-CO_2+H_2 system, including the reaction pathway, structure sensitivity, particle size effect and the active sites for the reaction[1,2]. However, the role of each Ni facet under realistic reaction conditions remains unsolved.

Here, we study the role of Ni(111) facets during CO_2 hydrogenation using *in situ* surface-sensitive infrared spectroscopy under ambient pressure and temperature conditions. Our findings suggest that the main reaction occurring on the Ni(111) surface is RWGS (rather than CO_2 methanation), which is composed of several surface reaction steps: dissociative adsorption of CO_2 to CO and atomic oxygen, oxygen reaction with hydrogen to form water and CO desorption. Hydrogen was found to affect the occupancy distribution of CO between hollow and top sites by eliminating oxygen from the energetically preferred hollow sites. Overall, a balance between oxygen production from CO_2 dissociation and oxygen removal by hydrogen determines the oxygen coverage and thereby the distribution of CO between top and hollow sites. We demonstrate that this balance strongly depends on the reaction temperature and the H_2/CO_2 partial pressures (schematically described in Figure 1).

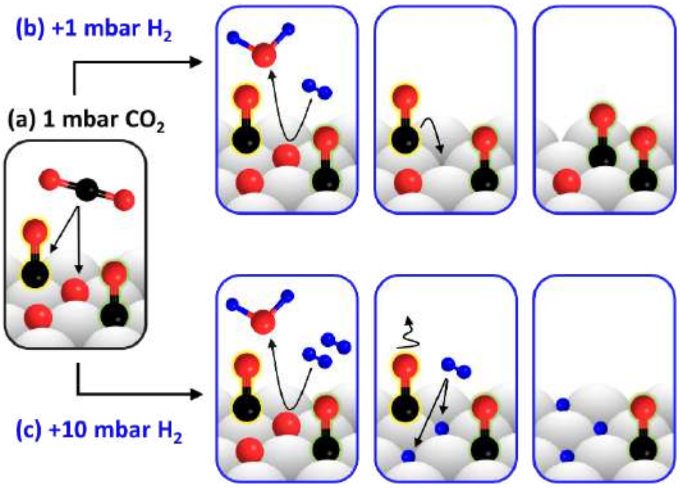


Figure 1: Schematic model of the surface processes and surface intermediates on Ni(111): **(a)** under 1 mbar CO_2, and following the addition of **(b)** 1 mbar H_2 and **(c)** 10 mbar H_2 (all at 25 °C).

References:

(1) Sterk, E. B.; Nieuwelink, A. E.; Monai, M.; Louwen, J. N.; Vogt, E. T. C.; Filot, I. A. W.; Weckhuysen, B. M. Structure Sensitivity of CO2 Conversion over Nickel Metal Nanoparticles Explained by Micro-Kinetics Simulations. *J. Am. Chem. Soc.* **2022**, *2* (12), 2714–2730. https://doi.org/10.1021/jacsau.2c00430.

(2) Vogt, C.; Groeneveld, E.; Kamsma, G.; Nachtegaal, M.; Lu, L.; Kiely, C. J.; Berben, P. H.; Meirer, F.; Weckhuysen, B. M. Unravelling Structure Sensitivity in CO2 Hydrogenation over Nickel. *Nat. Catal.* **2018**, *1* (2), 127–134. https://doi.org/10.1038/s41929-017-0016-y.

Poster no. P_ESM_13

In-gap States and Carrier Recombination in Quasi-2D Perovskite Films

Bat-El Cohen [a], Ron Alafi [b], Jonathan Beinglass [c], Adva Shpatz Dayan [a], Oren Goldberg [c , Shachar Gold* [d], Isaac Balberg [c], Leeor Kronik [d], Lioz Etgar [a], Oded Millo [c], and Doron Azulay [b, c]

[a] *Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.*

[b] *Azrieli College of Engineering, Jerusalem 9103501, Israel.*

[c] *Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.*

[d] *Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovoth 7610001, Israel*

E-mail: shachar.gold@weizmann.ac.il

In-gap states and their effect on recombination rates in quasi-2D lead–iodide-based perovskites, intercalated with various spacer molecules, are studied using a combination of scanning tunneling spectroscopy and temperature-dependent photoconductivity measurements. The results are further analyzed by a Shockley–Read–Hall model. Indications for shallow in-gap states, positioned at about 0.15–0.2 eV below the bottom of the conduction band, are found. These states are identified as dominating the recombination route of photogenerated carriers in these systems, with a relatively large capture coefficient of about $10^{-5} - 10^{-6}\ \mathrm{cm^3 s^{-1}}$ at room temperature. First-principles calculations based on density functional theory imply that these states are not an intrinsic effect of the inclusion of the spacer molecules, but rather one that arises from chemical defect formation or structural deformation of the perovskite layers. The results suggest that further improvement of the performance of solar cells that are based on quasi-2D perovskites requires, along with enhancing carrier mobility, efforts to suppress the concentration of these detrimental defect states

Acknowledgements: D.A., O.M., and I.B. thank the support of ISF (grant no. 576/21). O.M. thanks the Harry de Jur, Chair in Applied Science. L.E. acknowledges the Israel Ministry of Energy for its financial support. L.K. thanks the Minerva Centre for Self-Repairing Systems for Energy & Sustainability, the Aryeh and Mintzi Katzman Professorial Chair, and the Helen and Martin Kimmel Award for Innovative Investigation, for their support.

Poster no. P_ESM_14

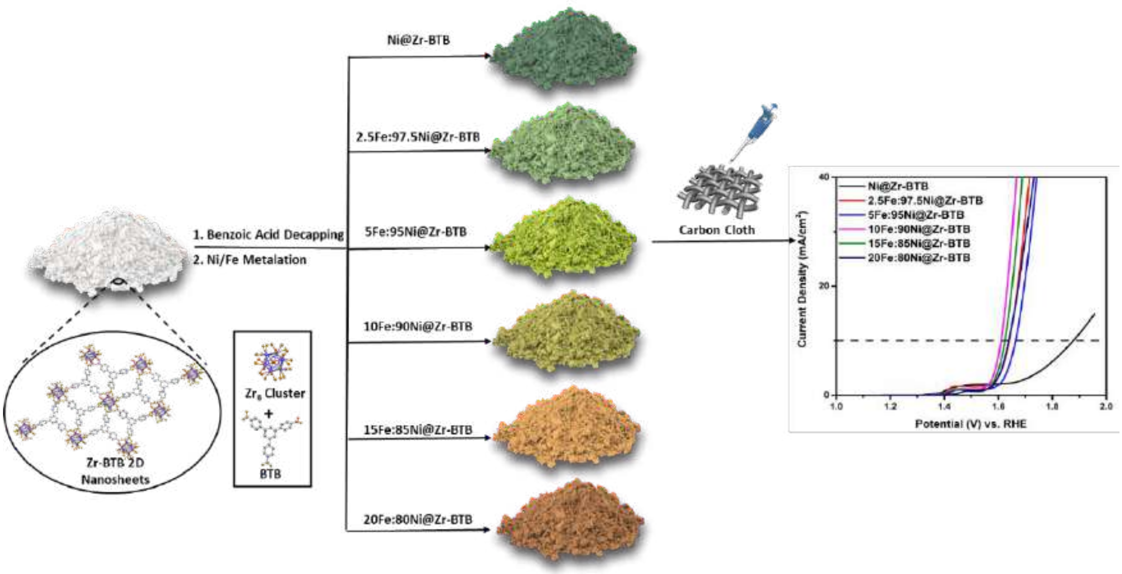
Nickel Iron Modified 2D MOF as a Precatalyst for Highly Efficient Water Oxidation Reaction

Shahar Binyamin[a] and Idan Hod* [a]

[a] *Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel*

E-mail: bishahar@post.bgu.ac.il , hodi@bgu.ac.il

Today's growing demand for energy consumption results in escalating amount of green-house gases emitted to the Earth's atmosphere, leading to harmful impact on the environment and global warming. Electrochemical water splitting to produce green H_2 fuel is a promising approach for reducing fossil fuels usage. Oxygen Evolution Reaction (OER), the anodic water splitting half reaction, generally exhibits sluggish kinetics and thus determines the overall catalytic rate. The project I will present focuses on designing new approaches to improve OER performance. Generally, Ni-Fe based oxides are known to be highly active OER electrocatalysts. Here, we chose to construct a layered Ni-Fe oxide catalyst by modifying a 2D Metal-Organic Framework (MOF) porous scaffold. Using this MOF as a template enables modification with varied Ni-to-Fe molar ratios to obtain tunable OER catalysts. This class of MOF derived materials reveals high intrinsic activity despite low metal loadings, while avoiding mass-transport limitation during electrocatalysis, and eventually improving overall OER rates.



Scheme 1: Schematic synthesis of the MOFs after metalation denoted *Ni@Zr-BTB, 2.5Fe:97.5Ni@Zr-BTB, 5Fe:95Ni@Zr-BTB, 10Fe:90Ni@Zr-BTB, 15Fe:85Ni@Zr-BTB* and *20Fe:80Ni@Zr-BTB* and their electrochemical performance during OER.

References:

1. Wang, Y., Feng, L., Pang, J., Li, J., Huang, N., Day, G. S., Cheng, L., Drake, H. F., Wang, Y., Lollar, C., Qin, J., Gu, Z., Lu, T., Yuan, S., Zhou, H.-C.," Photosensitizer-Anchored 2D MOF Nanosheets as Highly Stable and Accessible Catalysts toward Artemisinin Production", Adv. Sci. 2019, (6), 1802059
2. Shimoni, R.; Shi, Z.; Binyamin, S.; Yang, Y.; Liberman, I.; Ifraemov, R.; Mukhopadhyay, S.; Zhang, L.; Hod, I., “Electrostatic Secondary-Sphere Interactions That Facilitate Rapid and Selective Electrocatalytic CO_2 Reduction in a Fe-Porphyrin-Based Metal–Organic Framework“, Angewandte Chemie Int. Ed., e202206085
3. Singh, C.P.; Liberman, I.; Shimoni, R.; Ifraemov, R. ; Hod, I. “Pristine versus Pyrolyzed Metal-Organic Framework Based Oxygen Evolution Electrocatalysts: Evaluation of Intrinsic Activity Using Electrochemical Impedance Spectroscopy“. Journal of Physical Chemistry Letters, 2019, 10, 3630−3636
4. He, W.; Gao, H. M.; Shimoni, R.; Lu, Z. Y.; Hod, I. “Synergistic Coupling of Anionic Ligands to Optimize the Electronic and Catalytic Properties of Metal-Organic Framework-Converted Oxygen-Evolving Catalysts“ ACS Appl. Energy Mater., 2019, 2 (3), 2138–2148.

Poster no. P_ESM_15

Bringing order to the Bio-mess From Diverse Waste Coffee to Reproducible Carbon Catalyst

Shir Tabac-Agam,[a] Shelly Burda, [a] and David Eisenberg.[a]

[a] Schulich Faculty of Chemistry, the Resnick Sustainability Center for Catalysis, and the Grand Technion Energy Program, Technion – Israel Institute of Technology, Israel.

E-mail: shir.tabac@campus.technion.ac.il

Biomass surrounds us everywhere and is an abundant carbon source for electrocatalysis and energy applications. One major challenge presented by biomass is its diversity and variability of composition, which raises a meaningful question – can it become a source for precise carbon electrodes?[1]

Here, we present a method for producing carbon catalysts from waste coffee grounds (WCG). We use chemical activation to handle resource variability and to control the structure and composition. Generally, these methods improve porosity, change carbon morphology and exhibit higher surface area.[2,3] For example, earlier work shows that chemical activation with molten salt and potassium salts resulted in carbons with a high specific surface area. In line with this, different chemically-activated carbon samples were produced using different potassium salts (KOH, K_2CO_3, KH_2PO_4) and different pyrolysis temperatures (700°C, 800°C, 900°C). When impregnated with iron,[4] these carbons show an improved catalytic activity and current density (Figure 1) for hydrazine oxidation reaction (hydrazine is an important energy carrier for fuel cell technology).[5]

These promising results have led us to develop a strategy to produce and investigate renewable and sustainable single atom catalysts (SAC) for hydrazine oxidation from waste coffee grounds. Important parameters within this enquiry are pyrolysis temperature and activating reagent and their effect on catalyst surface area, graphitization, porosity and activity. Since coffee is a well-known catalyst for human productivity, and our goal is to use its waste for catalysts in renewable energy.

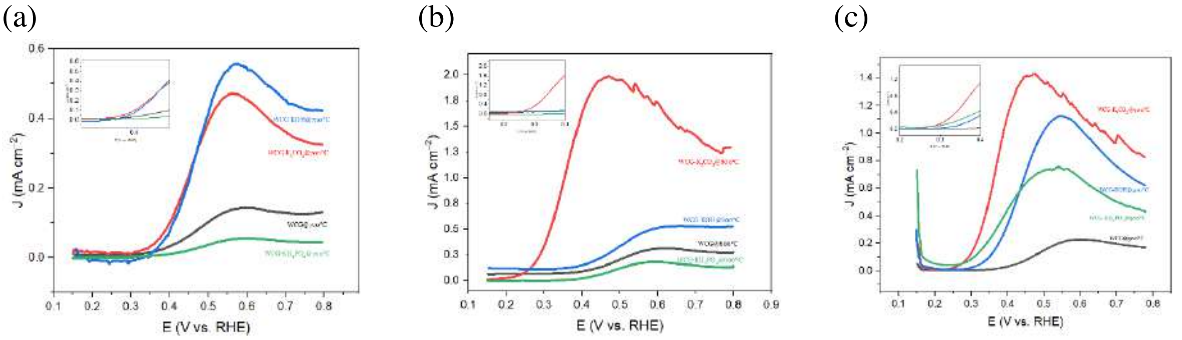


Figure 1 - Cyclic voltammetry showing hydrazine oxidation for WCG-derived Fe-SACs, following chemical activation with different potassium salts and at different pyrolysis temperatures: not only did the chemical activation technique worked in terms of electrochemical activity, but the K_2CO_3 -activated sample at 800°C showing remarkable onset potential at 0.21V vs. RHE as well as samples at 900°C exhibiting early onset and high currents.

References

1. Tabac, S. & Eisenberg, D. Pyrolyze this paper: Can biomass become a source for precise carbon electrodes? *Curr. Opin. Electrochem.* **25**, 100638 (2021).
2. Liu, X. & Antonietti, M. Molten salt activation for synthesis of porous carbon nanostructures and carbon sheets. *Carbon* **69**, 460–466 (2014).
3. Guerrera, J. V. *et al.* Evaluation of Two Potassium-Based Activation Agents for the Production of Oxygen- and Nitrogen-Doped Porous Carbons. *Energy Fuels* **34**, 6101–6112 (2020).
4. Yang, H. *et al.* A universal ligand mediated method for large scale synthesis of transition metal single atom catalysts. *Nat. Commun.* **10**, 4585 (2019).
5. Serov, A. & Kwak, C. Direct hydrazine fuel cells: A review. *Appl. Catal. B Environ.* **98**, 1–9 (2010).

Poster no. P_ESM_16

Ternary compounds of NiSe and CoSe as efficient electrochemical & photothermal catalysts for water-splitting reactions

Shir Abramovich[a], Maya Bar-Sadan*[a]

[a] Chemistry Department, Ben-Gurion University of the Negev, Beer Sheva blvd 1, 84105 Beer Sheva, Israel.

E-mail: barsadan@bgu.ac.il

In recent years, metal chalcogenides have emerged as prominent candidates for low-cost catalysts in green technology applications, particularly in processes related to renewable energy, such as the hydrogen evolution reaction. The scientific community has expressed significant interest in hydrogen due to its potential as a clean alternative to fossil fuels, devoid of CO_2 emissions, and its impressive energy density. [1]

This project focuses on the investigation of NiSe, CoSe, and their ternary compounds, selected for their noteworthy electro-catalytic and photothermal properties. These properties, and especially the ability to generate a substantial increase in temperature, are anticipated to enhance reaction kinetics (as per Arrhenius) and potentially impact the thermodynamics of these reactions positively. [2]

Previous efforts in this project concentrated on the synthesis, characterization, and examination of the basic electrochemical and photothermal properties of nanostructures. Synthesis of NiSe, CoSe, and ternary compounds with varying metal ratios yielded hexagonal nanoparticles in the size range of 15-30 nm. These nanoparticles exhibited enhanced electro-catalytic activity in the hydrogen evolution reaction and demonstrated significant heating performance across different solvents and electrolytes. Furthermore, these nanoparticles were employed in the advancement of solar-driven membrane distillation technology, as part of a collaborative endeavor with Italian researchers. [3]

Subsequently, the focus shifted to developing stable and suitable fluorine-doped tin oxide (FTO) electrodes for a new system. This system allows for the investigation of how the photothermal properties of nanoparticles influence the kinetics of the electrochemical hydrogen evolution reaction under illumination. It was determined that the conductive polymer PEDOT:PSS served as the most stable binder for attaching the nanoparticles to the FTO. It is noteworthy that when used as a thin layer, PEDOT:PSS remains nearly transparent to visible light. The subsequent phase involved examining how the heating of the reaction surroundings (electrolyte) impacts the kinetics and thermodynamics of the reaction. During these measurements, the activation energy values for each material were extracted.

These values offer insights into the degree to which temperature variations can impact the kinetics of an electrochemical reaction. Additionally, they can provide additional explanations for the differences in the activity observed among various catalysts. [4] A comprehensive analysis of kinetic parameters, including the activation energy of nanoparticles under various conditions, was conducted. In some instances, the nanoparticles exhibited lower activation energy than platinum (Pt). Additionally, an initial experiment integrating the new electrodes and the new system was conducted. Future work will focus on optimizing the conditions of photo-assisted electrochemistry in the new setup, with a focus on exploring catalytic activity under illumination and leveraging the photothermal effect.

References:

1. LÓPEZ, C., current challenges in energy. *Front. Knowl* **2009,** *2*, 257-269.
2. Zheng, Y.; Jiao, Y.; Jaroniec, M.; Qiao, S. Z., Advancing the electrochemistry of the hydrogen-evolution reaction through combining experiment and theory. *Angew. Chem. Int. Ed.* **2015,** *54* (1), 52-65.
3. Abramovich, S.; Dutta, D.; Rizza, C.; Santoro, S.; Aquino, M.; Cupolillo, A.; Occhiuzzi, J.; Russa, M. F. L.; Ghosh, B.; Farias, D., NiSe and CoSe Topological Nodal-Line Semimetals: A Sustainable Platform for Efficient Thermoplasmonics and Solar-Driven Photothermal Membrane Distillation. *Small* **2022**, 2201473.
4. Zeradjanin, A. R.; Narangoda, P.; Masa, J.; Schlögl, R., What Controls Activity Trends of Electrocatalytic Hydrogen Evolution Reaction?– Activation Energy Versus Frequency Factor. *ACS Catal.* **2022,** *12* (19), 11597-11605.

Poster no. P_ESM_17

Synthesis and Characterization of Aucore-Irshell Nanoparticles for Oxygen Evolution Reaction Catalysis

S. Sisorov[1], A. Keilin[1], D. Kaplan[1,2], G. Markovich[1], E. Peled[1]

[1]School of chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel Aviv 6997801, Israel

[2]Nuclear Research Center - Negev, Beer-Sheva, Israel, 84190

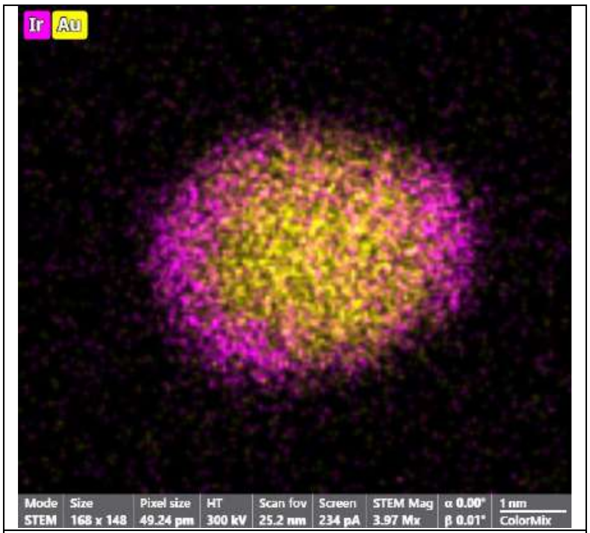
Email: gilmar@tauex.tau.ac.il, peled@tauex.tau.ac.il

The widespread production of green hydrogen through water electrolysis faces a significant challenge attributed to the high overpotential associated with the oxygen evolution reaction (OER). Catalysts play a crucial role in mitigating this overpotential, and iridium-based catalysts have demonstrated a superior balance between catalytic activity and stability. Nevertheless, the extensive scarcity and elevated cost of iridium present obstacles to the widespread adoption of pure iridium-oxide in water electrolyzers. In response to this challenge, the reduction of iridium loading on nanocatalysts has become a focal point of intensive research in both academia and the industry. Our study is dedicated to the synthesis and characterization of Au_{core}-Ir_{shell} nanoparticles with reduced iridium content as part of an effort to promote wide-scale green hydrogen production.

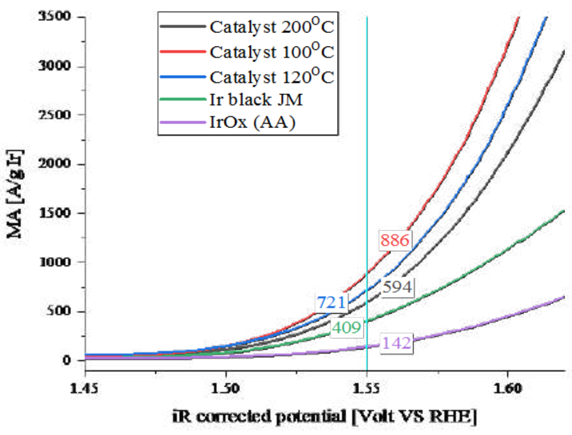
Gold nanoparticles (Au-NPs) were synthesized in ethylene glycol by the reduction of an Au-precursor with NaBH4. Subsequently, these Au-NPs were coated with Ir using the polyol method at various temperatures. The resulting catalytic powder underwent electrochemical and physical characterization to investigate its electrochemical properties, metal composition, and nanostructure.

Electrochemical measurements, employing cycling voltammetry and linear sweep voltammetry were conducted in a three-electrode cell with a rotating disk electrode (RDE). H_{upd} desorption and iridium-oxide pseudo-capacitance peaks were employed for ECSA measurements. Mass activity (MA) and specific activity (SA) were determined at 1.55V vs RHE after iR correction. Characterization of the catalyst's composition was accomplished through SEM-EDS, while the nanostructure was elucidated using STEM-EDS mapping.

Comparative analysis revealed that the synthesized catalysts exhibited nearly twice the MA and comparable SA for the Oxygen Evolution Reaction (OER) when compared to commercially available Ir-based catalysts. This study sheds light on the potential of Au-Ir bimetallic nanoparticles as efficient and cost-effective electrocatalysts for OER applications.



A representative STEM-EDS mapping of a Au_{core}-Ir_{shell} nanoparticle



OER polarization curves of commercial Ir black and commercial Ir-oxide catalysts and the synthesized Au_{core}-Ir_{shell} catalysts normalized by wt% of Ir in the catalyst.

Poster no. P_ESM_18

SmMnOx catalyst for nitrate reduction

Thierry K. Slot,[a] Omer Zaltzberg,[a] Yair Shahaf,[a] and D. Eisenberg[a]*

[a] *Schulich Faculty of Chemistry, the Resnick Sustainability Center for Catalysis, and the Grand Technion Energy Program, Technion – Israel Institute of Technology, Haifa 3230003, Israel*

E-mail: tkslot1@gmail.com

Thanks to the invention of the Haber-Bosch process in 1909, we can, to this day, produce ammonia industrially at immense scales.[1,2] While this is great feat of science and engineering, it comes at a cost: it consumes 1-2% of the world's energy and relies heavily on fossil fuels.

We investigate another approach: a zero-emission process that produces ammonia based on oxidation of nitrogen from air using plasma (Figure 1a). Oxidation of nitrogen generates NO_x species (NO, NO_2, N_2O). To capture and reduce the NO_x on site, we are building an electrolyzer which converts most of these species into ammonia. We will share our latest results of our novel Sm-based nitrate reduction catalyst, which shows good NO_3 reduction activity and an interesting activation process based on repeated cycling. Under cycling, this catalyst forms a new catalytic phase with nitrate-reduction onset potentials as high as -0.2 V vs RHE (Figure 2b). We investigate the nature of this new catalytic phase and study the prerequisites for its formation.(Figure 2c).

Our dream is to produce a self-contained device, that combines a plasma NOx generator and nitrate reduction catalysts to generate "green" ammonia, using only electricity, water and air. (Figure 2d).

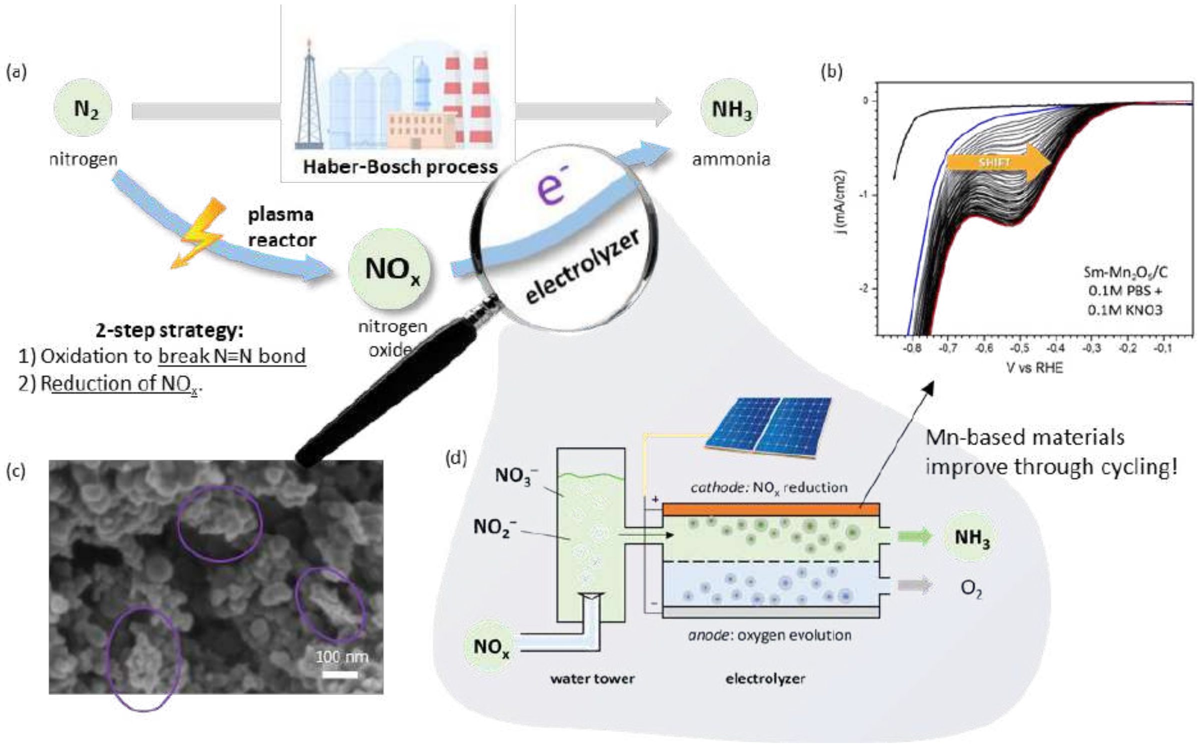


Figure 2. (a) schematic overview of our approach to make ammonia. (b) cyclic voltammetry of a novel SmMnOx catalyst (50 scans) (c) scanning electron micrograph of the SmMnOx catalyst showing regions (purple line, based on backscatter detector) where SmMnOx is deposited. (d) A schematic overview of the NOx capture device and electrolyzer setup.

Acknowledgements: This research is supported by an Azrieli Fellowship and The Israel Academy of Science and Humanities.

References:

Host-Guest Chemistry

Poster no. P_HGC_01

Guest Transition Metals in Host Keplerate Nanocapsules- Towards Inorganic Functional Mimics of Redox Metalloenzymes?

Eynat Haviv[a], Bo Chen[a], Raanan Carmieli[b], Lothar Houben[b], Hagai Cohen[b], Gregory Leitus[b], Liat Avram[b], and Ronny Neumann[a]
[a]Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot 76100, Israel
[b]Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel
E-mail: (eynat.haviv@weizmann.ac.il)

Host-guest solution chemistry with wide range of organic and organometallic hosts is an important and established research area, while the use of inorganic hosts is a more nascent area of research. In the recent past in a few cases, Keplerate-type molybdenum-oxide based porous, spherical clusters, shorthand notation $\{Mo_{132}\}$, have been used as hosts for organic guests[1]. In a previous publication[2] we demonstrated a procedure to encapsulate transition metal cations, from an organic solvent, by design into a Keplerate capsule. By this methodology three first row transition metal cations ($M^{2+} = Mn^{2+}$, Fe^{2+}, Co^{2+}) were encapsulated as guests into a porous Keplerate inorganic host, $\{Mo_{132}\}$ containing phosphate ligands. Different from previous research[3], the methodology allows control by design of the average number of guest cations introduced into the capsule, in the range of 1-10 guests cations per capsule.

An additional development of our methodology was recently achieved, and allows the encapsulation process from aqueous solution based on the affinity of transition metal cations to different functional groups, such as thiols, carboxylic acids and imidazole rings. Thus, by changing the ligands inside the capsule we can achieve variety of host guest systems with different properties.

In the work presented here, the synthesis and application of such an assembly contains Cu(II) cations encapsulated inside $\{W^{VI}_{72}Mo^{V}_{60}\}$ inorganic capsule with Imidazole acetate ligands is described. This host gust complex demonstrated as a catalyst for the cathodic oxidation of different aliphatic substrates. Using electrochemistry we provide electrons and protons to the encapsulated Cu (II) cation in order to catalyze the activation of molecular oxygen and the oxygenation of different alkanes and alkenes. The catalytic activity of this assembly presents monooxygenase type reactivity, and can be compared with the activity of Methane Monoxygenase enzyme (pMMO). This is an example of how this new system, which contain transition metal sites inside porous confined space in aqueous environment can be a functional mimic of redox enzymes.

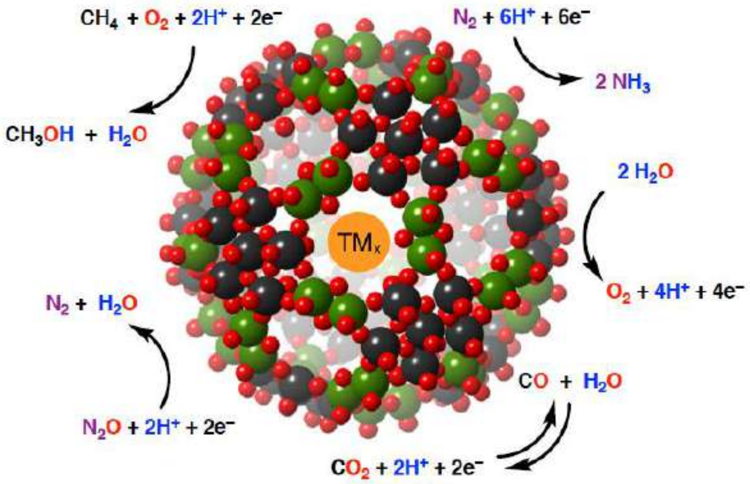


Figure 1: proposed catalytic guest-host complex with the suggested catalytic transformations. Black-W^{VI}/Mo^{VI}, Green-Mo^{V}, Red- oxygen.

References:

1. (a) *Angew. Chem. Int. Ed.* **2016**, 55, 4476 –4481. (b) *Chem. Eur. J.* **2016**, 22, 15231 – 15236.

2. *J. Am. Chem. Soc.* **2020**, 142, 14504-14512.

3. *Angew. Chem., Int. Ed*, **2003**, 42, 5039-5044.

Poster no. P_HGC_02

Conformationally-adaptive thio-hemicucurbiturils exhibit promiscuous anion binding by induced fit

Raghuram Gujjarappa,[a,b] Raman Khurana,[a,b] Natalia Fridman,[b] Ehud Keinan,*[b] and Ofer Reany*[a]

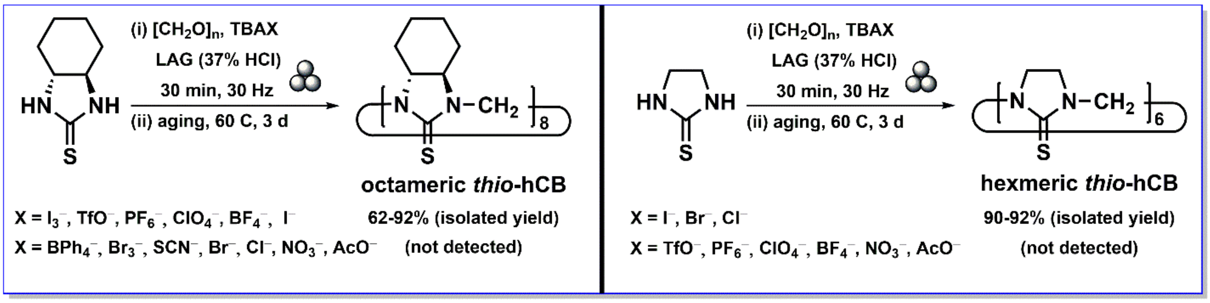
[a] Department of Natural Sciences, The Open University of Israel, Ra'anana 4353701, Israel. [b] The Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Technion City, Haifa 3200003, Israel.

E-mail: *oferre@openu.ac.il; keinan@technion.ac.il*

Most oligomeric host macrocycles exhibit one or two hoops of single bonds interconnecting the repeating subunits, dubbed either "single-stranded" or "double-stranded" host molecules. The fixed interior of double-stranded cavitands can optimally accommodate guests of complementary dimensions. In contrast, the conformationally flexible single-stranded host molecules allow for more promiscuous host-guest complexation, with the cavitand's walls adapting to the guest's shape and size to maximize the available stabilizing interactions. This induced-fit process, well-known in proteins and other bio-macromolecules, has become increasingly relevant also for small molecules.

Here, we report on the synthesis of *thio*-hemicucurbit[n]urils (*thio*-hCB[n], n = 6,8), which represent a new family of host molecules readily available via liquid-assisted grinding (LAG) coupled with thermal aging (Scheme 1). The monomer-dependent, hexameric, or octameric macrocycles are obtained in nearly quantitative yields using an appropriate anion template. The mixture of linear oligomers, initially formed by mechanochemistry, converges to a single macrocycle upon aging in the presence of an anion template. Apparently, the templating power of various anions in the synthesis of octameric *thio*-hCB stems from their thermochemical ionic radius and the melting point of their salt. With the smaller hexameric *thio*-hCB, the templating power of anions stems solely from their spherical shape.

Based on the crystallographic data of *thio*-hCB complexes, these macrocycles feature induced fit transformation in response to different anionic guests. Using ^{1}H and ^{19}F NMR in titration studies illustrates the *thio*-hCB host-guest properties and selectivity in solution. Isothermal titration calorimetry (ITC) shows that the *thio* analog binds anions more strongly than the parent *oxo* analog by two orders of magnitude, probably due to the higher polarizability of thiourea relative to urea.



Scheme 1: Mechanochemical synthesis of *thio*-hCB macrocycles.

Acknowledgements: We thank the OUI and Technion for financial support.

References:

1. Gujjarappa, R.; Khurana, R.; Fridman, N.; Keinan, E.; Reany, O., Conformationally-adaptive thio-hemicucurbiturils exhibit promiscuous anion binding by induced fit, A manuscript on this study will be submitted shortly.

Poster no. P_HGC_03

Co-crystal Structure Prediction (Co-CSP)

Yury Torubaev *

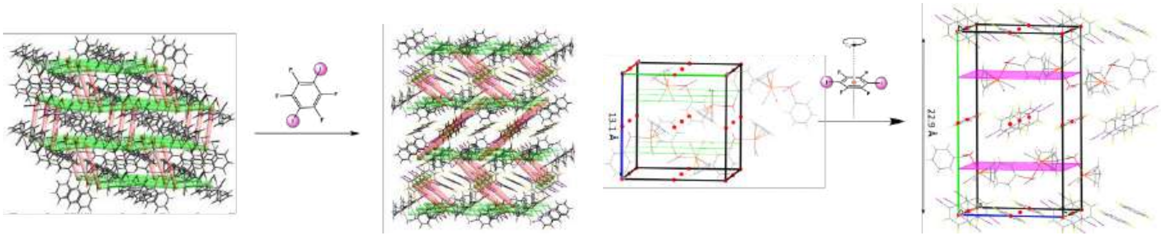
Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

E-mail: torubaev@bgu.ac.il

Crystal structure prediction (CSP) is one of the central and most challenging tasks in physical chemistry, spanning over 70 years [1]. It is not only academically significant but also of high practical importance (consider the polymorphism problem in the pharmaceutical industry). The complex interplay between thermodynamic and kinetic factors during the crystallization process, along with the existence of multiple local minima of energy, are just a few factors that make the CSP task challenging, even with the current level of computational techniques and resources. On the other hand, when considering not a single-component crystal but a two-component one, or in other words, a *co-crystal*, the CSP task appears not twice as complicated but, *au contraire*, much more simplified. This is, of course, assuming that the crystal structure of its parent components (co-formers) is known.

A comparative analysis of the packing patterns in parent crystals (deposited in the Cambridge Structural Database (CSD)) with the new co-crystals resulting from co-crystallization demonstrates that, in certain cases, certain packing patterns (molecular chains, stacks, layers, etc.) of the parent crystals may reappear almost intact in their co-crystals. Supported by the calculations of energy frameworks in the parent crystals, this allows for a more chemically reasonable and rational understanding of the supramolecular reactions and, therefore, a rational prediction of their crystalline outcome [2].

For example, upon the insertion of a halogen bond donor molecule (1,4-diiodo-tetrafluorobenzene) into the layered structure of $CpFe(CO)_2TeI_2Ph$, we can expect that it will target the electrostatic Te---I halogen bonds between the layers (shown in red), leaving the van der Waals-associated layers (green) almost intact.



a **b**

Figure 1: (a) 1,4-DITFB molecules target the electrostatic Te---I interactions between the layers; (b) centrosymmetric molecules of 1,4-DITFB appears exactly at the inversion centers (orange dots) of parent $CpFe(CO)_2TeI_2Ph$ unit cell. Notice that the cell dimensions increase only in one direction:
$P2_1/c$ a 9.6807(17) b 13.128(2) c 13.045(2) β 95.738(3) (CSD code: AHICIE, $CpFe(CO)_2TeI_2Ph$)
$P2_1/n$ a 9.5865(11) b 22.895(3) c 13.5008(15) β 90.777(2) (new co-crystal $CpFe(CO)_2TeI_2Ph$ 1,4-DITFB (1:1))

This particular case demonstrates how we can (a) provide an illustrative, computationally-based description of supramolecular reactions; (b) presume the packing pattern of their co-crystalline product; (c) estimate the change in unit cell dimensions. More examples, including the prediction of macroscopic characteristics such as crystal habit [3], will be given in the report.

Acknowledgements:

References:

(1) Desiraju, G. R. Cryptic crystallography. *Nature Materials* **2002**, *1* (2), 77-79. DOI: 10.1038/nmat726.
(2) Torubaev, Y.; Skabitsky, I.; Lyssenko, K. A. Stages of Kitaigorodsky Aufbau Principle Detached in the Cocrystals of Cp_2MX_2 (M = Ti, Zr; X = Cl, Br, I) with σ- and π-Hole Donors. *Crystal Growth & Design* **2021**, *22* (2), 1244-1252. DOI: 10.1021/acs.cgd.1c01207.
(3) Torubaev, Y. V.; Howe, D.; Leitus, G.; Rosokha, S. V. The relationship between the crystal habit and the energy framework pattern: a case study involving halogen bonding on the edge of a covalent bond. *CrystEngComm* **2023**, *25* (23), 3380-3390. DOI: 10.1039/d3ce00316g.

Industrial and Analytical Chemistry

Poster no. P_IAC_01

The mechanical properties of epoxy microfibers in varying diameters

Hagar Shitrit[1], Mark Shcneider[2]
[1] Yitzhak Navon (Ironi H) high school, Modi'in and Alpha program at Weizmann Institute of Science, [2] Department of Materials and Interfaces, Weizmann Institute of Science
E-mail: shtrithagar@gmail.com mark.schneider@weizmann.ac.il

Epoxy is a thermoset material which forms cross-linked, polymeric structure with high strength and low strain. Epoxy is often used as glue, however. Its fibrous structure is still unknown. Previous studies suggested that the strength is dependent on its diameter. In this work, we aimed to evaluate the effect of the fiber diameter on its rheological properties (mechanical and resistance). To that end, we used epoxy fibers with different diameters, and by using a tensile test we measured the fibers' Young's modulus, yield point, extension percentage and ductility. The diameters of the fibers were measured before and after the test. We found that smaller diameter fibers are more resistant to extension, and that the fiber's true stress was 41% higher than its engineering stress. This result has a great significance in the context of the application of these fibers in the industry where engineering stress is mainly used, therefore it can be concluded that when using low diameter epoxy fiber as a structural material, its strength will be higher.

Poster no. P_IAC_02

Elastomer Nanocomposites: Mechanical and Electrical Relaxation Properties

Adi Keezl, Lev Rovinsky*, Dr. Noa Lachman*

Lev Rovinsky: levrovinsky@mail.tau.ac.il
Dr. Noa Lachman: noala@tauex.tau.ac.il

Department of Materials Science and Engineering, Faculty of Engineering, Tel Aviv University

Email: adi.keezl@gmail.com, levrovinsky@mail.tau.ac.il

Silicon-elastomer-based composite materials solve the limitation of traditional rigid electronics, enabling the creation of compliant electronic devices. Composite material combine the properties of its constituents, a host and a reinforcement, creating a property set unreachable or impractical to reach otherwise, with the property transfer occurring at the interface between the constituents. Nanocomposites are composite materials, in which the reinforcements are on the nanoscale, exhibiting very large surface area, and enhancing the efficiency of the property transfer. By reinforcing the material with two types of reinforcement, we enhance the degrees of freedom for tailoring the properties. In this project, we investigate the electrical and mechanical relaxation properties of silicone rubber nanocomposites, reinforced with both carbon nanotubes and carbon black. Samples were put into varying levels of continuous strain in different periods while their electrical conductivity and stress applied on them were measured.

The electrical conductivity decrease showed further reduction in tests, which involved a greater strain level. Additionally, an examination of the correlation between conductivity of electrical current and mechanical relaxation revealed a separation between the factors which dictate the mechanical and electrical behavior. As can be seen in figure 1, the graphical results did not present a pattern or relation between the current and the stress values, which suggested the possibility that the two are not correlated. A comparison between the length of the mechanical and electrical relaxation (the electrical relaxation being the cause of the change in current) confirmed that the two mechanisms do not happen in conjunction and therefore cannot be correlated (see figure 2). Based on this result, it was found that the mechanical characteristics, being strain behavior and stress response in this case, were mainly affected by the rubber host particles, while the electrical properties were found to be generated and affected by the presence of the conductive fillers. Further research to investigate the behavior and properties of similar nanocomposites will be the key to allowing the use of these materials in new technology.

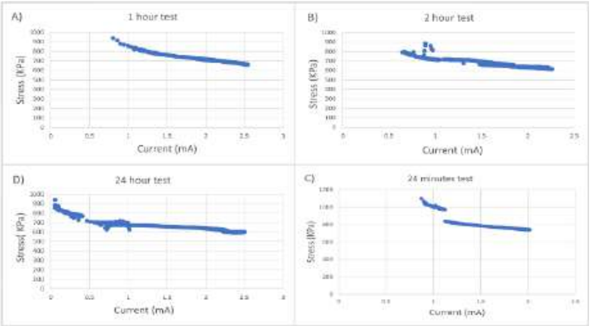


Figure 1 - Ration between the stress and the current flowing in the circuit. The graphs describe the tests as follows: A. two-hour test, B. one hour test, C. 24 minute test, D. 24 hour test.

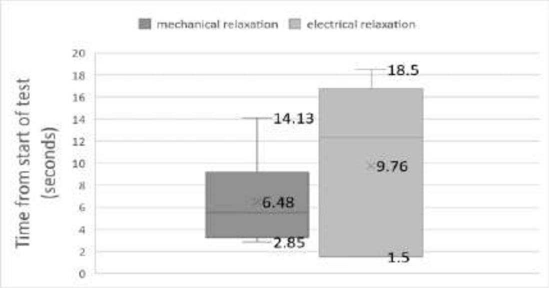


Figure 2 - This graph presents a comparison between the time which the material required to perform 50% out of the mechanical and electrical relaxation processes. The values shown are the minimum, average and maximum values.

Poster no. P_IAC_03

A highly practical, metal-free colorimetric fluoride sensor

Jenisha John Peter,[a] Vincent Joseph,[a] Tanya Bachu,[b] Flavio Grynszpan,[a] and Mindy Levine[a]*

[a] Department of Chemical Sciences, Ariel University, 65 Ramat HaGolan Street, Ariel, Israel.
[b] Brownell Talbot College Preparatory School, Omaha, Nebraska, USA.
* CORRESPONDING AUTHOR Mindy Levine, Department of Chemical Sciences, Ariel University, 65 Ramat HaGolan Street, Ariel, Israel.
E-mail: (Vincent Joseph: vincentkunnathukuzhy@gmail.com; Jenisha John Peter: jenishaktg15@gmail.com; Tanya Bachu : tanyabachu7@gmail.com; Flavio Grynszpan: flaviog@ariel.ac.il; Mindy Levine: mindyl@ariel.ac.il)

In chemical literature, the necessity for fluoride detection systems that function in complex environments has been extensively reported.[1] However, the systems that are now in use frequently have poor sensitivity, selectivity, or general applicability, or they contain hazardous metal cations as key sensor components. The development of fluoride detection devices that are metal-free, versatile, and high-performing is still an unsolved issue.

Herein, we present a metal-free fluoride detection system characterized by rapid, sensitive, and selective color changes upon fluoride exposure. The mechanism of action of this system is based on the interaction between fluoride and bromocresol green (compound **1**), which results in rapid response times, excellent sensitivity (limits of detection as low as 0.22 ppm), and high selectivity (nearly no response to other halide anions). Notably, the system also functions when compound **1** is non-covalently adsorbed on filter paper[2], although the colorimetric response changes from being linearly dependent on the concentration of fluoride for solution-state detection, to a non-linear dependence with presumed sensor saturation for on-paper detection. Mechanistic studies focused on the lack of colorimetric changes observed with moderate changes in the solution pH and ^1H NMR spectroscopic confirmation of close-range interactions between fluoride and compound **1**, both of which point to a fluoride-specific impact. Furthermore, the colorimetric response of compound **1**-functionalized paper to fluoride in commercial (toothpaste and mouthwash)[3] and agricultural (orange and bell pepper) products showed the wide-ranging applicability of this colorimetric sensor.

These findings emphasize the capability of bromocresol green (compound **1**) to respond to fluoride and serve as a foundation for a practical colorimetric fluoride sensor. The outcomes provide a valuable foundation for creating a commercially feasible colorimetric fluoride chemosensor, demonstrating its wide-ranging applicability in various real-world situations.

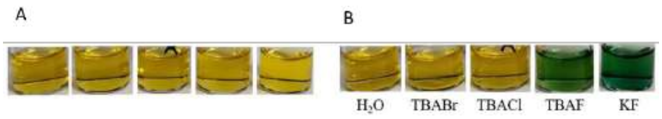


Figure 1: Photograph of solutions of compound **1** (100 μM): (A) before the addition of analytes; and (B) after the addition of various analytes (H_2O, TBABr, TBACl, TBAF, and KF)

Acknowledgements: We gratefully acknowledge Ariel University for providing the Levine group with research funding, and for providing V. J. and J. J. P. with scholarships to support their doctoral research work. Dr. Vered Marks is acknowledged for her role in maintaining the NMR facility at Ariel University, and Dr. Rami Krieger is thanked for his assistance in maintaining the plethora of analytical chemistry instruments available for use. Ms. Miriam Meir Mrouat and Ms. Ikhlas Abu Muammar are thanked for their assistance in conducting preliminary colorimetric experiments.

References:

1. Lu, W; Jiang, H.; Hu, F.; Jiang, L.; Shen, Z. A Novel Chemosensor Based on Fe(III)-Complexation for Selective Recognition and Rapid Detection of Fluoride Anions in Aqueous Media. *Tetrahedron* **2011**, *67*, 7909–7912.
2. Joseph, V.; Warhaftig, O.; Klein, S.; Levine, M. Paper-Based Manganese and β-Cyclodextrin Sensors for Colorimetric Sulfur Dioxide Detection. *Anal. Chim. Acta* **2022**, *1200*, 339629.
3. Rajendiran, M.; Trivedi, H. M.; Chen, D.; Gajendrareddy, P.; Chen, L. Recent Development of Active Ingredients in Mouthwashes and Toothpastes for Periodontal Diseases. *Molecules* **2021**, *26* (7), 2001.

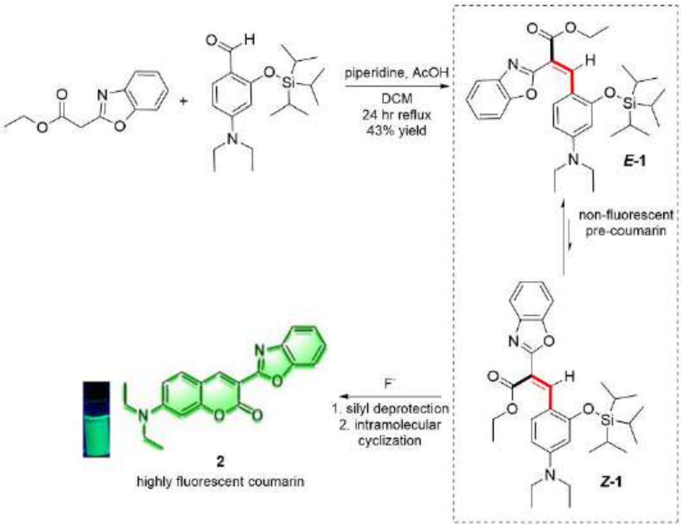
Poster no. P_IAC_04

Shining light on fluoride detection: a comprehensive study exploring the potential of coumarin precursors as selective turn-on fluorescent chemosensors

Vincent Joseph, [a*] Sara Amer, [a*] Bat-El Oded,* Vered Marks,* Flavio Grynszpan,* and Mindy Levine*
a These authors contributed equally to this work.
* Department of Chemical Sciences, Ariel University, Ariel,
E-mail: vincentkunnathukuzhy@gmail.com, pacsaraice59@gmail.com, b0546797403@gmail.com,
veredmarks@gmail.com, flaviog@ariel.ac.il, mindy.levine@gmail.com

The quantitative detection of fluoride is a highly significant research objective, as fluoride has both beneficial health effects at low concentrations and deleterious health effects at elevated concentrations (i.e., fluorosis[1] and osteoporosis[2]). Although currently used methods can detect fluoride with extraordinary sensitivity and selectivity, the requirements for costly instrumentation and trained laboratory personnel limit their broad-based applicability. To address this concern, more practical colorimetric[3] and fluorometric,[4] fluoride sensors are needed.

In this study, we report a fluoride chemosensor based on the use of a non-fluorescent pre-coumarin,compound **1**. This compound undergoes selective fluoride-triggered formation of coumarin **2**,with a concomitant turn-on fluorescence signal. Although compound **1** exists as a mixture of alkene isomers (2:1 in favor of the *E* isomer), only the minor *Z*-isomer undergoes cyclization (Scheme 1). Nonetheless, comprehensive computational and experimental studies provide evidence that *in situ* isomerization of ***E*-1** to ***Z*-1**, followed by fluoride-triggered phenolate evolution and intramolecular cyclization, facilitates the generation of coumarin **2** in high yield. Moreover, this system acts as an effective turn-on fluorescence sensor for fluoride anions, and displays outstanding selectivity (limited response to other commonly occurring analytes), sensitivity (lowest reported limits of detection for this sensor class), and practicality (works in solution and on paper to generate both fluorometric and colorimetric responses). Ongoing efforts are focused on expanding this paradigm to other pre-coumarin scaffolds, which also undergo analyte-specific coumarin formation accompanied by turn-on fluorescence.



Scheme 1. Illustration of the synthesis of compound **1** (***E*-1**:***Z*-1** ~ 2:1) and how fluoride-induced silyl deprotection of **1** followed by intramolecular cyclization leads to the formation of highly fluorescent coumarin **2**

Acknowledgements: We gratefully acknowledge Ariel University for providing research funding.

References:

---

[1] Akuno, M. H.; Nocella, G.; Milia, E. P.; Gutierrez, L. Factors Influencing the Relationship Between Fluoride in Drinking Water and Dental Fluorosis: A Ten-Year Systematic Review and Meta-Analysis. *J. Water Health* **2019**, *17*, 845-862; DOI: 10.2166/wh.2019.300.

[2] Demos, L. L.; Kazda, H.; Cicuttini, F. M.; Sinclair, M. I.; Fairley, C. K. Water Fluoridation, Osteoporosis, Fractures—Recent Developments. *Australian Dental J.* **2008**, *46*, 80-87; DOI: 10.1111/j.1834-7819.2001.tb00561.x.

[3] Wu, H.; Li, Y.; He, X.; Chen, L.; Zhang, Y. Colorimetric Sensor Based on 4-Mercaptophenylboronic Modified Gold Nanoparticles for Rapid and Selective Detection of Fluoride Anion. *Spectrochim. Acta A: Molec. Biomolec. Spectroscopy* **2019**, *214*, 393-398; DOI: 10.1016/j.saa.2019.02.039.

[4] Yang, J.; Yuan, X.; Wang, Y.; Liu, H.; Pu, S. A Novel Turn-On Type Fluorescent Probe with a Large Red-Shift Based on TPE for Detection of F⁻. *Tetrahedron* **2022**, *129*, 133167; DOI: 10.1016/j.tet.2022.133167.

Poster no. P_IAC_05

Development of a on-line Biotoxicity Sensing and Control Unit for Wastewater Treatment

Yuejun Yu,[a] Zach Shidlovsky,[a] Andraz Suligoj,[a] Dina Shachar,[b] Sima Yaron[b] and Yaron Paz *[a]

[a] Wolfson Department of Chemical Engineering, Technion, Israel. [b] Department of Biotechnology and Food Engineering, Technion, Israel.

E-mail: (yuejun@campus.technion.ac.il; simay@bfe.technion.ac.il; paz@technion.ac.il)

Wastewater is known to contain large variety of organic and inorganic pollutants originating from industrial, agricultural, or domestic activities. Unfortunately, a single wastewater treatment method can hardly handle wastewater with complicate composition. Biological treatment and photocatalytic treatment, as two techniques that are frequently used in contaminated water purification, suffer from their own drawbacks in practical wastewater treatment.

The combination of these two methods may provide a way to solve the problems under complicate environments and can significantly reduce the operation cost of the process. This reactor should be able to overcome the limitations of the two techniques, thus increasing the efficiency of polluted water purification in harsh situation.

Here we report on the developing of a unit that automatically measures the extent by which polluted water might put at risk a biological treatment unit. The sensing unit monitors in real time the viability of the reporting bacteria Bacillus Subtilis, using resazurin. The toxic compounds were modelled by three antibiotics (chloramphenicol, tetracycline and ciprofloxacin). The potential of embedding the sensing unit in a multi-technology system (AOP-biological) was demonstrated by connecting the sensing unit to a photocatalytic reactor and controlling the number of operating lamps in the photocatalytic reactor autonomously according to predetermined toxicity setpoint. The approach can be easily applied to almost any AOP-biotreatment tandem system, while altering any controllable parameter (residence time, light, etc.) of the AOP unit according to needs.

This method was applied in two field studies: connected to the sewage system of Yoseftal hospital in Eilat and as part of a water treatment facility, handing streams arriving from olive oil mills. Following successful operation, the concept is currently extended to take into account not only toxicity but also the turbidity of the contaminated stream.

Acknowledgements: This work was performed as part of PROJECT ˆO: “Demonstration of planning and technology tools for a circular, integrated and symbiotic use of water” financed by the European Union Program Horizon 2020, grant No. 776816.

Inorganic Chemistry and Nano Science

Poster no. P_ICN_01

Exploring the Synthesis Mechanisms of Novel $CsPbBr_3@MoS_2$ Nanostructures toward their implementation in the field of renewable energy

Achiad Goldreich [a], Lena Yadgarov [a]

[a] *Department of Chemical Engineering, Ariel University, Ariel, 4076414, Israel*

E-mail: achiod@ariel.ac.il, lenay@ariel.ac.il

The capacity to capture and convert solar energy into efficient, environmentally friendly, and renewable power sources has wide-ranging implications globally, spanning across scientific and technological domains. Halide perovskites (HPs) exhibit remarkable performance in optoelectronics and photovoltaic devices, making them promising materials for a vast gamut of applications.[1] Within the halide perovskites family, the nanocrystals of $CsPbBr_3$ stand out with their extraordinary photoelectric properties, positioning them as a highly promising option for photovoltaic devices. Nonetheless, their widespread adoption faces obstacles due to their intrinsic instability and toxicity, resulting in detrimental phase changes and decomposition when exposed to environmental factors.[2] To surmount these challenges, a well-established and effective approach entails the development of a protective shell surrounding the core perovskite. This shell acts as a physical barrier, providing stability to the perovskite and augmenting the optical characteristics of the core material. Previous studies have demonstrated the potential of transition metal dichalcogenides (TMDs) as agents for surface passivation and exhibiting outstanding optoelectronic properties.[3] Moreover, owing to the TMD's semiconductor features, their bandgap and work functions can be modified by various methods, such as doping or induced strain. Indeed, it was shown that MoS_2 doped with sulfur deficiency serves as an additive to solar cells and produces very stable devices. Herein, we developed a new synthetic strategy for stabilizing HPs and boosting their optoelectronic properties by sheeting the NCs with TMDs. We investigate the synthesis mechanism by analyzing each step using a gamut of analytical methods. Namely, we study the mechanism of MoS_2 shell formation around the $CsPbBr_3$ NCs by examining the impact of the reaction temperature and the concentration of the precursors. Moreover, the analysis of the optical properties of the core-shell nanostructures indicates a charge transfer from the conduction band (CB) of the $CsPbBr_3$ NCs to the CB of MoS_2. The findings from our study are anticipated to facilitate the integration of halide perovskites into sustainable energy applications and pave the way to their rapid commercialization.

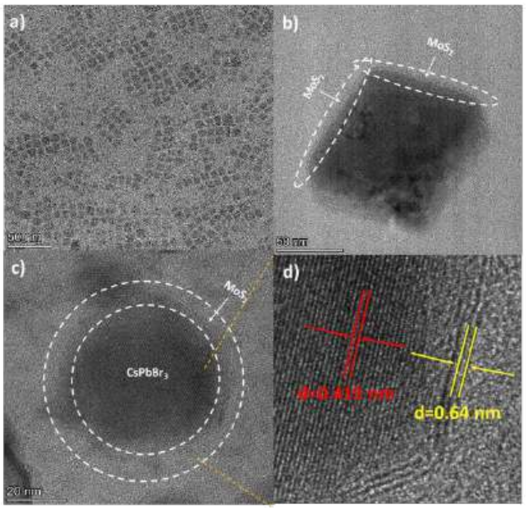


Figure 1. TEM images of (a) $CsPbBr_3$ NPs, (b) $CsPbBr_3$ with a MoS_2 partial coating, (c) complete encapsulation of MoS_2 on $CsPbBr_3$ NPs, (d) HR-TEM images of $CsPbBr_3$ with a lattice spacing of 0.419 nm (red), and MoS_2 with 0.64 nm (yellow)

References:

[1] A. Swarnkar, A. R. Marshall, E. M. Sanehira, B. D. Chernomordik, D. T. Moore, J. A. Christians, T. Chakrabarti, J. M. Luther, *Science (New York, N.Y.)* **2016**, *354*, 92-95.

[2] A. Buin, P. Pietsch, J. Xu, O. Voznyy, A. H. Ip, R. Comin, E. H. Sargent, *Nano letters* **2014**, *14*, 6281-6286.

[3] aP. N. Immanuel, S. J. Huang, V. Danchuk, A. Sedova, J. Prilusky, A. Goldreich, H. Shalom, A. Musin, L. Yadgarov, *Nanomaterials (Basel, Switzerland)* **2022**, *12*; bY. Lin, B. Adilbekova, Y. Firdaus, E. Yengel, H. Faber, M. Sajjad, X. Zheng, E. Yarali, A. Seitkhan, O. M. Bakr, A. El-Labban, U. Schwingenschlögl, V. Tung, I. McCulloch, F. Laquai, T. D. Anthopoulos, *Advanced materials* **2019**, *31*, 1902965.

Poster no. P_ICN_02

Manganese Substituted Polyoxometalates as Dioxygenase Catalysts for Indole Oxidation with Molecular Oxygen

Adi Herman[a] and Ronny Neumann[a]

[a] *Department of Molecular Chemistry and Material Science, Weizmann Institute of Science, Rehovot, Israel.*

E-mail: adi.herman@weizmann.ac.il, ronny.neumann@weizmann.ac.il

Oxidation chemistry is an important and large branch of organic chemistry. Molecular oxygen is the most ecologically benign oxidant for oxidative transformations but requires catalyst for its activation. In nature, molecular oxygen is activated toward oxygenation reactions by oxygenase enzymes which contains transition metals at their active sites. Polyoxometalates (POMs) containing transition metals are known and can be used as redox catalysts and, therefore, they are good candidates to be used as inorganic catalysts for molecular oxygen activation. There are several mechanistic pathways for molecular oxygen activation by transition metals. In this research we have carried out an oxygenation reaction by activation of both atoms of molecular oxygen, a so-called dioxygenase reaction.

Indoleamine 2,3-dioxygenase (IDO) and tryptophane 2,3-dioxygenase (TDO) are two heme-containing dioxygenase enzymes that catalyze the first step of the kynurenine pathway.[1] Different organometallic compounds containing iron, manganese and cobalt were studied in order to mimic and understand the mechanism of the enzyme.[2,3]

Here, manganese and manganese-zinc substituted Keggin POMs were synthesized. We showed by EPR spectroscopy that there are interactions between molecular oxygen and the different POMs to form manganese superoxide which is known to react with 2,3-dimethyl indole (2,3-DMI). The oxygenation of 2,3-DMI with O_2 in the presence of the different manganese POMs were carried out resulting in high yields and selectivity of a dioxygenated product (Figure 1). The products were characterized by GC-MS and LC-MS and also by $^{18}O_2$ labeling experiments.

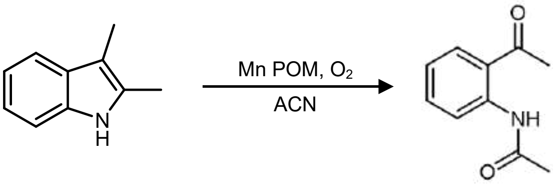


Figure 1: Oxidation of 2,3-dimethylindole.

References:

1. Savitz, J. The kynurenine pathway: a finger in every pie. *Mol. Psychiatry 25*, 131 - 147 (2020).
2. Dufour, M. N., Crumbliss, A. L., Johnston, G., Gaudemer, A. Reaction of indoles with molecular oxygen catalyzed by metalloporphyrins. *J. Mol. Catal.* 7, 277 - 287 (1980).
3. J. J. D. Sacramento and D. P. Goldberg, Oxidation of an indole substrate by porphyrin iron(III) superoxide: relevance to indoleamine and tryptophan 2,3-dioxygenases. *Chem. Commun. 56*, 3089 - 3092(2020).

Poster no. P_ICN_03

Highly Dense Monolayers of PbTe Quantum Dots Fabrication Using Spin Coating Method

Alina Sermiagin[a], Svetlana Lyssenko [a,b], Michal Amar[a], Refael Minnes[a]*

[a] *Department of Physical Sciences, Ariel University, Israel.* [b] *Department of Chemical Sciences, Ariel University, Israel.*

E-mail: refaelm@ariel.ac.il

Pb-chalcogenide semiconductor quantum dots (QDs) such as PbS, PbSe, and PbTe have drawn a generous amount of attention, mainly due to their chemical, physical, and optical properties. The bandgap tunability of Pb-X (X=S, Se, Te) QDs can be manipulated by simply changing the physical size of the nanocrystals (NCs). This makes it possible to create devices covering the entire solar spectrum with a series of different-sized QDs. In this work, we demonstrate the fabrication of thin, large-area, tightly packed, highly ordered monolayers of PbTe quantum dots (PbTe QDs) in various sizes.

The experiments were conducted using a spin coater in accordance with the solid-state ligand exchange method. We examine the key factors influencing layer production, including QD morphology, concentration, spin coater parameters, wetting, and solvent effect. We successfully created layers of PbTe QDs ranging from 6-13 nm on TiO_2/ITO. Our findings indicate that the spin coater method is favorable for small spherical QDs of 6-9 nm and unfavorable for cubical QDs. Additionally, we found that substrate surface roughness, QD fluid concentration, viscosity, and evaporation rate significantly impact the layer production process. We also explored layer-by-layer fabrication techniques and achieved bilayers of various sizes. Lastly, we discuss the spin coating method's ability to generate smooth, crack-free thin films on a large scale.

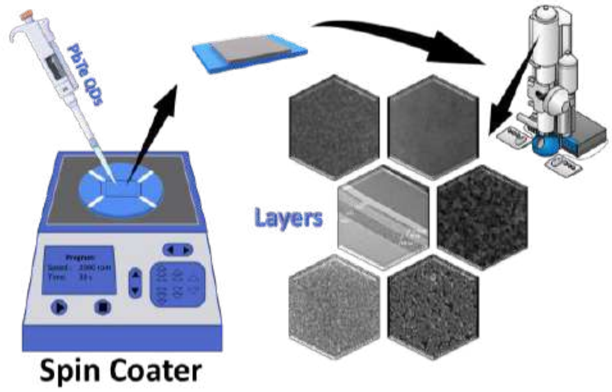


Figure 1: A schematic representation of the spin coating method for layer fabrication

Poster no. P_ICN_04

Laser-Assisted Direct Coating of Graphene-Based Films on Plastic Substrates with Bactericidal Properties

Aneena Lal[1], Hani Porat[1], Rivka Cahan[2], Lea Ouaknin Hirsch [2], Arie Borenstein[1*]

1- Department of Chemical Sciences, Ariel University, Ariel, Israel

2- Department of Chemical Engineering, Ariel University, Ariel, Israel

*- corresponding author. Email: arieb@ariel.ac.il

Bacterial growth on surfaces is a major problem in medical equipment, fresh food storage, and water supply industries. Antibacterial coatings offer a preferred method to prevent this dangerous hazard. However, to provide a complete solution, the developed coating must not only efficiently prevent bacterial growth and consist of cost-effective, stable, and bio-friendly materials but also offer a simple coating method. In this work, we use novel laser processing that offers significant advancements, including (1) fast, single-step, and waste-free synthesis, (2) allowing direct printing of graphene over any substrate, including thermal-sensitive materials (i.e., polymers), and (3) micron-resolution patterning of the coated materials. We use an intense laser beam to fabricate metal-oxide/graphene nanoparticle composite films directly on plastic surfaces. The metal-oxide nanoparticles (cobalt and copper) are tested for antibacterial activity. Due to the combined formation, the metal-oxide nanoparticles are highly dispersed and firmly adhered to the graphene matrix. Notably, the structure and properties of the laser product, such as the nanoparticle's size and the graphitization level, can be controlled by tuning laser parameters. The composite coatings demonstrate excellent antibacterial activity. Studying substrates coated with different metal compositions found that 4.5-5 % of metal contents have antibacterial activity (percentage inhibition) by 89 % (PBS). Additionally, leaching studies demonstrate that the fabricated substrates are stable in different pH solutions.[1]

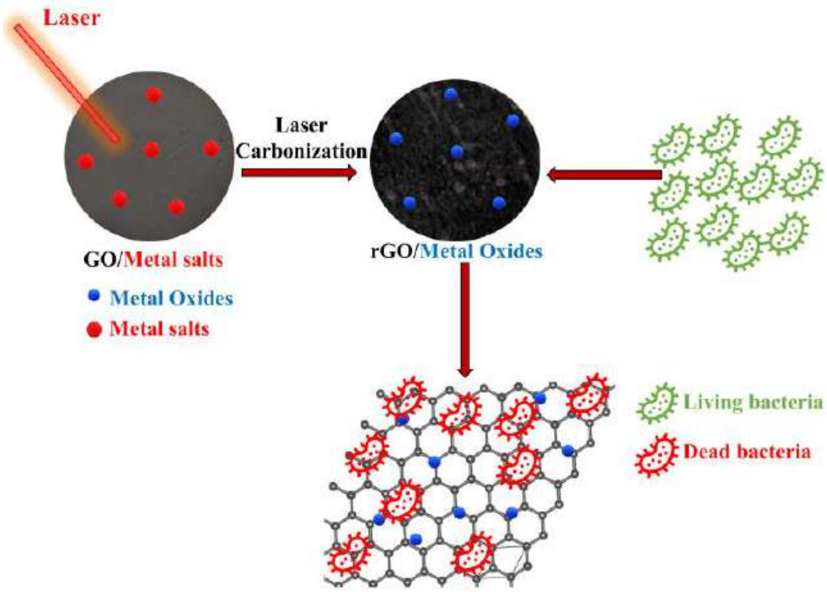


Figure 1. Schematic illustration of the synthesis procedure for laser-induced metal-oxide/rGO composites coatings and the antibacterial activity.

Poster no. P_ICN_05

Silica-encapsulated plasmonic heat sources unlocking photothermally driven colloidal synthesis of nanoparticles

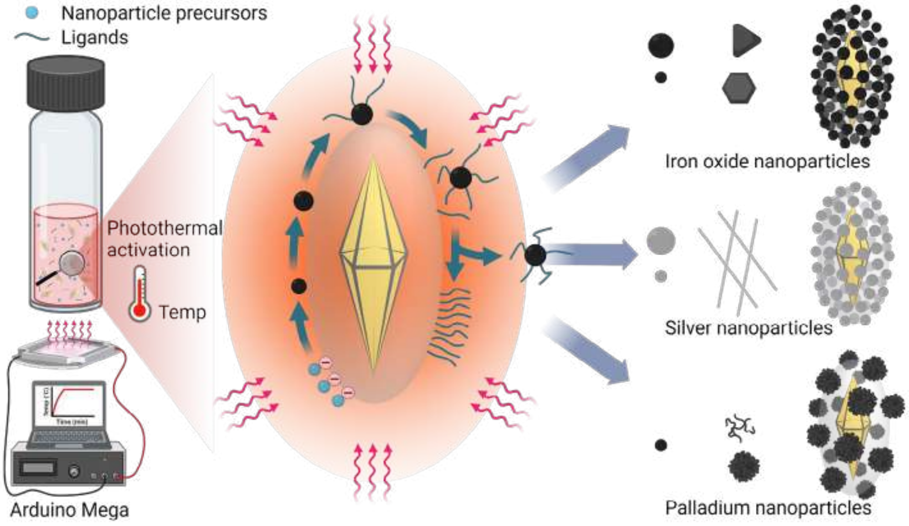
Aritra Biswas,[a] **and Yossi Weizmann***[a,b,c]

[a]Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
[b]Ilse Katz Institute for Nanotechnology Science, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
[c]Goldman Sonnenfeldt School of Sustainability and Climate Change, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

E-mail: aritrab@post.bgu.ac.il; yweizmann@bgu.ac.il

Plasmonic nanomaterials exhibit phenomena such as local field enhancement, hot electron carriers, and photothermal conversion, all stemming from resonant oscillations of surface electrons.[1] Consequently, extensive efforts have focused on unraveling the mechanisms governing these plasmonic effects for diverse applications. Recently, interest in plasmon-mediated light-to-heat conversion has surged, particularly in fields like photothermal catalysis, imaging, and photothermal therapy. While previous studies indicate temperatures exceeding 200 °C near the surface of photothermal nanoparticles, current research often emphasizes applications requiring lower temperatures and mostly not in solution.[1]

Our work targeted the photothermal synthesis of nanoparticles in solution using silica-encapsulated gold-bipyramids (SiO_2@AuBPs) as heat sources.[2] Plasmonic materials we used efficiently convert visible and infrared light to heat facilitating nucleation and growth. Notably, our study introduced light-assisted colloidal synthesis of iron oxide, silver, and palladium nanoparticles. The silica surface chemistry and localized thermal hotspots generated by plasmonic nanoparticles significantly influence the formation mechanism, enabling growth at temperatures considerably lower (difference from ≈30-100 °C) than conventional methods with higher yields. This research further extended the photothermal approach to anisotropic geometries, allowing the synthesis of intricate assemblies previously inaccessible. In summary, our study showcased the potential of plasmonic-driven photothermal synthesis for nanoparticle production in solution.



Scheme 1: Thermoplasmonic abilities of SiO_2@AuBPs to initiate the nucleation-growth of nanoparticles and control the formation of intricate assemblies.

Acknowledgements: We thank the support of the Zuckerman STEM Leadership Program, and the Israel Science Foundation (ISF), grant No. 2491/20.

References:

1. Baffou, G.; Cichos, F.; Quidant, R. Applications and challenges of thermoplasmonics. *Nat. Mater.* **2020**, *19*, 946–958.
2. Biswas, A.; Lemcoff, N.; Shelonchik, O.; Yesodi, D.; Yehezkel, E.; Finestone, E. Y.; Upcher, A.; Weizmann, Y. Photothermally heated colloidal synthesis of nanoparticles driven by silica-encapsulated plasmonic heat sources, *Nat. Commun.* **2023**, *14*, 6355.

Poster no. P_ICN_06

1D transition-metal dichalcogenides/carbon core-shell composites for the hydrogen evolution reaction

Asmita Dutta[a], Arie Borenstein[a]

a-Department of Chemical Sciences, Ariel University, Israel

arieb@ariel.ac.il

2D transition metal dichalcogenides (TMDCs) have recently been proposed as an excellent catalytic substitute for noble metals in the hydrogen evolution reaction (HER). When assembled in a 1D nanotube configuration, TMDCs show enhanced performances originating from the curved lattice strain and nanosize. However, WS_2 nanotubes (NTs) have minor electron mobility and low number of active edge sites, which hinder their effective use in electrocatalytic reactions. In this work, we present the synthesis of the core–shell structure of WS_2 NTs coated with carbon. WS_2 NTs were coated with nitrogen-doped graphitic carbon in three steps. After physical adsorption and annealing, excessive carbon was removed by CO_2 gas, which acts as a mild oxidizer. Finally, recrystallization of the carbon coating at 800 °C was done by thermal annealing in the presence of N_2. Products after each reaction step were chemically analyzed. Following the recrystallization, the heterostructure WS_2 nanotubes/carbon showed significantly improved HER performance, exhibiting an overpotential of 172 mV compared to 540 mV for the uncoated NTs. The improved activity was confirmed in different pH electrolytes. Moreover, the carbon coating significantly improved the electrochemical stability of the WS_2 by protecting it upon prolonged reductive operation. The formation of carbon-coated WS_2 NTs composite material provides a promising way to obtain a pH-universal, cost-effective electrocatalyst for energy conversion.

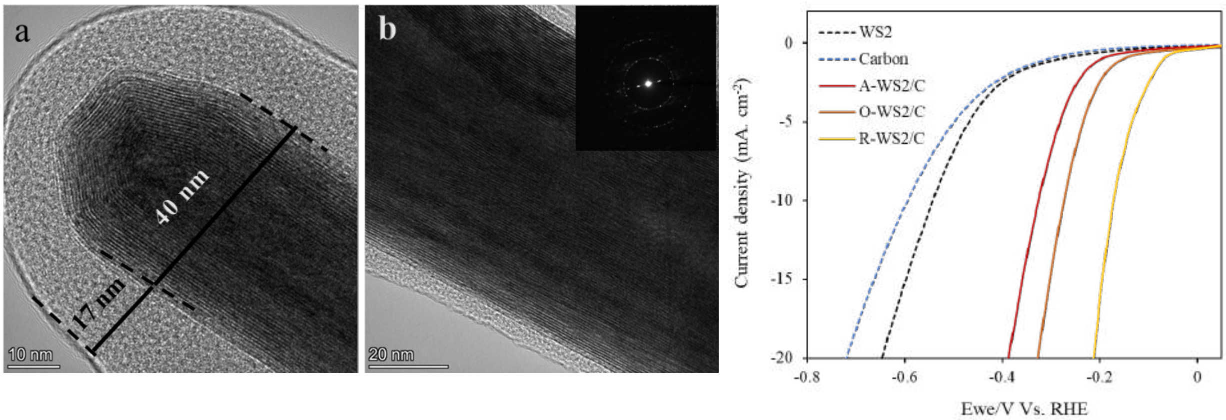


Figure 1. (Left) TEM magnification image of WS_2 nanotube coated by carbon layers. (Right) LSV curves showing H_2 evolution reaction in 0.5 M H_2SO_4.

Acknowledgments: We express our gratitude to ICS for their financial assistance and for creating a platform for scientific discussions.

References: Wei, Shuangying; Serra, Marco; Mourdikoudis, Stefanos; Zhou, Huaijuan; Wu, Bing Dekanovsky, Lukas; Sturala, Jiri; Luxa, Jan; Tenne, Reshef; Zak, Alla; Sofer, Zdenek. Improved Electrochemical Performance of NTs-WS_2@C Nanocomposites for Lithium-Ion and Sodium-Ion Batteries. *ACS Appl. Mater. Interfaces* 2022, 14, 41, 46386–46400

Poster no. P_ICN_07

Using Thermogravimetric Analysis (TGA)/Differential Scanning Calorimetry (DSC) As A Tool To Analyze The Low Temperature Oxidation (LTO) of Coals

Presenting Author: Aviv Hassid, Mr, Department of Chemical Sciences, Ariel University, Ariel, Israel
Contact Information: aviv.hassid@gmail.com

uthors: Mathias Klinger, Dr.-Ing, Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie Freiberg, Freiberg, Germany
Contact Information: mathias-klinger@gmx.de

uthors: Steffen Krzack, Dr.-Ing, Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie Freiberg, Freiberg, Germany
Contact Information: Steffen.Krzack@iec.tu-freiberg.de

Co-Authors: Haim Cohen, Prof., Department of Chemical Sciences, Ariel University, Ariel, Israel
Contact Information: hcohen@ariel.ac.il

:

ds as the preeminent energy resource globally, prominently harnessed for power generation and sustenance of the steel
and is anticipated to persist as the predominant source in the immediate future. The principal coal variants employed for
poses include Lignites (commonly known as brown coal) and Bituminous coals, specifically Steam Coal.
characterized by their inability to be stored for prolonged durations, necessitate immediate utilization post-mining. In
Bituminous coals, can be stored and transported prior to utilization.
, the storage of Bituminous coals presents potential risks, manifesting in self-heating phenomena concomitant with the
toxic and fire-hazardous gases. Under extreme conditions, the latent risk of self-ignition arises, primarily stemming from
perature Oxidation (LTO) of the coal, occurring at temperatures ranging from room temperature to 150°C.
y, integrating the combined Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC) alongside Ga
ography and on-line Mass Spectrometry to learn about the potential hazards associated with the emission of toxic and
gases during the spontaneous heating process inherent to both Lignites and Bituminous coals.

Poster no. P_ICN_08

Modified Successive Ionic Layer And Adsorption Reaction (SILAR) to introduce Vertically grown SnS nanosheets

Chandradip D. Jadhav[a] Girish P. Patil[a] Refael Minnes*[a]

[a] *Department of Physics, Faculty of Natural Sciences, Ariel University, Ariel, Israel.*

E-mail: ((refaelm@ariel.ac.il & minnesr@gmail.com))

We describe a modified Successive Ionic Layer And Adsorption Reaction (SILAR) technique **(Figure 1)** for the controlled production of vertically developed SnS nanosheets over a large substrate surface (16 cm^2). The enhancement entails fine-tuning the SILAR settings to gain improved control over the growth process, allowing the creation of well-defined and vertically aligned SnS nanosheets.

X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and X-ray Photoelectron Spectroscopy (XPS) were used to analyze the developed nanomaterials. The crystalline nature of the vertically developed SnS nanosheets was shown by XRD examination, with distinct peaks corresponding to the orthorhombic phase of tin sulfide. The nanosheets' large-area coverage and vertically grown nature were highlighted by SEM imaging, offering unique insights into their shape and structure.

A further microscopic study using TEM revealed the detailed structural elements of the nanosheets, confirming their sheet-like topography, fringe spacing, and crystallinity nature. The XPS examination revealed elemental composition and chemical state information, offering insight into the surface chemistry of the produced SnS nanosheets.

The modified SILAR approach presented here not only enables large-scale development of SnS nanosheets but also provides a route for modifying their structural and morphological features. The extensive characterization of the produced nanomaterials using XRD, SEM, TEM, and XPS methods offers a detailed knowledge of them, making them interesting candidates for use in optoelectronic devices, energy storage systems, and catalysis. This study advances controlled nanomaterial manufacturing and broadens the possible uses of SnS nanosheets in a variety of technical sectors.

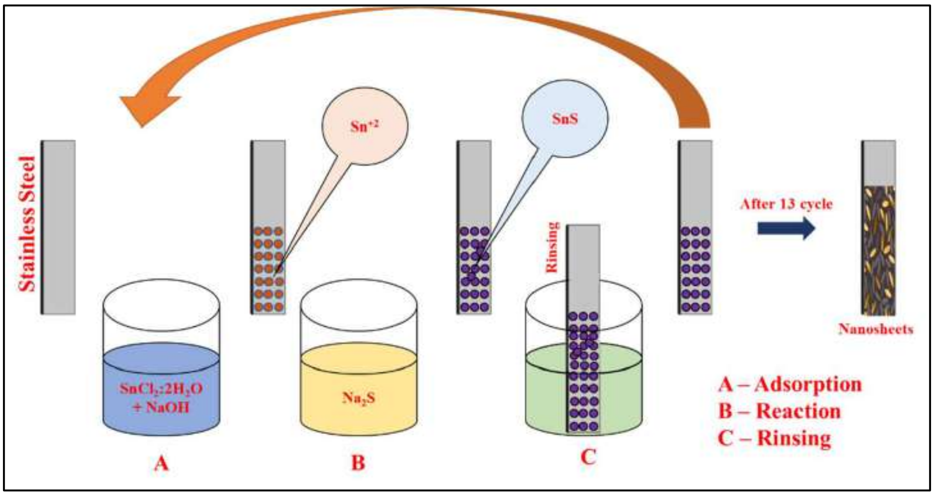


Figure 1: Schematic illustration of Vertically grown SnS nanosheets

Acknowledgements: We express our gratitude to Ariel University for providing PhD scholarship support.

Poster no. P_ICN_09

The Reaction Mechanism of $Co^{II}(HCO_3)_n^{2-n}$ with Carbonate Anion Radicals

Dalia Gitin[1], Dan Meyerstein [1] and Tomer Zidki[1]

[1]*Department of Chemical Sciences, Ariel University, Ariel 40700, Israel*

E-mail: daliag@ariel.ac.il, danm@ariel.ac.il, tomerzi@ariel.ac.il

Radicals have been of great importance in chemical, environmental and biological processes. There are numerous radical reactions that occur in the presence of transition metals, metal complexes, nanoparticles and organic substances. A large part of these processes are biological processes that are critically important in living organisms. In our study, we plan to study mainly reaction of carbonate anion radicals. Carbonates and bicarbonates are found in all neutral and alkaline solutions. While usually considered buffers or proton donors, recent research found that they play a vital role in oxidation-reduction processes, some of which are of major importance in biological and environmental processes. Carbonate is a strong, hard base and excellent σ donor, enabling it to stabilize transition metal complexes in high oxidation states. Carbonate complexes with transition metals can function as electrocatalytic catalysts for water oxidation.

In our work, we produced carbonate anion radicals ($CO3^{\cdot -}$) using ionizing radiation. In preliminary experiments the reaction of $CO_3^{\cdot -}$ with cobalt(II) carbonate complexes, $Co^{II}(HCO_3^-)_m(H_2O)_{6-m}^{2-n}$ was studied. Applying the pulse-radiolysis technique. Immediately after the pulse two peaks at 600 nm and 300 nm appeared. After around 2.5 milliseconds the 600 nm peak disappeared, while the absorption at 300 nm increased along with the emergence of new peaks at 450 nm and 650 nm. We established that the 600 nm peak is due to the carbonate radical anion, the 300 nm peak is attributed to a cobalt(III) carbonate charge transfer complex, and the 650 nm and 450 nm peaks the d-d transitions of this complex. In addition, the rate constant of the reaction $Co^{II}(HCO_3^-)_m(H_2O)_{6-m}^{2-m} + CO_3^{\cdot -} \rightarrow Co^{III}(CO_3^{2-})_{m+1}(H_2O)_{5-m}^{1-2m} + mH^+$ processes high $k = 1.0\text{x}10^7\ M^{-1}s^{-1}$. This reaction is followed by the ligand exchange reaction: $Co^{III}(CO_3^{2-})_{m+1}(H_2O)_{5-m}^{1-2m} + HCO_3^- \rightleftharpoons Co^{III}(CO_3^{2-})_{m+2}(H_2O)_{4-m}^{-(2m+1)} + H^{+/-}, k = 3 \times 10^7 M^{-1}s^{-1}$. The latter reaction affects the spectra of the complexes.

Poster no. P_ICN_10

Anisotropic Etching of Au@Ag Nanobars by Circularly Polarized Light

Monika Ghalawat[1], **Daniel Feferman[1]** and Gil Markovich[1]

[1] *School of chemistry, faculty of exact sciences, Tel-Aviv university, Tel-Aviv 6997801, Israel*

Email: Fefermand@mail.tau.ac.il

Plasmon-induced reactions of coinage metal nanoparticles have inspired many interests in the last few decades both in research and industry. Chiral metallic nanostructures have stronger chiroptical response than conventional small chiral molecules, and can be utilized in fields like enantioselective sensors, metasurfaces and medical applications[1–3]. Forming chiral metal nanoparticles is challenging. The symmetry breaking in such systems can be achieved using various routes, including plasmon induced chemical processes, as shown by Tatsuma *et. al.*, who demonstrated asymmetric oxidation of Pb ions on gold nanocuboids deposited on surfaces to create chiral gold/PbO_2 nanoparticles[4].

Our aim is to break symmetry in metal nanoparticles in colloidal solution by exciting asymmetric plasmon modes through illumination with circularly polarized light (CPL). Govorov and coworkers have theoretically shown[5] that although the asymmetry induces by the CPL is averaged out by the free rotation of nanoparticles in solution, there might be a small asymmetry left. Here we experimentally show that significant optical activity appears in Au@Ag core-shell nanocuboids which are oxidized under CPL illumination. The mechanism of the effect could involve hot holes excitation by localized asymmetric plasmon modes which could then oxidize the silver. Another mechanism is that the local fields created by the plasmonic hot spots could reduce energy barriers for oxidation of the silver.

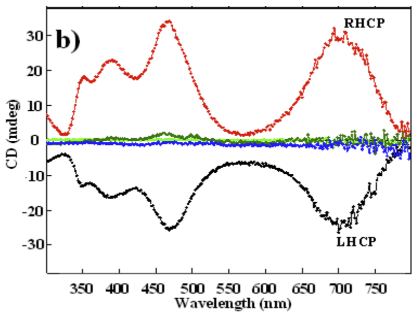


Figure 1 – CD spectra of AgNBs before (light green) and after plasmon-induced etching in dark conditions (blue), under unpolarized light (dark green), under right- or left circularly polarized light (red and black, respectively).

1. Li, W. *et al.* Circularly polarized light detection with hot electrons in chiral plasmonic metamaterials. (2015) doi:10.1038/ncomms9379.
2. Tullius, R. *et al.* 'Superchiral' Spectroscopy: Detection of Protein Higher Order Hierarchical Structure with Chiral Plasmonic Nanostructures. *J. Am. Chem. Soc* **137**, 8383 (2015).
3. Bhanushali, S. *et al.* Photomodulated Spatially Confined Chemical Reactivity in a Single Silver Nanoprism. *ACS Nano* **14**, 11100–11109 (2020).
4. Saito, K. & Tatsuma, T. Chiral Plasmonic Nanostructures Fabricated by Circularly Polarized Light. (2018) doi:10.1021/acs.nanolett.8b00929.
5. Besteiro, L. V. *et al.* Local Growth Mediated by Plasmonic Hot Carriers: Chirality from Achiral Nanocrystals Using Circularly Polarized Light. *Nano Lett* **21**, 10315–10324 (2021).

Poster no. P_ICN_11

Colloidal nanoparticles with a perovskite periodic heterostructure of $(PbBr_2)_2(AMTP)_2PbBr_4$ composition

Emma H. Massasa[a], *Lotte T. J. Kortstee*[c], *Rachel Lifer*[a], *Saar Shaek*[a], *Boaz Pokroy*[a], *Ivano E. Castelli*[c], *Yehonadav Bekenstein*[a,b]

[a] *Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 32000 Haifa, Israel.*

[b] *The Solid-state institute, Technion – Israel Institute of Technology, 32000 Haifa, Israel.*

[c] *Department of Energy Conversion and Storage (DTU Energy), Technical University of Denmark, Anker Engelunds Vej 411, DK-2800 Kongens Lyngby, Denmark.*

E-mail: bekenstein@technion.ac.il

Heterostructure nanoparticles challenge our common understanding of interfaces due to quantum confinement and size effects, giving rise to synergistic properties. An alternating heterostructure in which reoccurring interfaces appear in a single nanocrystal is hypothesized to accentuate such properties. We developed a colloidal synthesis for perovskite layered heterostructure nanoparticles to prove the concept and advance our understanding of perovskite heterostructures. We produce a layered heterostructure containing ($PbBr_4$) octahedra akin to perovskite structure and a non-perovskite layer of ($(PbBr_2)_2(AMTP)_2$) where AMTP is the organic molecule 4-(ammoniomethyl)-Tetrahydropyran. These two layers keep repeating one on top of the other.

Adding organic molecules attached to the surfaces of the nanocrystals limits the average crystal size and enables colloidal stability. By varying the synthetic parameters and selection of precursors, we control particle size, shape, and product priority. For example, as the synthesis temperature increases, the particle size decreases, in agreement with classic nucleation theory. Structural and spectroscopic studies fit reported bulk structures[1], reaffirming our results, with some changes, mainly in the photoluminescence of the nanocrystals.

We aim to utilize these new colloidal perovskite nanoparticle heterostructures and use their unique interfacial properties for applications that exploit such internal potentials as photovoltaics, photocatalysis, and optoelectronics. The heterostructure interfaces can facilitate faster charge carrier transfer, separation, tunable recombination rate, and higher efficiencies. The improved nanocrystal electronic structure and resulting properties may be used to engineer optoelectronic properties for lighting and solar applications.

Acknowledgments: This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 949682- ERC- HeteroPlates. We thank Dr. Iryna Polishchuk, Dr. Arad Lang, and Dr. Giorgia Confalonieri for their help in the synchrotron measurements. Diffraction experiments were performed on beamline ID22 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

References:

(1) Aubrey, M. L.; Saldivar Valdes, A.; Filip, M. R.; Connor, B. A.; Lindquist, K. P.; Neaton, J. B.; Karunadasa, H. I. Directed Assembly of Layered Perovskite Heterostructures as Single Crystals. Nature 2021, 597 (7876), 355–359.

Poster no. P_ICN_12

Modifying the Properties and Performance of Degradable Polymers with Atomic Layer Depositio

G. Menasherov, T. Segal-Peretz

Department of Chemical Engineering, Technion, Haifa, Israel

Email – Gil.m@campus.technion.ac.il , Tamarps@technion.ac.il

Degradable polymers offer a viable solution to the harmful environmental impact of conventional, non-degradable plastics. However, their widespread adoption is impeded by their lower performance compared to conventional polymers. Degradable polymers are often sensitive to elevated temperatures, UV radiation, and exposure to solvents, as well as have poor mechanical properties and high oxygen and water permeability (Nakajima, Dijkstra, and Loos 2017). One potential avenue for overcoming these challenges lies in the development of organic-inorganic hybrid materials. Vapor phase processes, such as sequential infiltration synthesis (SIS) - a method derived from atomic layer deposition (ALD), have emerged as a promising technique for synthesizing hybrid materials. In SIS, polymers are exposed to gaseous precursors that diffuse and interact with the polymers, leading to growth of inorganic materials within the polymer matrix (Leng and Losego 2017).

This research aims to modify degradable polymers, including poly(lactic acid) (PLA) and poly(hydroxyalkanoates)(PHA), using SIS to create hybrid materials with enhanced properties. First we investigated the growth of AlO_x within and ontop PLA and PHA thin films and explored the precursor-polymer interactions using *in-situ* quartz crystal microbalance (QCM) microgravimetric measurements and electron microscopy. This fundamental understanding was further applied in finding the favorable conditions for SIS processes on 3D printed models of PLA and PHA. The hybrid AlO_x-polymer showed improved properties such as resistance to solvent vapors. These findings contribute to the development of environmentally friendly materials by harnessing the potential of SIS to enhance the properties of degradable polymers, thus addressing the global plastic accumulation problem.

References:

Leng, Collen Z., and Mark D. Losego. 2017. "Vapor Phase Infiltration (VPI) for Transforming Polymers into Organic–Inorganic Hybrid Materials: A Critical Review of Current Progress and Future Challenges." *Materials Horizons* 4 (5): 747–71. https://doi.org/10.1039/C7MH00196G.

Nakajima, Hajime, Peter Dijkstra, and Katja Loos. 2017. "The Recent Developments in Biobased Polymers toward General and Engineering Applications: Polymers That Are Upgraded from Biodegradable Polymers, Analogous to Petroleum-Derived Polymers, and Newly Developed." *Polymers* 9 (10): 523. https://doi.org/10.3390/polym9100523.

Poster no. P_ICN_13

Facile hydrothermal synthesis and electrochemical properties of Copper Telluride (Cu_2Te) nanoparticles in aqueous electrolyte

Girish P. Patil[a], Chandradip D. Jadhav[a], Refael Minnes[a]*

[a]*Department of Physics, Faculty of Natural Sciences, Ariel University, Ariel, Israel*

E-mail: refaelm@ariel.ac.il

Abstract:

Copper telluride (Cu_2Te) nanoparticles were successfully synthesized through the hydrothermal method and subjected to comprehensive characterization using X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED). The resulting Cu_2Te nanoparticles exhibited an average diameter of 60 nm. Electrochemical supercapacitive investigations were conducted on these nanoparticles employing stainless steel (SS -304 grade) as the current collector in a three-electrode system. Notably, a specific capacitance of 381 F/g was achieved at a scan rate of 2 mV/s, and a capacitance of 338 F/g was observed at a current density of 0.47 A/g. Beyond their application in supercapacitors, Cu_2Te nanoparticles hold promise for various other fields, including solar cells, LEDs, sensors, and batteries.

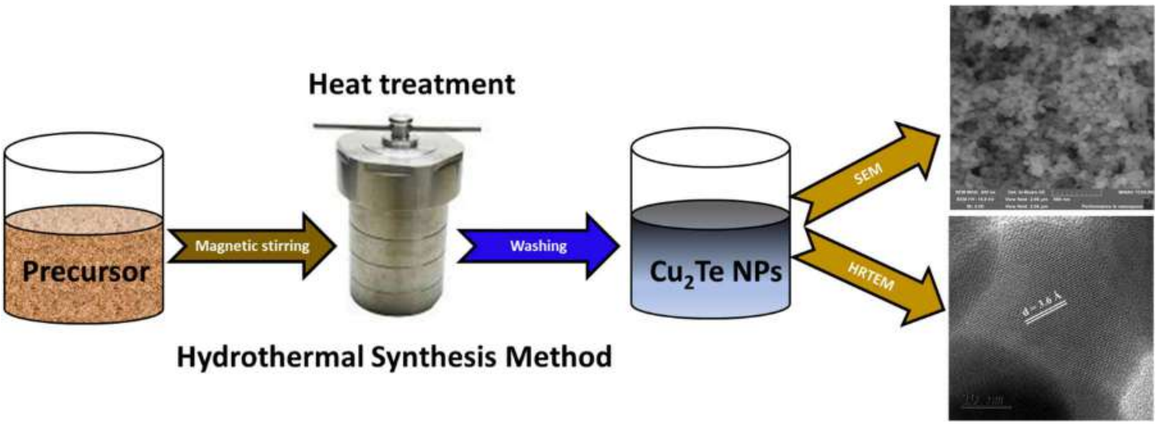


Figure 1: Schematic representation of hydrothermal synthesis

Acknowledgements: GPP And CDJ acknowledge to Ariel university for providing PhD Scholarship

Poster no. P_ICN_14

From Ions to Metallic Micro-deposition: Unveiling Mechanism and Nanostructure of Laser-Induced Photo-Thermal Reduction

Ehud Greenberg, Keren Chaika, Jonathan Ben-Moshe, Tamar Rozevich, Nina Armon, & Hagay Shpaisman*

Chemistry Department & Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan, Israel

E-mail: Hagay.shpaisman@biu.ac.il

Laser-guided assembly of materials into microstructures is garnering considerable interest due to its potential for creating intricate patterns and forming 2D and 3D structures. The precision of this technique, capable of achieving micron/sub-micron resolution, coupled with its efficiency in reducing energy and material waste compared to conventional top-down methods, makes it a promising approach for a wide range of applications, including sensing, medical devices, and microelectronics. Assembly from liquids provides smaller feature sizes than powders and has advantages over other states of matter in terms of relatively simple setup, easy handling, and recycling. However, the simplicity of the setup conceals a variety of underlying mechanisms, which cannot be identified simply according to the starting or resulting materials.

Here, we illuminate one of the mechanisms through systematic analysis of photo-thermal reaction products forming metals and oxides from their corresponding ions at different interfaces. Examination of the nanostructure of deposits on a substrate using high-resolution transmission electron microscopy and selected area diffraction pattern analysis reveals a combination of both amorphous and crystalline moieties. We have found that crystalline nanostructures are formed inside the liquid while a thermal microbubble directs these crystalline nanostructures to its base while also forming amorphous moieties at the liquid/gas/solid interface. We provide insights on how these findings can be leveraged to develop methodologies that enable precise control over material properties, such as the degree of amorphousness or crystallinity in metals and oxides, using laser technology. Our system is unique as the origin of the two moieties arise from different mechanisms, so they could be tuned separately. Moreover, we suggest formation of composite metallic microstructures and alloys with control over the distribution of the various nano-sized components by depositing mixtures of metallic ions with nano-particles. The main advantage of the proposed method compared to known methods of composite formation lies in its modularity and flexibility. As there is no a-priori requirement for chemical affinity between the metallic matrix and nano additives, composites that would otherwise require several production stages could be formed in a single step.

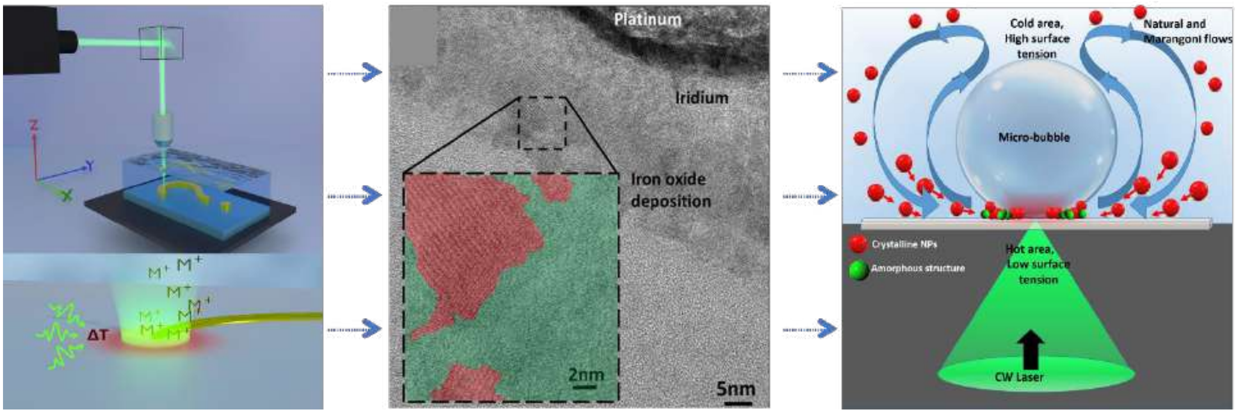


Figure 1: (Left) Setup and general phenomenon. Determining (Middle) nanostructure unveils (Right) proposed mechanism.

Poster no. P_ICN_15

Measuring and understanding the nanomechanical properties of halide perovskites and their correlation to structure.

Irit Rosenhek-Goldian[3], Isaac Buchine[1], Naga Prathibha Jasti[1], Davide R. Ceratti[3,4], Sujit Kumar[1,2], David Cahen[1,2] & Sidney R. Cohen[3]

[1] Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ. Ramat Gan Israel.

[2] Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel.

[3] Dept. of Chemical Research Support, Weizmann Inst. of Science Israel.

[4] CNRS, UMR 9006, IPVF, Institut Photovoltaïque d'Ile-de-France, 18 Boulevard Thomas Gobert, 91120 Palaiseau, France.

E-mail: (irit.goldian@weizmann.ac.il)

Halide perovskites, HaP, and especially Pb-based ones exhibit a plethora of remarkable properties. Of these, their photovoltaic properties are the most widely studied due to the proven potential these materials hold for significant technological impact. In addition to photoresponse, this material class is characterized by interesting physical properties, of which mechanical properties enjoy special attention, not only because of potential use in flexible devices, but also from a fundamental science point of view. The mechanical response can shed light on the materials' behavior including dynamic processes and strain-related effects on optoelectronic behavior.

In the context of these studies, particular emphasis has been placed on environmental factors which can alter, especially degrade, material functionality and device performance. Exposure to humidity, light, and oxygen rank prominently amongst these factors.

In this study we measure the humidity influence on the mechanical properties, i.e., elastic modulus (E) and hardness (H), for two series of lead halide perovskite single crystals, varying either by cation or by anion type. Our conclusions are based on comparing results obtained from several different nano-indentation techniques, which separate surface modulus from that of the bulk, and probe different manifestations of the hardness. These studies reveal the different crystalline parameters governing influence of humidity on the mechanics at the surface and in the bulk.

An atypical inverse correlation between E and H was measured (as seen in the **figure 1 a**). Furthermore, humidity influenced these two properties in opposite fashion – humidity exposure led to lower H, but to higher E (**figure 1 b**). This trend is opposite to that found in most materials where hydration lowers both E and H. We suggest a link between dynamic disorder, self-healing, and the intriguing relation between E and H.

Poster no. P_ICN_16

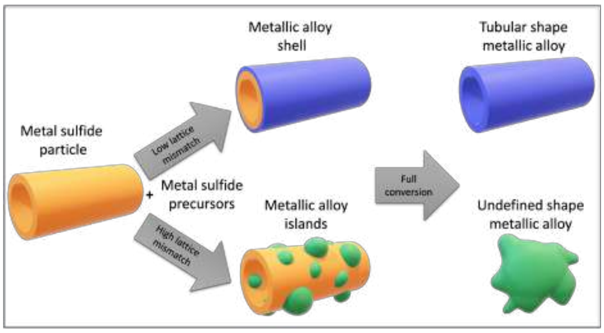
Unconventional Synthesis of Metal (Ni, Co, Ag) Antimony Alloy Particles

Karam Shreteh[a], Sandhiya Murugesan[a], Iman Alkrenawi[a], Noa Afik[a], Michael Volokh[a] and Taleb Mokari*[a] [b]

[a] *Department of Chemistry, and* [b] *Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel*

E-mail: mokari@bgu.ac.il

Bimetallic alloy materials attract interest owing to their properties and stability compared to pure metals, especially alloys with nanoscale dimensions. Metal antimony (MSb) alloys, specifically NiSb, are widely used for charge storage applications due to their high stability. Most synthetic approaches to form these materials require drastic conditions (e.g., high temperature, potent reducing agent, extended reaction times) limiting control over the final morphology. The other viable approach is a galvanic replacement that uses unstable materials as precursors. In this work, we present a new and facile method to prepare several MSb (M = Ni, Co, Ag) alloys with shape control by reacting Sb_2S_3 particles with metal(M)-sulfide single source precursor in trioctylphosphine (TOP) under mild conditions. Furthermore, we explore the role of TOP as a reducing agent and demonstrate how both alloy constituents are crucial for mutual stabilization. Electrochemical studies are also performed on these NiSb particles, showing their ambipolar nature and allowing their utilization as the active ingredient in the demonstrated high-energy density symmetric supercapacitor.



Scheme 1: Schematic illustration of an unconventional method for producing metallic alloys through the reaction of metal-sulfide tubular particles with metal-sulfide precursors. The diagram highlights the crucial role of lattice mismatch between the materials in preserving the desired shape.

Acknowledgements: This work was supported by the Israel Science Foundation (grant No. 1507/22). KS thanks the Chemo–tech fellowship from the Kreitman School of Advanced Graduate Studies, Ben-Gurion University of the Negev, and the Council for Higher Education fellowship for outstanding doctoral students from the Arab community.

References:

1. Shreteh Karam, Murugesan Sandhiya, Alkrenawi Iman, Afik Noa, Volokh Michael, Mokari Taleb. Unconventional Synthesis of Metal (Ni, Co, Ag) Antimony Alloy Particles. *Inorganic Chemistry,* **2023**, *Accepted*.

Poster no. P_ICN_17

Preferential photocatalytic degradation of enantiomers of Penicillamine by molecular imprinting and ALD

Lital Felzenshtein,[a] and Yaron Paz[a]

The Wolfson Department of Chemical Engineering, Technion – Israel Institute of Technology

E-mail: litalfel@campus.technion.ac.il, paz@technion.ac.il

Enantiomeric separation has a critical role in pharmaceutical and chemical industries, especially in the production of enantiopure drugs. Traditional methods, such as chiral chromatography and stereoselective crystallization, encounter limitations in terms of efficiency and selectivity. This study presents a novel approach for preferential degradation of enantiomers through chiral molecular imprinting on a photocatalytic substrate, focusing on Penicillamine.

The proposed method involves imprinting the distomer (undesired enantiomer) onto the surface of a photoactive semiconductor, creating a chiral template. Subsequently, an inert layer is deposited through atomic layer deposition (ALD), forming a chiral cavity. This unique configuration facilitates selective degradation of the distomer under UV light, resulting in the enrichment of the desired enantiomer, eutomer.

The primary objectives of this research included expanding the arsenal of separable chiral compounds, enhancing separation selectivity, and minimizing the reaction time. The model system comprises of P25 titania as the photocatalyst, alumina as the inert layer, Penicillamine as the targeted compound, with kinetics monitored using high-performance liquid chromatography (HPLC).

Preliminary findings indicated successful preferential degradation of Penicillamine in experiments conducted with single enantiomer solutions. Selectivity was demonstrated with accelerated degradation rates of the imprinted enantiomers on the imprinted films, with L-Penicillamine being degraded 2.78 times faster than D-penicillamine on L-imprinted films, and D-Penicillamine being degraded 4.41 times faster than L-Penicillamine on D-imprinted films. Unfortunately, the preferentiality was found to be much lower whenever the measurements were performed with racemic mixtures. In part, this was due to the instability of D-Penicillamine manifested by hydrolysis above 10°C.

An additional approach for racemate experiments was conducted, in which a bulky side group was covalently attached to the chiral center, aiming for increasing the geometric shape difference between the two enantiomers. In this set of experiments, a selectivity ratio of 1.22 was obtained on L-imprinted films in measurements with racemic mixtures. When D was imprinted - a lower selectivity of 1.05 was measured.

The findings of this research hold promise for broader applications in the pharmaceutical and chemical industries, paving the way for advancements in tuneable and efficient enantiomer enrichment methodologies. Ongoing research will focus on optimization and exploration of additional compounds, emphasizing pharmaceutically relevant compounds.

Acknowledgements: We thank the Technion, the Chemical engineering department and ICS for financial support.

Poster no. P_ICN_18

Enhancing Stability and Solar Cell Efficiency of $CsPbBr_3$ Nanowire Arrays Grown on Anodized Aluminum Oxide: Insights into Light-Matter Interactions

Neena Prasad [a] and Lena Yadgarov *[b]

[a] *Department of Chemical Engineering, Ariel University, Ariel, Israel*

E-mail: neenaphy@gmail.com and lenay@ariel.ac.il

Metal halide perovskites (HPs) are being recognized as a novel category of semiconductor nanomaterials because of their fascinating properties and potential applications. Among different HPs nanostructures one-dimensional (1D) HPs possess exceptional optical properties, extended charge diffusion length, and prolonged lifetime, making them promising for various cutting-edge technologies. However, the instability of HP materials when exposed to air, moisture, polar solvents, oxygen, and heat poses a challenge, leading to phase transformation and decomposition. Additionally, the lack of a facile and effective synthetic protocol for the stable 1D nanostructure limits their commercialization, prompting significant efforts to address and overcome these limitations. To address this, we present a study on the growth of $CsPbBr_3$ nanowire (NW) arrays within anodized alumina oxide (AAO) templates using the inverse temperature crystallization (ITC) method. The AAO serves as both a growth template and stabilizing medium, facilitating the formation of physically confined vertically aligned NW arrays. The study employs theoretical Finite Difference Time Domain (FDTD) simulations to explore the near-field light-matter interaction within the periodic arrays of $CsPbBr_3$ NWs in the AAO pore, optimizing pore geometry for enhanced light-matter interaction. This allows optimization of the pore diameter inter-pore distance, geometry, etc. to achieve maximum light-matter interaction. Intriguingly, the ITC method led to the filling of nearly all pores in the AAO template with NWs, which were observed from the Scanning electron microscopic (SEM) image. Our comprehensive structural analysis using X-ray Diffraction (XRD) provided strong evidence of the successful formation of stable orthorhombic phase $CsPbBr_3$. Notably, the experimental absorption results closely aligned with the simulated absorption spectra, validating the precision of the theoretical findings. Finally, the outer exposed edges of the/HPs structure are stabilized by encapsulating the surfaces with electron and hole-transporting layers (ETL and HTL) for the optoelectronic device applications. Two-dimensional layered molybdenum sulfide (MoS_2) can serve as an ETL by facilitating efficient electron extraction from the $CsPbBr_3$ layer. MoS_2 is expected to improve charge separation, minimize recombination losses, and enhance the efficiency of the system. Hence, FDTD simulations were employed to find the efficiency of the vertical $CsPbBr_3$ NW-based solar cells, particularly when integrated with MoS_2 as an HTL, suggesting that a maximum Jsc can be achieved with 4 layers of both HTL and ETL. Overall, this study is a significant reference for future advancements in developing highly stable HP NW-based devices and the effective use of layered MoS_2 as ETL, opening doors for diverse applications in the field of photonics or renewable energy.

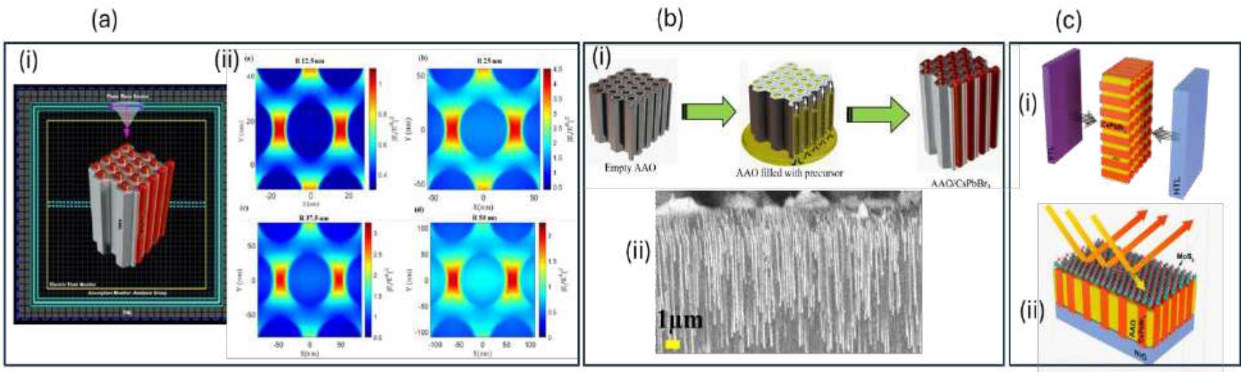


Figure 1: (a) Theoretical FDTD simulations (i) FDTD Simulation setup and layout; (ii) Simulated Electric field distribution of AAO/HPs structure with different diameters and interpore distances: (b) Experimental (i) The schematic of the ITC-assisted templated growth process of CsPbBr3 NWs in AAO membranes (ii) cross-sectional scanning electron microscopic image of AAO/HPs structure: (c) Solar cell device application (i) Design HPs/AAO photoreactor by active HTL and ETL (ii) Checking the solar generation of HPs/AAO photoreactor with NiO as HTL and MoS_2 as ETL

Poster no. P_ICN_19

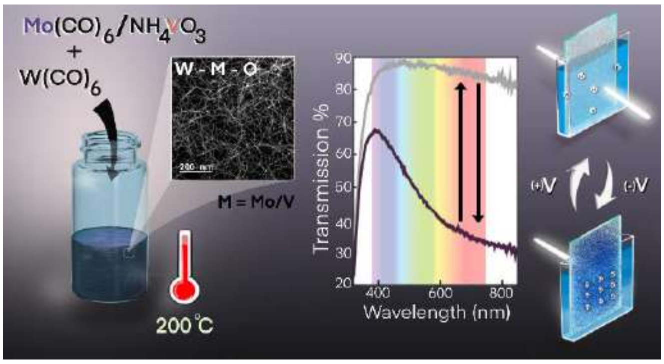
Synthesis and Electrochemical Properties of Ultrathin Alloy (Mo, V)- Tungsten Oxide Nanowires

Noa Afik,[a] Sandhiya Murugesan,[a] Karam Shreteh,[a] Helena Fridman,[a] Yara Hijaze,[a] Michael Volokh,[a] and Taleb Mokari*,[a,b]

[a] Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel. [b] Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel

E-mail: mokari@bgu.ac.il

Doped and alloyed transition metal-oxides (TMOs) attract vast attention owing to their tunable electronic properties (e.g., conductivity, band gap, optical absorption), making them appealing for many (photo)electronic, chromic, and green energy applications. Pure tungsten-oxides exhibit distinctive electrochromic (EC) properties but attain low energy density compared to other TMOs (e.g., MoO_3 and V_2O_5). The coloration efficiency and energy density can be enhanced by controlling the morphology, size, and composition of the nanoscale TMOs constituting the active EC film. Herein, we demonstrate a straightforward and facile synthesis of crystalline Mo / V alloyed tungsten-oxide ultrathin nanowires (uNWs) that does not require a further annealing process. The new properties (compared to untreated tungsten-oxide) these alloys exhibit, such as additional absorbance peaks, lead to improved specific capacitance and, in the case of W-Mo-O, better coloration efficiency.



Scheme 1: A simple synthesis is presented: mixing precursors in octadecanol and heating forms ultrathin alloy (Mo, V)-tungsten oxide nanowires. Thereafter the ultrathin nanowires are deposited on ITO, and electrochromic features are attained when applying different potentials.

Acknowledgments: We thank Dr. Natalya Froumin for assistance in XPS characterization and analysis, Dr. Vladimir Ezersky for assistance with HRTEM, and Nitzan Shauloff for graphical support. This work was supported by the Israel Science Foundation (grant No. 1507/22). NA thanks the Darom fellowship from the Kreitman School of Advanced Graduate Studies, Ben-Gurion University of the Negev.

References:

1. Afik, N.; Murugesan, S.; Shreteh, K.; Fridman, H.; Hijaze, Y.; Volokh, M.; Mokari, T., Synthesis and Electrochemical Properties of Ultrathin Alloy (Mo, V)-Tungsten Oxide Nanowires, *submitted.*
2. Moshofsky, B., & Mokari, T., Length and diameter control of ultrathin nanowires of substoichiometric tungsten oxide with insights into the growth mechanism. *Chem. Mater.* **2013**, 25, 1384-1391.

Poster no. P_ICN_20

Alloy Nanowire Arrays with Controlled Compositions Templated by Block Copolymers

Ofer Burg, Roy Shenhar*

Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Israel.

E-mail: roys@huji.ac.il

Metallic nanowire arrays are promising components for nanotechnology thanks to their directional, continuous, longitudinal structure. Nanowires made from alloys of two or more metals are beneficial for applications such as catalysis and magnetism. The alloy composition influences the properties of the nanowires, and certain metal ratios show improved properties compared to their individual constituents. Yet, creating these nanowire arrays requires enhanced control over their composition and organization. This requirement may be answered by using block copolymer films, which provide three advantages: (a) they exhibit periodic arrays with typical periodicities of a few tens of nanometers; (b) the domains could be aligned using patterned substrates; (c) impregnation of the films with metal precursors and subsequent plasma treatment affords metallic nanowires that are organized in periodic arrays.[1]

In this work, we use films of polystyrene-block-poly(2-vinylpyridine) to create arrays of alloy nanowires with controlled compositions. We achieve this control by studying how different impregnation parameters affect the amount of metal in the nanowires and the metal ratio in alloys. Namely, impregnating the film with palladium precursors, followed by platinum precursors for different durations, shows how one metal increases over the other, and the rate of metal precursor replacement in the film. Additionally, impregnating with a mixture of palladium and platinum precursors in different ratios gives different Pd-Pt alloys, and elucidates the affinity of each metal to the film. These experiments give an understanding of the interaction between the metal precursors and the pyridine groups in the polymer and lay a foundation for fabricating alloy nanowires with controlled compositions.

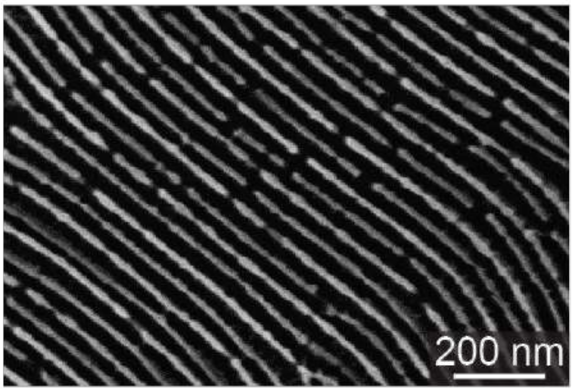


Figure 1: SEM image of a Pd-Pt alloy nanwire array

References:

1. Burg, O., Sanguramath, R. A., Michman, E., Eren, N., Popov, I., & Shenhar, R. (2021). Periodic nanowire arrays with alternating compositions and structures fabricated using a simultaneous nanowire formation step. *Soft Matter*, 17(43), 9937-9943.

Poster no. P_ICN_21

Structure-function effects of Na-K alloying in double perovskite nanocrystals

Offir Zachs [a] Yehonadav Bekenstein [a] [b]

[a] *Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 32000 Haifa, Israel.*

[b] *The Solid-state institute, Technion – Israel Institute of Technology, 32000 Haifa, Israel.*

E-mail: bekenstein@technion.ac.il

In the past few years, inorganic perovskites have gained interest for their electro-optic properties, especially lead-halide perovskites. Since lead is a toxic substance, other alternatives, including lead-free double perovskites, are currently being investigated. In order to match the properties of their lead-based counterparts, material engineering techniques are required.

Here, we are using antimony doping and Na-K alloying to allow the breaking of the forbidden symmetry transitions and promote the emissive self-trapped exciton mechanism. We show how nano-particles of $Cs_2Na_{1-x}K_xIn_{0.9}Cl_6Sb_{0.1}$ with different ratios between the Na and K concentrations, manifest in tunable photoluminescence emission and tunable stocks shift.

Furthermore, we see a higher quantum yield in some ratios than those without alloying. Our high-quality synchrotron x-ray diffractograms depict a non-monotonic peak shift signifying a phase transition upon high potassium concentration or other non-trivial competing structural changes. We hypothesize that those structural changes allow the tuning and improvement of the electro-optic properties.

In an additional experiment, we show the phase transition of $Cs_2KIn_{0.9}Cl_6Sb_{0.1}$ with temperature-dependent X-ray diffraction. We start in the cubic phase in the colloidal synthesized nano-crystals to a tetragonal phase after hitting the sample to receive a bulk-like material.

Acknowledgements:

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 949682- ERC and from the Israel Science Foundation under grant agreement No 890015.

Poster no. P_ICN_22

Light-induced MOF synthesis enabling composite photothermal materials

Ofir Shelonchik[1*], and Yossi Weizmann[1,2,3]

1Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

2Ilse Katz Institute for Nanotechnology Science, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

3Goldman Sonnenfeldt School of Sustainability and climate Change, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

E-mail: ofirshe@post.bgu.ac.il

Metal-organic frameworks (MOFs) represent a class of porous materials renowned for their large surface areas, making them a focal point of interest in the scientific community over recent decades. Despite their potential, conventional MOF syntheses often involve prolonged solvothermal processes conducted at elevated temperatures. Addressing this limitation, our study introduces an innovative approach—an accelerated light-induced synthesis of MOFs leveraging the plasmonic photothermal capabilities of bipyramidal gold nanoparticles (AuBPs).

Our methodology's versatility is evident as we successfully synthesized four distinct MOFs using three different wavelengths (520 nm, 660 nm, and 850 nm). The regulation of light exposure allowed for the strategic embedding of AuBPs within the MOF or their maintenance in the supernatant. Remarkably, the MOF with embedded AuBPs (AuBP@UIO-66) retained both its plasmonic properties and the remarkable surface area characteristic of MOFs. The photothermal AuBP@UIO-66 exhibited a pronounced light-induced heating response, a feature harnessed for ultrafast desorption and MOF activation.

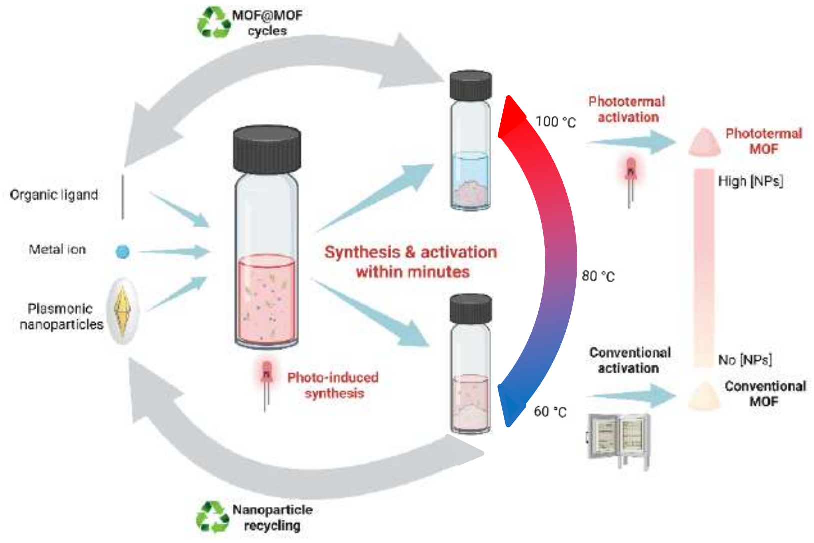


Figure 1: A scheme summarizing the photo-induced synthesis of MOFs research

References:

1. Shelonchik, O.; Lemcoff, N.; Shimoni, R.; Yehezkel, E.; Yesodi, D.; Hod, I.; Weizmann, Y., Light-induced MOF synthesis enabling composite photothermal materials. *Nat. Comm.*, **2024**, Just accepted.

Poster no. P_ICN_23

Catalysts Development for Redox Reactions

Pnina Gorodishev[1] and Tomer Zidki*[1]

[a] *Department of Chemical Sciences, Ariel University, Ariel 40700, Israel.*

E-mail: pninag@ariel.ac.il, tomerzi@ariel.ac.il

Abstract

As the demand for clean and renewable energy sources continues to rise, developing efficient and cost-effective methods for hydrogen production via water-splitting has emerged as a critical research area. Due to their unique structural and electronic properties, Prussian blue analogs (PBAs) have emerged as promising catalyst templates for driving the water-splitting reaction. This work explores the behavior of Fe-Co-PBA-based catalysts for water splitting, highlighting their exceptional catalytic activity, stability, and tunable composition. The compounds are synthesized by a quick and straightforward co-precipitation method. The potential applications of PBAs-based catalysts in different electrochemical and photoelectrochemical techniques are also examined.

Moreover, this project discusses the potential of PBAs as electrochemical catalysts, emphasizing the improvements in reaction conditions and stability of these derivatives. Overall, PBAs represent a promising avenue towards achieving efficient and environmentally friendly water splitting, paving the way toward a hydrogen-based economy. Considering previous work in this field,1 we aim to decrease the overpotential of the OER process and improve the conditions of this reaction.

References:

1. Sathiyan K., Mondal T., Mukherjee P., Patra S. G., Pitussi I., Kornweitz H., Bar-Ziv R., Zidki T. Enhancing the catalytic OER performance of MoS_2 via Fe and Co doping. *Nanoscale*, **2022**, *14*(43), 16148-16155.

Poster no. P_ICN_24

Liquid-Liquid Interface-Based Thiocyanate Surface Treatment for Bright and Stable $CsPbBr_3$ Nanocrystals

Rachel Lifer[a], *Saar Shaek*[a], *Nathan Rafisman*[a],[b], *Ivano E. Castelli*[c], *Lev Chuntonov*[b], and *Yehonadav Bekenstein**[a]

[a] Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 32000 Haifa, Israel. [b] Department of Chemistry, Technion – Israel Institute of Technology, 32000 Haifa, Israel. [c] Department of Energy Conversion and Storage (DTU Energy), Technical University of Denmark, Anker Engelunds Vej 301, 2800 Kongens Lyngby, Denmark.

E-mail: bekenstein@technion.ac.il

Abstract: Enhancing the efficiency and stability of lead halide perovskite devices is crucial for their practical application. Previous treatments with thiocyanate (SCN-) have demonstrated significant improvements in the photoluminescence quantum yield (PLQY) and stability of $CsPbBr_3$ nanocrystals (NCs), but the underlying mechanisms remain partially unresolved. Addressing the challenge of low SCN- solubility in traditional nonpolar solvents, our study introduces a novel urea-ammonium thiocyanate (UAT)-based ionic liquid surface treatment. This method facilitates a higher SCN-loading by creating a liquid-liquid interface that is compatible with the organic colloidal suspension, preventing NC degradation and achieving near-unity PLQY. Utilizing electron energy loss spectroscopy (EELS) mapping, we present high-resolution evidence of thiocyanate binding to NC surfaces, affirming the presence of thiocyanate and demonstrating that this modification enhances stability against ionic substitution while maintaining the perovskite structure intact. Our findings provide conclusive evidence that the primary mechanism of performance enhancement is the passivation of surface traps attributed to bromide vacancies rather than A site cationic doping. This novel surface treatment method slows ion migration, offering a significant advancement in the development of perovskite-based solar cells.

Acknowledgments: This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement **No 949682-ERC-HeteroPlates.** Special thanks to the scientific staff of our microscopy center (MIKA), and, specifically, Dr. Maria Koifman for discussing the 2D-GI-WAXS analysis. IC YB and SS thanks the EuroTech alliance program for their kind support. YB thanks the Nancy and Stephen Grand Technion Energy Program for their generous support and support of the Technion Russel Berrie Nanotechnology Institute, and of the Technion Helen Diller quantum center.

Poster no. P_ICN_25

Atomic Layer Depostion within Polymers Templates for Doped Materials

R. Azoulay,[a] T. Segal Peretz *[a]

a Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa, Israel

E-mail: azorotem@campus.technion.ac.il, tamarps@technion.ac.il

Today's nanofabrication techniques require multistep and costly processes in order to fabricate complex, multi-materials nanostructures. Performing atomic layer deposition (ALD) within polymeric templates can offer a simple solution for nanostructure fabrication. In this process, named sequential infiltration synthesis (SIS), high partial pressures and long exposures times lead to inorganic materials growth within polymers. Sequential polymer removal results in inorganic materials. While SIS shows great potential in fabricating a large variety of structures, it is currently limited to a single material growth process.

In our research, we utilized SIS properties to achieve doped materials. For the first time, we demonstrated simultaneous growth using a multi-material SIS process with control over the percentages of the dopant.

We studied SIS within polymer films and developed multi-material SIS, where two metal oxides are grown together in a single process, with precise control over their ratios. We used epoxidized isoprene films as the polymeric template and DEZ (diethyl zinc), TMA (trimethyl aluminum) as the organometallic precursors to fabricate Al-doped ZnO films. We performed structural characterization using scanning and transmission electron microscopy (SEM and TEM, respectively) to characterize the films and energy-dispersive X-ray spectroscopy (EDS) TEM to quantify each element and evaluate the doping percentage. This research opens new pathways for multi-materials nano scale structure fabrication through ALD-based growth within polymers.

Poster no. P_ICN_26

Synergetic Effects of Non-thermal Plasma for Catalytic NH_3 Synthesis

Rutvija Dange, [a] Kaifeng Zheng, Prof. Anatoly Frenkel
and Charlotte Vogt*[b]

[a, b] *Schulich Faculty of Chemistry, Technion–Israel Institute of Technology, Haifa 3200003, Israel*

E-mail: c.vogt@technion.ac.il

Plasma catalysis is seen as a potential alternative to the energy-intensive Haber-Bosch (HB) process for sustainable NH3 synthesis.[1] Plasmas are ionized gases that can be generated by applying a large electrical potential between two electrodes, shielded by a dielectric material, thereby generating chemically active species using relatively low energy inputs. The focus of our research is to study the synergy between plasma and catalyst materials. That is, plasma could affect the geometry of nanoparticles (NPs), as well as other physical and chemical properties of supports, and, finally, micro discharges, simply described as the localized formation of plasma, can occur as a function of the catalyst material properties.[2] These effects, in turn, can greatly influence the mechanistic pathway of plasma catalytic NH_3 synthesis.

To understand the influence of plasma on NP geometry, we aim to generate an experimental library of X-ray absorption spectra to deconvolute different shapes of NPs using a neural network approach. In the first step, we synthesized NPs with distinct shapes and deposited them on different supports. For the neural network approach, we collaborate with Prof. Dr. Anatoly Frenkel at Stonybrook University in the USA and have travelled to the synchrotron facilities at Brookhaven light source to perform XAS.[3]

After initial data analysis, we observed differences in the XAS spectra of synthesized NPs in suspension form vs deposited NPs, further study on geometry is still under process. In the future, we plan to perform operando XAS spectroscopy and compare the results with the generated library to better understand the geometry changes. For these operando plasma XAS studies, we will modify our operando plasma-catalytic DRIFTS reactor by introducing a path for X-rays near the sample holder. This approach is expected to enhance understanding of the relationship between NP shape and catalytic performance.

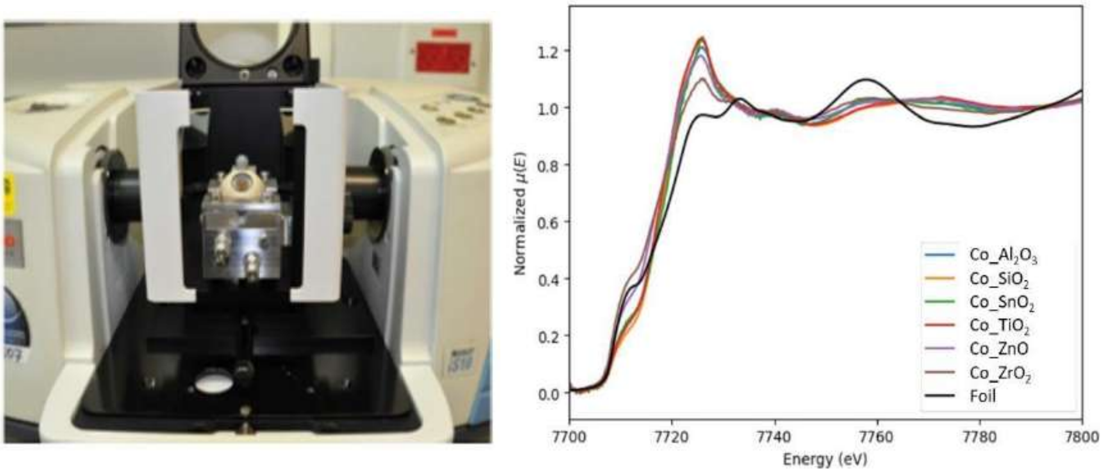


Fig. 1. Home-built operando plasma-catalytic DRIFTS cell setup and Initial results obtained by XAS of reduced colloidally prepared Co NPs deposited on different supports.

Acknowledgments: The authors thank the Technion - Israel Institute of Technology for financial support, and Dr. Anatoly Frenkel for the initial study of XAS for the training set development of geometric effect.

References:

1. Gorbanev, Y. *et al.* Al2O3-Supported Transition Metals for Plasma-catalytic NH3 Synthesis in a DBD Plasma: Metal Activity and Insights into Mechanisms. *Catalysts* **11**, (2021).
2. Van't Veer, K., Engelmann, Y., Reniers, F. & Bogaerts, A. Plasma-Catalytic Ammonia Synthesis in a DBD Plasma: Role of Micro discharges and Their Afterglows. *Journal of Physical Chemistry C* **124**, 22871–22883 (2020).
3. Frenkel Anatoly, T. J. System and Method for Structural Characterization of Materials by Supervised Machine Learning-based Analysis of their Spectra. 1–31 (2021).

Poster no. P_ICN_27

Utilized treated oil shale ashes as alternatives for cement and fine aggregates in the concrete industry

Sarit Nov[1], Shay Barak [2], Haim Cohen[1,3] and Yaniv Knop[4]

[1]*Department of Chemical Sciences, Ariel University, Ariel 40700, Israel*

[2]*Department of Chemical Engineering, Ariel University, Ariel, 40700 Israel*

[3]*Department of Chemistry, Ben Gurion University of the Negev University, Beer Sheva 84105, Israel*

[4]*Department of Civil Engineering, Ariel University, Ariel, 40700 Israel*

E-mail: saritno@ariel.ac.il, shay.bruks@cemex.com, hcohen@ariel.ac.il, yanivkn@ariel.ac.il

Abstract

The growing global demand for energy and concerns about the environmental impact of fossil fuels underscore the necessity for alternative approaches. The combustion of fossil fuels, particularly coal and oil shale, not only contributes to greenhouse gas emissions but also results in substantial ash residues, presenting environmental challenges.

This research specifically explores the potential of thermal treatment to refine oil shale bottom ash (OSBA) for its application as a substitute for cement in concrete. This addresses the economic viability of oil shale combustion and the environmental issues associated with ash waste management. The study's outcomes significantly impact the economic and environmental sustainability of utilizing oil shale combustion in construction.

By improving the properties of OSBA, this investigation makes a noteworthy contribution to advancing greener energy solutions and more efficient waste management practices in both the energy and construction sectors.

References:

Nov, S., Barak, S., Cohen, H., & Knop, Y. Treated Oil Shale Ashes as Cement and Fine Aggregates Substitutes for the Concrete Industry. *ACS Omega*, **2023**, *8*(49), 46608–46613.

Poster no. P_ICN_28

Tuning Collective Exciton Interactions in Halide Perovskite Nanocrystal Superlattices

Shai Levy[a,b], Orr Be'er[a,b], Saar Shaek[a,b], Alexey Gorlach[b], Einav Scharf[c], Yonatan Ossia[c], Rotem Strassberg[a,b], Ido Kaminer[b], Uri Banin[c], and Yehonadav Bekenstein*[a,b]

[a] *Department of Materials Science and Engineering, Technion-Israel Institute of Technology, 32000 Haifa, Israel.*

[b] *The Solid-State Institute, Technion – Israel Institute of Technology, 32000 Haifa, Israel.*

[c] *Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, 91904, Jerusalem, Israel.*

E-mail: bekenstein@technion.ac.il

Ordered halide perovskite nanocrystal superlattices exhibit collective emission, due to dipole-dipole interactions between several simultaneously excited emitters. This coupling, enabled below a critical temperature of 180-200K, changes both the transition energy and emission rate compared with individual emission of uncoupled nanocrystals. Collective emission behavior as a result of dipole-dipole interactions between emitters, is a well-known phenomenon communly found in clusters of organic molecules, known as H/J-aggregates. In these organic systems, the excitons are highly localized Frenkel excitons, positioned mainly between the electron donating and electron withdrawing groups. As a result, the type of interactions between emitters is mainly dictated by the relative orientation of molecules in the cluster. However, in halide perovskite semiconductor nanocrystals the excitons are Wainer-Mott excitons, which are free to move within the volume of the nanocrystal. This opens the possibility for changing the coupling without influencing nanocrystal packing in the superlattice. We demonstrate here how quantum confinement governs the type of coupling through synthetical control over nanocrystal size, and by compositional control over the Bohr radius via anion exchange. The confinement modifies the preferred alignment of transition dipoles in the nanocrystals, shown by angular-dependent emission patterns, changing the relative dipole orientation between adjacent nanocrystals, and the resulting optical behavior of the ensemble. In superlattices made of weakly confined nanocrystals, the collective emission is red-shifted with faster emission rate, showing characteristics of superfluorescence. In contrast, the collective emission of superlattices made of strongly quantum-confined nanocrystals is blue-shifted with a slower emission rate. This demonstrated tunability of collective light emission from perovskite nanocrystals is especially important for future implementation of these nanomaterials in optoelectronic applications utilizing the collective properties of the nanocrystal ensemble.

Acknowledgements: We gratefully thank Dr. Yaron Kauffmann, and Dr. Maria Koifman-Khristosov for their help in TEM and SEM-EDS characterization, and to Dr. Inna Popov, and Dr. Ilya Torchinsky for their help in CL measurements. This project is supported by the European Union's Horizon 2020 research and innovation program under grant agreement No 949682- ERC.

References:

1. Rainò, Gabriele, et al. "Superfluorescence from lead halide perovskite quantum dot superlattices." Nature 563.7733 (**2018**): 671-675.
2. Levy, Shai, et al. "Tuning the Colloidal Softness of $CsPbBr_3$ Nanocrystals for Homogeneous Superlattices." Nano Letters 23.15 (**2023**): 7129-7134.
3. Masson, Stuart J., and Ana Asenjo-Garcia. "Universality of Dicke superradiance in arrays of quantum emitters." Nature Communications 13.1 (**2022**): 2285.

Poster no. P_ICN_29

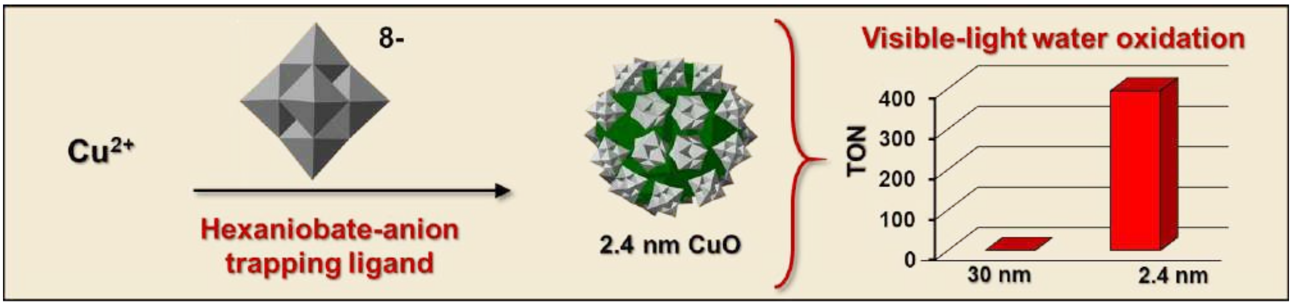
Sensitizer-Free Visible-Light Water Oxidation Upon Hexaniobate-Ligand Entrapment of Quantum-Confined Copper-Oxide Cores

Shubasis Roy, [a] and Ira A. Weinstock*[a]

[a]Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel.

E-mail: iraw@bgu.ac.il

Among non-toxic, earth-abundant transition-metal oxides, hematite, α-Fe_2O_3, is unique in its ability to serve as a stable catalyst for visible-light driven water oxidation with no added dopants or photosensitizers. In this context, an intriguing question is whether quantum confinement that emerges upon decrease in size to within a few multiples of Bohr-exciton radii might provide other earth-abundant metal oxides with a similar ability to catalyze visible-light driven water oxidation. We now show that entrapment of 2.4 nm monoclinic CuO nanocrystals (NC) by hexaniobate, $[Nb_6O_{19}]^{8-}$, cluster-anion protecting ligands imparts the resultant water-soluble macro-anion like complexes with an unprecedented ability to catalyze visible-light water oxidation with no added photosensitizers or applied potentials, at rates comparable to those of hematite. More generally The findings point to polyoxoniobate ligand entrapment as a potentially general method for harnessing the size dependent properties of small semiconductor NCs by utilizing them as the cores of versatile, entirely inorganic complexes.



Scheme: Sensitizer-free visible-light water oxidation by CuO was acheived by using water-soluble hexaniobate cluster-anions to entrap quantum-confined nanocrystals of this familiar earth-abundant metal oxide.

Acknowledgements: Kreitman School of Advanced Graduate Studies of the Ben-Gurion University of the Negev for the doctoral fellowship.

References:

1. Tiwari, C. K.; Roy, S.; Tubul-Sterin, T.; Baranov, M.; Leffler, N.; Li, M.; Yin, P.; Neyman, A.; Weinstock, I. A. "Emergence of Visible-Light Water Oxidation Upon Hexaniobate-Ligand Entrapment of Quantum Confined Copper-Oxide Cores", Angew. Chem. Int. Ed., **2023**, *62*, e202213762.

2 Raula, M.; Gan Or, G.; Saganovich, M.; Zeiri, O.; Wang, Y.; Chierotti, M. R.; Gobetto, R.; Weinstock, I. A. "Polyoxometalate complexes of anatase-TiO_2 cores in water", Angew. Chem. Int. Ed., **2015**, *54*, 12416-12421.

3. Zhang, G.; Baranov, M.; Wang, F.; Poblet, J. M.; Kozuch, S.; Leffler, N.; Shames, A. I.; Clemente-Juan, J. M.; Neyman, A.; Weinstock, I. A. "Soluble Complexes of Cobalt Oxide Fragments Bring the Unique CO_2 Photoreduction Activity of a Bulk Material into the Flexible Domain of Molecular Science", J. Am. Chem. Soc., **2021**, *143*, 20769-20778.

4. Chakraborty, B.; Gan-Or, G.; Duan, Y.; Raula, M.; Weinstock, I. A. "Visible-Light-Driven Water Oxidation With a Polyoxometalate-Complexed Hematite Core of 275 Iron Atoms", Angew. Chem. Int. Ed., **2019**, *58*, 6584-6589.

Poster no. P_ICN_30

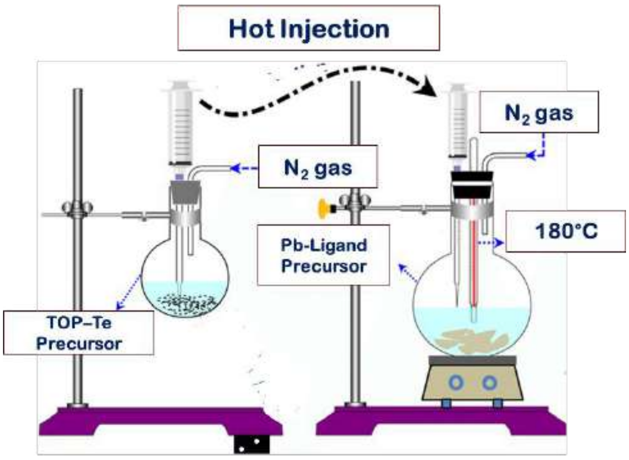
PbTe QDs Shape and Size Control by Ligand Length

Svetlana Lyssenko [a,b], Alina Sermiagin[b], Michal Amar[b], Refael Minnes[b]*

a Department of Chemical Sciences, Ariel University, Israel
b Department of Physical Sciences, Ariel University, Israel
E-mail: (refaelm@ariel.ac.il)

Pb-chalcogenide quantum dots (QDs) (PbS, PbSe, and PbTe) are known for their ability to exhibit a quantum confinement effect. For this reason, they demonstrate significant promise in various applications: telecommunications, photoelectrics, thermoelectrics, as well as photovoltaics. The size and morphology of Pb-chalcogenide QDs can be tuned by the capping ligand and its concentration. In this work, we report the size-controlled hot-injection synthesis of cubooctahedral 10-16 nm PbTe QDs using a combination of oleic acid (OA) with shorter carboxylic acids (octanoic (OctA), decanoic (DA) and lauric acids (LA)).

In this research, we found out that different volumetric ratios between the acids lead to various morphologies. The volumetric ratios of OA to the short ligands were 5.5:0.5, 5:1, 4.5:1.5, 4:2, and 3:3. We found out that at low concentrations of the short ligand, a cubical morphology was achieved. However, with the increase in short ligand concentration, a shape transformation from cubical to cubooctahedral takes place. It was shown that the transformation occurs by destroying the crystallinity of the nanocrystals (NCs). Additionally, a higher volumetric ratio of the short ligand in the synthesis results in PbTe NCs with a crystallite core and an amorphous shell. Our main observations for the mixed capping ligand hot-injection method are the tunability and precise control we achieved over the PbTe QDs. The shorter the capping ligand, the more monodispersed the PbTe QDs are. Moreover, the OctA ligand leads to big cubooctahedral PbTe QDs up to 16 nm. On the other hand, the closer the similarity in length between the mixed capping ligands, the more unstable and untenable the synthesis.



Scheme 1: A schematic representation of the hot-injection synthetic method.

Acknowledgments: SL thanks to Ariel University for PhD scholarship.

Poster no. P_ICN_31

Surface-Guided Growth of Bi2Se3 Nanowires

Tamir Forsht,*[a] Noga Levinson,[a] Lothar Houben,[b] Katya Rechav,[b] Olga Brontvein,[b] and Ernesto Joselevich*[a]

[a] Department of Molecular Chemistry and Materials Scinece, Weizmann Institute of Science. [b] Chemical Research Support, Weizmann Institute of Science.

E-mail: tamir.forsht@weizmann.ac.il

Ernesto.joselevich@weizmann.ac.il

Topological materials exhibit exotic electronic properties, which make them promising for non-conventional electronics and spintronics. For instance, integrating nanowires of topological insulators into devices could be used for dissipationless electronics, quantum switches, generating and braiding Majorana fermions and quantum computing. However, the assembly of nanowires with controlled orientation on surface remains one challenge preventing their integration into practical devices. A possible solution that was demonstrated in our group in the past few years is the guided growth of horizontal nanowires by epitaxy or graphoepitaxy on crystal surfaces.

In this work, we demonstrate the guided growth of Bi_2Se_3 nanowires on flat and faceted sapphire surfaces. Bi_2Se_3 is a layered material with weak VdW interaction between its layers. It is also a topological insulator with narrow band gap in the bulk and topologically protected conducting states on its surface, as well as a thermoelectric material. The growth direction of these nanowires and their crystallographic orientation are controlled by the relations with the sapphire substrate, allowing the growth of ordered nanowires without the need for post-growth processes. To the best of our knowledge, this is the first example of guided growth of nanowires made of layered materials, which demonstrates the generality of the guided growth approach.

Poster no. P_ICN_32

Cryogenic X-Ray Photoelectron Spectroscopy for Study Kinetics of the CaF_2 Nanocrystal Evolution

Reut Mashiach,[a] Dana Cohen,[a] Amnon Bar-Shir,[a] and Tatyana Bendikov*[b]

Departments of [a]Molecular Chemistry and Materials Science and [b]Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel

E-mail: (tatyana.bendikov@weizmann.ac.il)

Fluoride inorganic nanocrystals (NCs), in particular CaF_2, have drawn increasing attention in the last few years due to their unique chemical and physical properties.[1-3] CaF_2 colloids are widely used in the industry, medicine and for scientific purposes. Therefore, understanding their characteristics and growth evolution during synthesis is of great importance for the rationalization of the desired properties.

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique (top 10-15 nm) with sensitivity down to single atomic layer. XPS provides unique information about elemental composition and on the chemical and electronic state of the element in the material and is widely used for study of the variety of substances, their surfaces and interfaces.

For some research goals, it is essential that not only the composition, but also the morphology and native fabrication environment of the sample be preserved during the measurements. This is particularly important in the studies of biological objects and natural products and for evaluating the kinetics of chemical reactions. High vacuum requirements (pressure ~ $1 \cdot 10^{-9}$ - $1 \cdot 10^{-10}$ torr) make practically impossible analysis of this kind of samples by XPS. However, if the morphology and/or synthetic conditions of the sample are preserved by freezing, and the sample can be kept frozen during the measurements, it becomes similar to the nonvolatile solid samples and can be easily analyzed by XPS. The sample (liquid or highly volatile solid) is freezing during the loading, using the fast freezing procedure[4-5] (**Figure 1**) and remains frozen up to its removal from the XPS instrument.

In this work we use Fast Freezing Cryo-XPS to evaluate kinetics of the CaF_2 NCs growth in the presence of the 2-ammonium ethyl phosphate (AEP) ligand. By analyzing frozen reaction solutions at different reaction times we follow the NCs growth process showing the crucial role of the synthetic conditions in the evolution of the AEP-CaF_2 nanocrystals in aqueous solutions.

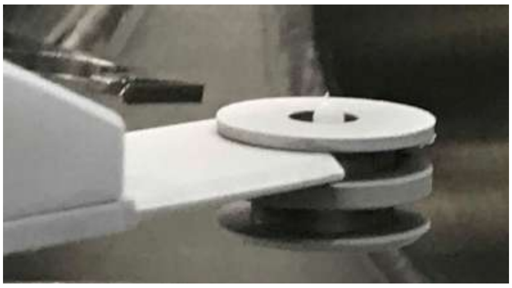


Figure 1: Frozen liquid sample in the loading compartment of the XPS instrument.

References:

1. Mashiach R. et al., *Nat. Commun.,* **2021**, *12*, 229.
2. Cohen D. et al., *ACS Nano,* **2021**, *15*, 7563-7574.
3. Galisova A. et al., *Chem. Commun.,* **2023**, *59*, 5502-5513.
4. Burger K. et al., *Inorg. Nucl. Chem. Lett.,* **1974**, *10*, 171-177.
5. Schukarev A., *Surf. Interf. Anal.*, **2006**, *38*, 682-685.

Poster no. P_ICN_33

Mechanism of WS_2 nanotube formation revealed by in situ/ex situ imaging

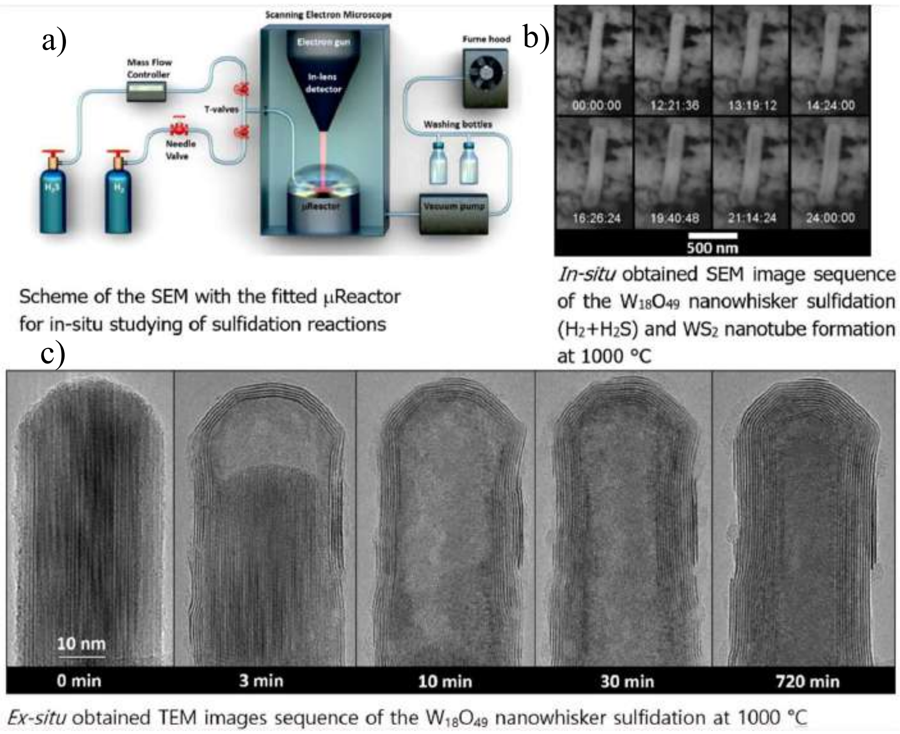
Vojtech Kundrat,*[a,b] Libor Novak, [b] Kristyna Bukisova, [b] and Reshef Tenne*[a]

[a] *Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot, Israel.* [b] *Thermo Fisher Scientific , Brno, Czech Republic.*

E-mail: vojtech.kundrat@weizmann.ac.il reshef.tenne@weizmann.ac.il

Metal dichalcogenide nanotubes, and in particular those made of WS_2, are known for over 30 years and have been investigated extensively. Synthesis of macroscopic amounts of such nanotubes has been demonstrated in past.[1] The tungsten suboxide $W_{18}O_{49}$ nanowhiskers are converted to WS_2 nanotubes by high-temperature reaction in the stream of a gaseous mixture of H_2S and H_2.

Scanning and transmission electron microscopy (SEM and TEM) play a crucial role in the structural characterization of nanomaterials. Various tools related to electron microscopy are available and under development for a deep understanding of reactions and nanostructures. The μReactor[2] technology allows in-situ observation of high-temperature heterogeneous reactions within a scanning electron microscope in a low-pressure atmosphere (up to 500 Pa). For the current work, the expedient SEM with a fitted μReactor was further developed for in-situ observation of sulfidation reactions. The coupling of in situ sulfidation in SEM and sequential ex situ TEM, both on the Micro Electromechanical System (MEMS) chip[2], revealed the mechanism of the WS_2 nanotube formation. Subsequent to the presentation of the modified μReactor and the experimental results, the growth mechanism of the nanotubes is discussed in light of the new growth environment.



Scheme of the SEM with the fitted μReactor for in-situ studying of sulfidation reactions

In-situ obtained SEM image sequence of the $W_{18}O_{49}$ nanowhisker sulfidation (H_2+H_2S) and WS_2 nanotube formation at 1000 °C

Ex-situ obtained TEM images sequence of the $W_{18}O_{49}$ nanowhisker sulfidation at 1000 °C

Figure 1: a) Scheme of μReactor SEM dedicated to sulfidation reactions b) sequence of *in situ* obtained images showing WS_2 nanotube formation upon sulfidation of $W_{18}O_{49}$ nanowhisker c) *ex situ* TEM obtained sequential analysis of WS_2 nanotube formation progression at selected times oft he reaction observed on the selected nascent nanotube

References:

1. Tenne, R., Margulis, L., Genut, M. *et al.* Polyhedral and cylindrical structures of tungsten disulphide. *Nature* **360**, 444–446 (1992). DOI: 10.1038/360444a0
2. Kundrat, V. *et al.* $W_{18}O_{49}$ Nanowhiskers Decorating SiO_2 Nanofibers: Lessons from In Situ SEM/TEM Growth to Large Scale

Poster no. P_ICN_34

Epitaxial MoS_2 Nanofins and Nanoribbons for Fast Photodetectors

Yarden Danieli[a], Lothar Houben[b], Katia Rechav[b] and Ernesto Joselevich*[a]

[a]Department of molecular chemistry and material science, [b]Chemical research support, Weizmann Institute of Science, Rehovot, Israe

* E-mail: ernesto.joselevich@weizmann.ac.il

2D materials are a versatile platform for optoelectronics, memory and energy-harvesting devices owing to their high-carrier mobility and strong light-matter interaction. Scientific efforts were invested during the last decade to tailor the physical properties of these materials by gaining control over their dimensionality. The synthesis of new structures with mixed dimensionalities, such as nanoribbons or nanofins, with controlled orientations, can give rise to a change of physical behavior and has many potential applications in electronics and optoelectronics. However, efficient synthetic methods for the bottom-up creation of aligned single-crystal nanoribbons and nanofins are still lacking.

Our group gained substantial knowledge regarding the aligned growth of 1D nanowires of different semiconductors, guided by different crystalline substrates, as part of the general guided-growth approach. This work aims to implement the guided growth approach to induce 1D growth of MoS_2 nanofins-nanoribbons with controlled direction and orientation. This unique hybrid structure is synthesized in a CVD system using epitaxy on C-plane sapphire and discussed in terms of crystal structure and morphology. Optical properties such as photoluminescence and Raman spectroscopy are also presented. The MoS_2 nanoribbons-nanofins were integrated into arrays of visible-light photodetectors and are showing high responsivity and short response times with respect to previously reported MoS_2-based photodetectors. Such growth of nanofins-nanoribbons can be generalized to other 2D materials, suggesting new structures that enable various device architectures with improved performance.

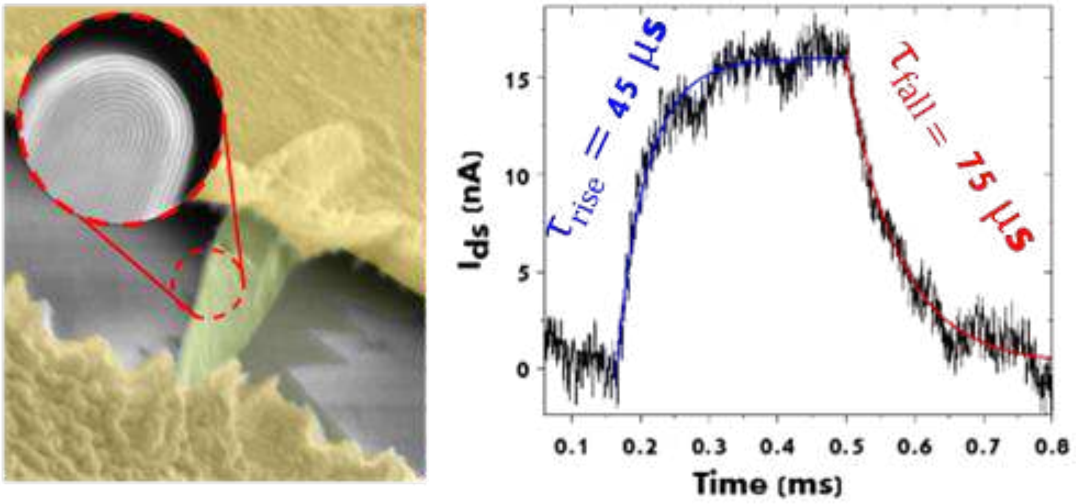


Figure 1: Left - False color SEM image of a MoS_2 nanofin-nanoribbon hybrid bridging source-drain electrodes in a photodetector. Zoom in picture is a cross-section TEM image of the nanofin. Right – A single on-off cycle of 450 nm light modulation of the device, exhibiting response times an the scale of 10^{-5} seconds.

Poster no. P_ICN_35

High-concentration aqueous colloids of metal and metal oxide nanoparticles free of steric stabilizers: preparation and characterization

Yuri Mikhlin,*[a] Denis Karpov,[b],[c] Sergey Vorobyev,[b] Yulia Antipova,[c] Sergey Zharkov,[c] Svetlana Saikova[b],[c]

[a] Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel; [b] Institute of Chemistry and Chemical Technology, Krasnoyarsk Science Center of the Siberian Branch of the Russian Academy of Sciences, Krasnoyarsk 660036, Russia; [c] Siberian Federal University, Krasnoyarsk 660041, Russia

E-mail: yumikh13@gmail.com, yury.mikhlin@biu.ac.il

"Wet" chemical synthesis is one of the main methods for preparation of nanomaterials, including colloid solutions as either intermediate or target products (e.g., nanofluids, inks). Colloids are usually considered as metastable systems with the particles stabilized by organic surfactants, interacting via the interplay of electrostatic repulsion and van der Waals forces, which are described by the DLVO theory. The typical aqueous colloids contain solid in the range of 0.1-10 g/L. Much more concentrated, up to several kg/L (55 vol.%) dispersions required for 2D/3D/4D printing, ceramics, soft robots, and prospective materials and technologies, are prepared with massive adding of organic stabilizers. Meanwhile, "bare" hydrophilic surfaces of nanoparticles are required in printed electronics, steric biomedical applications, sorbents, catalysts, sensors, and so on. There are known, and commercially available, in fact, just few high-concentration hydrosols without steric stabilizers: silica, alumina, titania, and magnetite/maghemite. Surprisingly, they have received very little attention up to now, and their application is hindered by the narrow choice and high price, poor understanding of their basic characteristics, such as the inner structure and colloidal stability mechanisms (probably beyond the DLVO), rheological, and other properties, and by scarce opportunities for their manufacturing and tailoring.

Recently, we developed simple preparation routes to electrostatically stabilized, repulsive colloids based on citrate-capped nanoparticles of very high, on the order of 1 kg/L and more, concentrations. As examples, we report here on the synthesis of hydrosols of spherical nanoparticles about 10 nm in diameter of metallic Ag and magnetite/maghemite Fe_3O_4, and CuO nanorods. Uniform Ag NPs were obtained using a modified Carey Lea method [1] via aqueous Ag^+ reduction with Fe^{2+} ions in the presence of citrate anions followed by several coagulation – filtration – water peptization cycles using sodium citrate as a coagulant and a minimal volume of water at the final stage [2]. The metal oxides were precipitated in alkaline media at 70-90 °C, and repeatedly washed with water, NaOH solutions and again water for purification and rendering the particle surfaces hydrophilic. Lower viscosity and colloidal stability of the dispersions having the superior concentrations can be achieved thanking to the removal of residual electrolyte by using ion-exchange resins and minimal quantities of citrate anions just necessary for the monolayer formation. Excessive water was eliminated by evaporation. The characteristics of the aqueous dispersions (viscosity, magnetic properties, conductivity and zeta potentials (after dilution)), and of the nanoparticles after drying were determined and analyzed. Particularly, SAXS measurements suggest that the fluids with the concentration above ~200 g/L are repulsive and possibly have an ordered, solid-like disposition of colloid particles, impeding the mobility and inducing the high sol viscosity that, however, can be reduced via tuning the colloid composition.

References:

1. Carey Lea, M. On Allotropic Forms of Silver. *Am. J. Sci*. **1889**, *37*, 476–491.
2. Vorobyev, S. A.; Likhatski, M. N.; Romanchenko, A. S.; Fetisova, O. Y.; Kazachenko, A. S.; Volochaev, M. N.; Mikhlin, Y. L. Fabrication of extremely concentrated silver hydrosols without additional stabilizers. *ACS Sustainable Chem. Eng*. **2020**, *8*, 17225–33.
3. Massart, R.; Dubois, E.; Cabuil, V.; Hasmonay, E. Preparation and properties of monodisperse magnetic fluids. *J. Magn. Magn. Mater*. **1995**, *149*, 1–5.
4. Vaseem, M.; Hong, A.-R.; Kim, R.-T.; Hahn, Y.-B. Copper oxide quantum dot ink for inkjet-driven digitally controlled high mobility field effect transistors. *J. Mater. Chem. C* **2013**, *1,* 2112–20.

Poster no. P_ICN_36

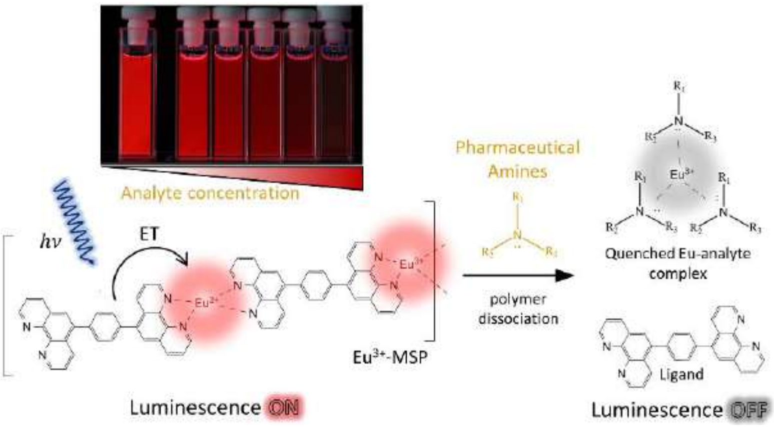
Stimuli-response of Eu^{3+} based metallo-supramolecular polymers towards pharmaceutical amines

Yuval Ben-Shahar*[a], Tamar Shamai Yamin[b], Sharon Marx[a], Naama Karton-Lifshin[c], Daniele Marciano*[c]

[a] Department of Physical Chemistry, Israel Institute for Biological Research, P.O. Box 19, Ness-Ziona 74100, Israel. [b] Department of Analytical Chemistry, Israel Institute for Biological Research, P.O. Box 19, Ness Ziona 741000, Israel. [c] Department of Organic Chemistry, Israel Institute for Biological Research, P.O. Box 19, Ness-Ziona 74100, Israel

E-mail: yuvalb@iibr.gov.il, Daniele.marciano@gmail.com

Metallo-supramolecular polymers offer a highly controllable platform for sensing. Their modular characteristics obtained by the ability of varying both building blocks, the metal ion and the organic ligand, provide tunability of their optical and chemical properties. Specifically, polymers based on lanthanide ions and conjugated aromatic ligands exhibit enhanced luminescence properties that can be altered by external stimulation. Herein, using europium-based polymer, we demonstrate the ability to detect different pharmaceutical amines such as illicit drugs and opioids, including in complex biological media, based on their luminescence quenching efficiency as a result of their polymer dissociation capacity. A combination of absorption, luminescence and NMR measurements reveals combined static and dynamic quenching mechanisms that enable selective sensing of strong basic amines with high pKa values.



Scheme 1: Schematic presentation of Eu-MSP quenching in the presence of amine analyte leading to polymer dissociation along with digital image of emitting pristine Eu-MSP solution (first from the left) and quenched Eu-MSP solution following 1-5 equivalent cocaine additions.

References:

1. Ben-Shahar Y., Shamai Yamin T., Marx S., Karton-Lifshin N., and Marciano D., Stimuli-response of Eu^{3+} based metallo-supramolecular polymers towards pharmaceutical amines, ACS Sens. **2023** 8 (4), 1481-1488.

Organic and Organometallic Chemistry

Poster no. P_OOC_01

Poly(lactic acid): New Architectures via Catalyst Design

Adi Urieli, Rami Hador, Sophia Lipstman, Moshe Kol*

School of Chemistry, Faculty of Exact Sciences , Tel Aviv University 6997801, Israel

Email: adiurieli@mail.tau.ac.il

Traditional plastics, while versatile and integral to various industries, pose environmental challenges due to their slow degradation and dependence on petroleum feedstock. PLA, derived from renewable resources and exhibiting biodegradability, emerges as a promising alternative. In this work, we describe a polymerization catalyst relying on a new zirconium complex of an amine tris(phenolate) ligand that combines several attractive properties, including: high activity, living character, and a pronounced tendency to consume *meso*-lactide in *meso*-lactide/L-lactide mixtures. Taking advantage of the living character of the catalyst, we prepared precise stereoblock copolymers of various microstructures by sequential monomer addition. Building on the stereoselectivity of this catalyst, we were able to prepare stereogradient copolymers from lactide stereoisomer mixtures, which were almost as precise. These stereogradient copolymers exhibited similar crystallinity as the stereoblock copolymers. Finally, we investigated the possibility of forming stereocomplexed PLA from enantiomeric pairs of stereogradient copolymers. We found that such stereocomplexes were indeed formed, and featured high crystallinities expressed in elevated melting temperatures, offering potential benefits over traditional PLA.

Poster no. P_OOC_02

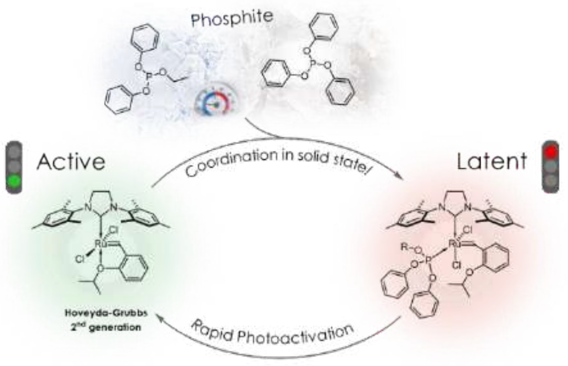
Latency for all: Enabling Latency of Hoveyda-Grubbs Second Generation Catalysts by Adding Phosphite Ligands (How to put Hoveyda to sleep with phosphites)

Anna Vaisman, [a] Yuval Vidavsky, [b] Mark Baranov, [a] Avi Lehrer, [a] Joshua H. Baraban[a] and N. Gabriel Lemcoff*[a]

[a] Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel. [b] Space Environment Department, Soreq NRC, Yavne 81800, Israel.

E-mail: (annava@post.bgu.ac.il, lemcoff@bgu.ac.il)

The Hoveyda-Grubbs® second generation catalyst (**HG2**, M720 Umicore) is one of the most commonly used catalysts for olefin metathesis, both because of its wide scope of substrates and its intrinsic stability. Given the usefulness of **HG2** and the great interest in developing latent olefin metathesis catalysts for numerous applications, we developed a method to introduce phosphite molecules as ancillary ligands to the precatalyst framework. This procedure inhibits the activity of the complex by displacing the oxygen chelating moiety with a phosphite ligand, changing the geometry from the active *trans*-dichloro form to a latent *cis*-dichloro species. Remarkably, stable coordination of the phosphite ligands to **HG2** occurs favorably only in solidified solutions (most likely due to entropic factors)[1] (Scheme 1). This very unusual synthesis afforded two latent complexes that can be manipulated and activated on demand by either heat or light stimuli. Thus, integrating phosphites with **HG2** opens the door to a new family of latent catalysts to be used in olefin metathesis applications that require latency. Of particular interest is the use of these latent catalysts in ring-opening metathesis polymerization (ROMP) reactions and 3D printing methods. Indeed, the novel complexes displayed the required latency towards ROMP monomers, even the most reactive dicyclopentadiene. Irradiation with 405 nm light readily results in the expeditious formation of the desired polymers. This novel approach provides a general and straightforward way to access efficient and well-defined latent olefin metathesis catalysts.



Scheme 1: synthesis and photoactivation of Hoveyda-Phosphite complexes.

References:

(1) Dragoe, N., Entropy Driven Synthesis of New Materials. *Materials Lab* **2022**, 1, 220001.
(2) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H., Efficient and Recyclable Monomeric and Dendritic Ru-Based Metathesis Catalysts. *J. Am. Chem. Soc.* **2000**, 122, 8168–8179.
for Olefin Metathesis. *ACS Catal.* **2018**, 8, 6413-6418.
(3) Eivgi, O.; Vaisman, A.; Nechmad, N. B.; Baranov, M.; Lemcoff, N. G., Latent Ruthenium Benzylidene Phosphite Complexes for Visible-Light-Induced Olefin Metathesis. *ACS Catal.* **2020**, 10, 2033-2038.
(4) Eivgi, O.; Vaisman, A.; Lemcoff, N. G., Latent, Yet Highly Active Photoswitchable Olefin Metathesis Precatalysts Bearing Cyclic Alkyl Amino Carbene (CAAC)/Phosphite Ligands. *ACS Catal.* **2021**, 11, 703-709.
(5) Vaisman, A.; Vidavsky, Y.; Baranov, M.; Lehrer, A.; Baraban, J H.; Lemcoff, N. G., Latency for all: Enabling Latency of Hoveyda-Grubbs Second Generation Catalysts by Adding Phosphite Ligands. *J. Am. Chem. Soc.* **2023,** Accepted, https://doi.org/10.1021/jacs.3c10826.

Poster no. P_OOC_03

How Can We Grow a Polymer Film One Monomer at a Time? Exploring Layer-by-Layer, Gas Phase Polymerization

Brian C. Welch [a,b]*, Vepa Rozyyev [b], Jeffery W. Elam [b], Tamar Segal-Peretz [a]

[a] *Department of Chemical Engineering Technion, Israel Institute of Technology, Haifa 3200003, Israel*
[b] *Argonne National Laboratory, Lemont, Illinois 60439, United States*

E-mail: bw@campus.technion.ac.il

Molecular layer deposition (MLD) is a solvent-free, layer-by-layer polymer film growth technique, derived from atomic layer deposition. In this process (Figure 1), sample surfaces were exposed to step-growth monomers one-at-a-time under vacuum. With each exposure, the vapor-phase reactants formed a monolayer through covalent bonds with surface functional groups. Film thickness was controlled with monomer-level precision according to the number of electophile-nucleophile cycles (MLD cycles) performed. With Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy, we analyzed the growth and chemistry of polyamide, polyurea and polyimine, whereby m-phenylenediamine was used as the nucleophile, paired with a bifunctional aromatic acyl chloride, isocyante or aldehyde electrophile. With in-situ ellipsometry, the per-cycle growth rates were measured at 0.22, 0.26 and 0.16 Å per MLD cycle at 130°C, respectively. These non-cross-linked chemistries had low growth rates at this temperature compared to a cross-linked polyamide chemistry (~3 Å/cycle) which involved a trifunctional acyl chloride. The networked structure appeared to mitigate “double reactions” where a monomer reacts with two substrate function groups, creating a molecular loop. We then analyzed the effect of growing these materials on common polymer substrates, including polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), polyethylene oxide (PEO) and polystyrene (PS). For PVA and PMMA, reactions were facilitated both at the surface and within the bulk of the samples, likely due to the presence of substrate hydroxyls. This held true, even for aldehydes, whose weak nuclephillic activity is acid-catylized in solution. PMMA and PS, however, had minimal material deposition due to a lack of functionality despite evidencing absorption of the vapor reactants. This work expands our understanding of MLD and vapor phase chemistry and paves the way for creating complex, multi-chemistry nanolaminate structures. Furthermore, the ability to infiltrate polymer substrates with organic vapor phase step-growth materials has the potential to enhance resilience to solvents, strengthen adhesives, and opens up the possibility of engineering hybrid polymer materials.

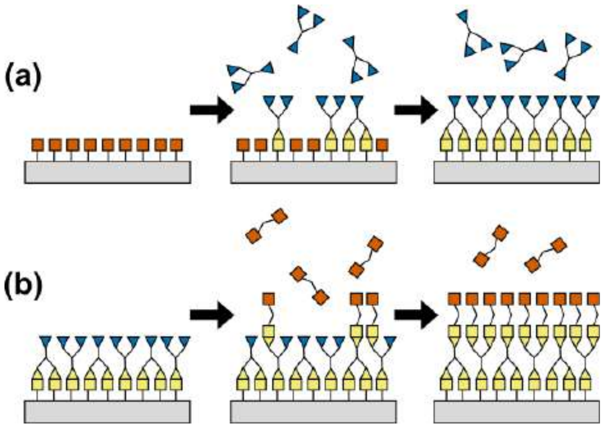


Figure 1: The MLD process. (a) The functional groups (orange squares) at the surface are exposed to vaporized monomers. The reactive funcitonal groups of the monomers (blue triangles) form covalent bonds (yellow) with the substrate. (b) After the surface is saturated and excess monomers are purged away, a second vaporized monomer is introduced in the same manner. This process may be cycled for controlled, step-wise growth of a polymer film.

Poster no. P_OOC_04

Stereoselective synthesis of 1,n dicarbonyl compounds through palladium catalyzed ring opening/ isomerization of densely substituted cyclopropanols

Charlotte S. Teschers[a]+, Anthony Cohen[a]+, Ilan Marek[a]*

[a]Schulich Faculty of Chemistry and the Resnick Sustainability Center for Catalysis, Technion – Israel Institute of Technology, Haifa 3200009, Israel

E-mail: chilanm@technion.ac.il

Remote functionalizations have gained momentum as they enable the editing of functional groups at a distal position from the initial reactive site.[1] As part of our research campaign on chain-walking remote functionalization involving cyclopropane ring-opening reactions,[2] we developed a highly diastereoselective protocol for the synthesis of 1,4 and 1,5-dicarbonyl compounds from densely substituted cyclopropanols. The methodology involves a palladium-catalyzed ring opening reaction followed by a “metal-walk” and oxidation of a remote hydroxyl group, as confirmed my mechanistic studies. The methodology represents a new application of cyclopropanols as initiation sites for chain walking remote functionalization. Importantly, this approach provides a straightforward access to highly valuable succinaldehyde derivatives bearing vicinal quaternary and tertiary stereocenters as single diastereomers.

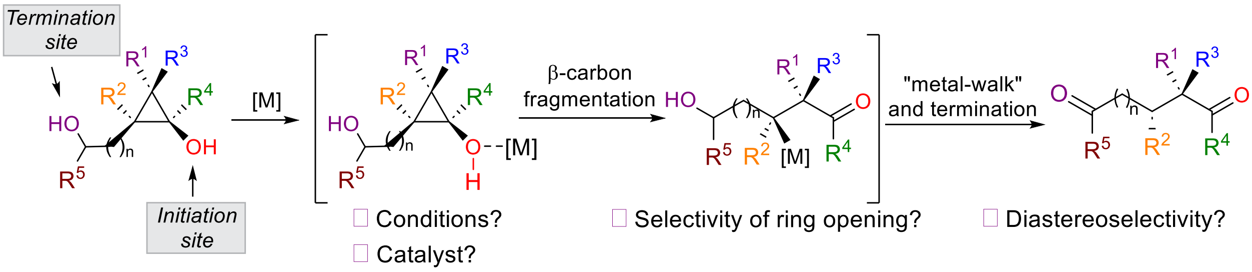


Figure 1: Conceptual framework for the synthesis of densely substituted dicarbonyl compounds from cyclopropanols via metal-walk.

Acknowledgements: This project received funding from the Israel Science Foundation administrated by the Israel Academy of Sciences and Humanities (grant 1625/22). The authors acknowledge generous support by the German research foundation (DFG, Walter Benjamin fellowship to CST).

References:

1. a) H. Sommer, F. Juliá-Hernández, R. Martin, I. Marek, *ACS Cent. Sci.* **2018**, *4*, 153–165; b) I. Massad, R. Suresh, L. Segura, I. Marek, *Nat. Synth.* **2022**, *1*, 37–48; c) A. Vasseur, J. Bruffaerts, I. Marek, *Nature Chem.* **2016**, *8* ,209–219

2. a) S. Singh, J. Bruffaerts, A. Vasseur, *Nature Comm.* **2017**, *8*, 14200; b) J. Bruffaerts, D. Pierrot, I. Marek, *Nature Chem.* **2018**, *10*, 1164-1170; c) S. Singh, M. Simaan, I. Marek, *Chem. Eur. J.* **2018**, *24*, 8553-8557; d) J. Bruffaerts, A. Vasseur, I. Marek, *Adv. Synth. Catal.* **2018**, *360*, 1389-1396; e) A. Cohen, J. Chagneau, I. Marek, *ACS Catal.* **2020**, *10*, 7154−7161; f) A. Cohen, A. Kaushansky, I. Marek, *JACS Au* **2022**, *2*, 687–696.

Poster no. P_OOC_05

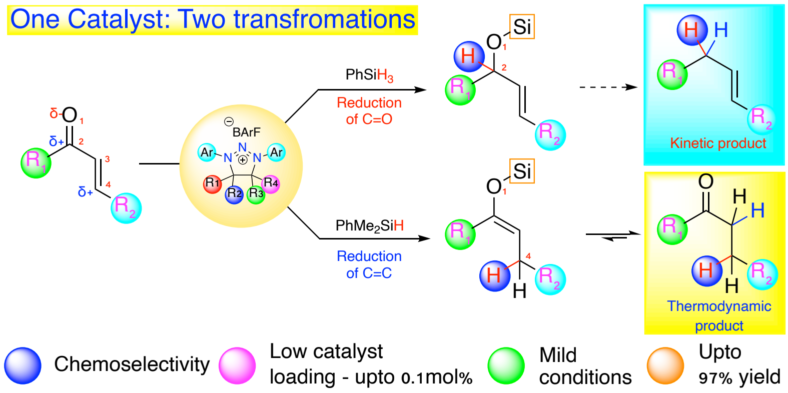
Nitrenium Salt-Catalyzed Chemo-selective Reduction of α,β-Unsaturated ketones

Deepak Ranolia[a], Guy Israeli[a], Natalia Fridman[a] and Mark Gandelman*[a]

[a] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel*

e-mail: chmark@technion.ac.il

Nitrenium salts are emerging as powerful contributors to the field of strong bond activation and catalysis(1-4). In this extensive unpublished research(5), we present a fresh category of nitrenium salts known as triazolinium salts. These innovative compounds are synthesized through a (3+2) dipolar cycloaddition process involving 1,3-diaryltriazene and highly strained tetra-substituted alkenes. The central focus of our investigation revolves around the synthesis and catalytic application of these triazolinium salts. We investigate the catalytic properties of triazolinium salts, especially in the context of silane-mediated reduction. In the course of our experimentation, it became evident that these triazolinium salts exhibit remarkable catalytic efficiency, particularly when applied to the reduction of conjugated ketones. What adds an exciting aspect to our study is the observation that a singular organo-catalyst nitrenium salt can be employed to selectively guide hydride transfer at either C_2 or C_4. This selectivity is achieved through the strategic variation of different silane reductants. The consequential outcome is the achievement of a highly selective reduction process, targeting either the carbonyl functionality (C=O) or the olefinic moiety (C=C), all accomplished under mild reaction conditions. This research not only introduces a new and synthetically valuable category of nitrenium salts but also elucidates their catalytic ability in effecting selective reductions. The ability to modulate hydride transfer and achieve targeted reductions under mild conditions stands as a demonstration of the potential practical applications and versatility of triazolinium salts in organic synthesis.



Scheme 1: Chemo-selective Reduction of α,β-Unsaturated ketones using nitrenium salts.

Acknowledgements: We thank the ICS for financial support.

References:

(1) Pogoreltsev, A.; Tulchinsky, Y.; Fridman, N.; Gandelman, M. Nitrogen Lewis Acids. *J Am Chem Soc* **2017**, *139* (11), 4062–4067.
(2) Avigdori, I.; Pogoreltsev, A.; Kaushanski, A.; Fridman, N.; Gandelman, M. Frustrated Lewis Pairs Comprising Nitrogen Lewis Acids for Si–H Bond Activation. *Angewandte Chemie International Edition* **2020**, *59* (52), 23476–23479.
(3) Singh, K.; Avigdori, I.; Kaushansky, A.; Fridman, N.; Toledano, D.; Gandelman, M. New Generation of Nitrenium Salts: Catalytic Hydrosilylation of Imines and a Mechanism of Action of Nitrogen Lewis Acids. *ACS Catal* **2022**, 6831–6839.
(4) Ranolia, D.; Avigdori, I.; Singh, K.; Koronatov, A.; Fridman, N.; Gandelman, M. Triazolium Salts as Lewis Acid Catalysts. *Org Lett* **2022**, *24* (22).
(5) Ranolia, D; Israeli, G; Fridman, N.; Gandelman, M. (Unpublished results).

Poster no. P_OOC_06

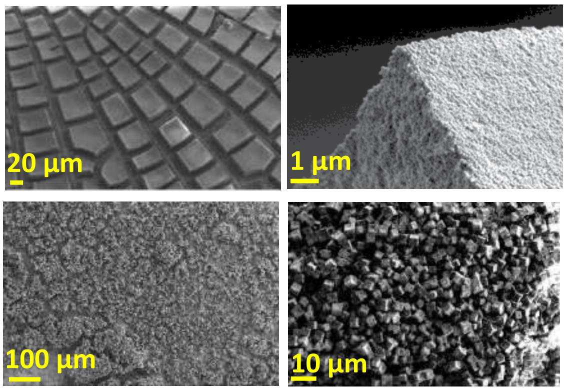
Self-assembled superstructures of imidazole-based metal-organic frameworks

Elad Gaver, Maria Chiara di Gregorio, Michal Lahav and Milko E. van der Boom

Weizmann Institute of Science, Department of Molecular Chemistry and Materials Science, 7610001, Rehovot, Israel.

Email: elad.gaver@weizmann.ac.il

Ve demonstrate sub-micron sized metal-organic frameworks (MOFs) that can assemble in large structures. Their ssembly properties are dependent on their size and morphology. Understanding the parameters that control the ssembly of sub-micron particles into suprastructures can result in the formation of crystal-from-crystals with usual roperties. These new MOFs were prepared by the solvent diffusion method using bivalent cobalt and nickel salts. A etrahedral ligand having four imidazole groups is used for coordination to first row metals. The coordination chemistry f imidazole groups for the formation of MOFs has been less explored than the coordination chemistry of pyridine nor arboxylates.[1] The use of imidazole coordination chemistry resulted in stable crystals with high level of uniformity in oth size and shape.[2] Imidazole coordination is weaker than that of carboxylate[1] and it is stronger than coordination of yridine-derivatives to the same metal centers.[3] It is plausible that during the crystal growth ligand-metal dissociation ccurs prior to formation of the obtained structures, Drop casting of the MOFs on silicon wafers resulted in omogeneous films that upon solvent evaporation formed the structures shown in **Figure 1** below.



igure 1. Scanning electron microscope (SEM) images of nickel (top) and cobalt (bottom) based metal-organic frameworks (MOFs) nd their self-assembled superstructures.

1] A. Nimmermark, L. Öhrström, J. Reedijk, *Zeitschrift fur Krist.* **2013**, *288*, 311–317.
2] M. C. di Gregorio, M. Elsousou, Q. Wen, L. J. W. Shimon, V. Brumfeld, L. Houben, M. Lahav, M. E. van der Boom, *Nat. Commun.* **2021**, *12*, 1–9.
3] A. Richaud, N. Barba-Behrens, F. Méndez, *Org. Lett.* **2011**, *13*, 972–975.

Poster no. P_OOC_07

Alternating current electrolysis: An alternative route for the efficient and scalable electrosynthesis

Evgeniy O. Bortnikov,* [a] and Sergey N. Semenov [a]

[a] *Weizmann Institute of Science, Department of Molecular Chemistry and Materials Science, 234 Herzl St., Rehovot 7610001, Israel*

E-mail: evgenii.bortnikov@weizmann.ac.il

Organic electrosynthesis is known as a powerful tool in synthetic chemistry, enabling a green and efficient route to perform a wide spectrum of organic transformations. The method of direct current (DC) electrolysis is widely used to achieve the reduction or oxidation of the starting materials to the desired products. At the same time, the periodical nature of alternating current (AC) limits the application of AC electrolysis method in organic electrosynthesis.

Recently, our group demonstrated that the use of AC may be highly efficient in Ni-catalyzed cross-coupling reactions. The redox-neutral catalytic cycle requires both oxidation and reduction in order to maintain the conversion of the starting aryl halide to the functionalized product; thus, cathodic reduction is required to enable oxidative addition to the metal center while anodic oxidation facilitates the reductive elimination step. The use of AC allows for performing both electron-transfer processes at the surface of the same electrode, eliminating the need in the interelectrode transfer of the reactive catalytic species. In our work, AC-assisted Ni-catalyzed amination, etherification, and esterification were successfully demonstrated on the diverse scope of aryl halide substrates with the yields and selectivity higher than those achieved using DC electrolysis method.[1]

Next, we found that the use of AC enables a unique strategy for scaling up electrosynthesis. If the inner volume of the reactor is filled with porous three-dimensional electrodes, the periodical switch of the polarity of the electrodes, inherent to AC, ensures that both cathodic reduction and anodic oxidation occur homogeneously throughout the reactor volume, even in the absence of stirring. This enables a straightforward scale-up approach for redox-neutral, reductive, and oxidative transformations, as demonstrated on up to a 50-mmol scale electrosynthesis. Particular attention was dedicated to the study of the frequency effect – while the reductive and oxidative processes could be performed efficiently even at very low frequencies, a particularly favorable frequency region was discovered for the redox-neutral reactions.[2]

References:

1. Bortnikov, E. O.; Semenov, S. N. Coupling of Alternating Current to Transition-Metal Catalysis: Examples of Nickel-Catalyzed Cross-Coupling. *J. Org. Chem.* **2021***, 86,* 782-793.
2. Bortnikov, E. O.; Smith, B. S.; Volochnyuk, D. M.; Semenov, S. N. Stirring-Free Scalable Electrosynthesis Enabled by Alternating Current. *Chem. Eur. J.* **2023**, *29*, e2022038.

Poster no. P_OOC_08

How low can we go? Enhancing polymer films resistance to solvents via infiltration of inorganic materials from vapor phase

Gilad Sasson, associate professor Tamar Segal Peretz, Doctor Brian Welch

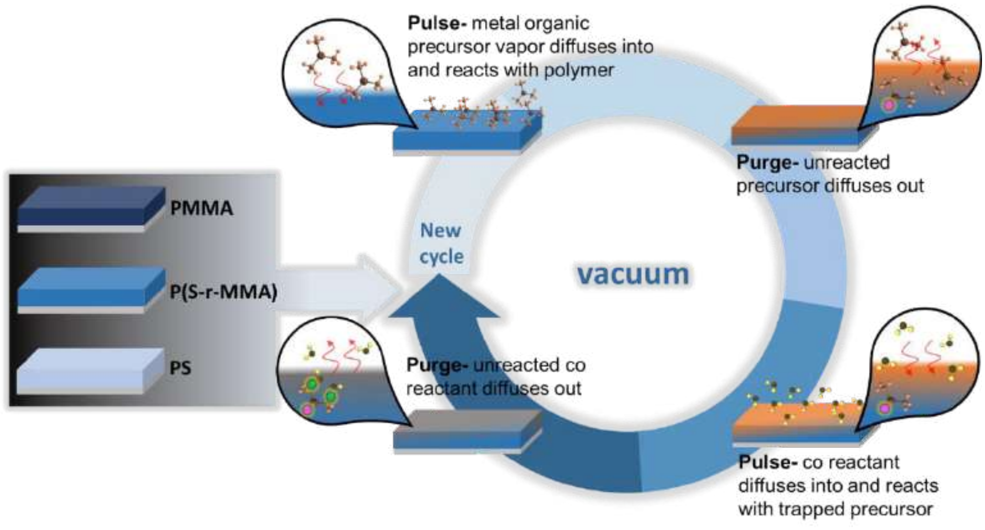
Chemical engineering, Technion, Haifa.

E-mail: ((gilad-sasson@campus.technion.ac.il, tamarps@technion.ac.il, bw@campus.technion.ac.il))

The performance of polymer products may suffer when they are exposed to organic solvents due to polymer dissolution. Sequential infiltration synthesis (SIS)- a new and promising technique for growth of inorganic materials within polymers, can be harnessed to protect polymer films and structures. In SIS, the polymer is exposed to a vapor phase organometallic precursor and its co-reactant sequentially. The precursors diffuses into the polymer, react, and form inorganic clusters within the polymer’s free volume, creating hybrid organic-inorganic material with tunable composition and concentration.

In this study, we ask if polymer film resistance to organic solvent be achieved with low concentration of functional groups that react in SIS, or in short- how low can you go? To that end, we have used polystyrene-random-polymethyl methacrylate copolymers, where the Al2O3 precursor- trimethyl aluminum (TMA) has selective interaction with PMMA, and varied the fraction of the reactive PMMA to control the level of Al2O3 growth within the polymer. We show that while nucleation of Al2O3 is linearly correlated to PMMA fraction, additional Al2O3 growth at high number of cycles occurs follows a different trend. Higher rates of alumina mass gain is achieved at lower PMMA fractions, due to the reduced diffusion of TMA at high Al2O3 concentration of the hybrid film.

We show the relation between the enhanced solvent resistance and the functional group densities within the polymer films. As expected, pure PS films that lack reactive groups remained immediately dissolved by toluene, even after SIS treatment, while pure PMMA films showed excellent resistance to dissolution. High resistance to dissolution by toluene was observed also in the PS-r-PMMA films after Al2O3 SIS. Interestingly, PS-r-PMMA samples with as little as 9% PMMA displayed excellent resistance to dissolution after SIS. This indicates that ~10% of well dispersed Al2O3 within the polymer is sufficient for creating the protecting inorganic cross-linking and maintaining the films stability in organic solvents.



Scheme or Figure 1: Sequential infiltration synthesis process scheme

Poster no. P_OOC_09

Towards New Polymers by ROMP of Tetra-Substituted Olefins

Habib Assy[a], Ofer Reany[b], N.Gabriel Lemcoff[a]

[a]Chemistry department, Ben Gurion University of the Negev, Beer-Sheba 84105, Israel.
[b]Department of Natural Sciences, The Open University of Israel, Ra'anana 4353701, Israel
assyh@post.bgu.ac.il

Olefin metathesis has allowed the synthesis of specialty polymers with mono-dispersed sizes, well-defined sequences, distinct stereochemistry, highly functionalized, and ready for further post-polymerization reactions. The great diversity and simplicity of these polymerization reactions have made olefin metathesis one of the most important and useful reactions dedicated to synthesis new polymers. Indeed, the ROMP methodology has produced very valuable polymers, both in industrial and academic settings. However, there are still areas in polymer chemistry that have not been explored. One of these areas is the ROMP of tetra-substituted olefins (TSO-ROMP). The reason for this is most likely the high steric strain involved during the coordination of a tetrasubstituted olefin to the metal center, and the concomitant reticence to initiate and propagate the reaction. However, a judicious design and synthesis of tetrasubstituted olefin substrates, coupled with a thorough screening of appropriate initiators may bring about a breakthrough in this area.

We present here the synthesis and design of a series of new tetrasubstituted alkenes based on fused bicyclic [3.3.0] structures as monomers for TSO-ROMP. Molecular models show a relatively planar structure for these monomers, as well as strained rings, which would allow the binding of the olefin to the catalyst and also provide the driving force for the ring-opening. If we succeed in 'ROMPing' these unique monomers, a completely new family of poly-macrocyclic chains connected by a carbon-carbon double bond with possibly unique properties and applications may be obtained. The final scope embraces the inclusion of other heteroatoms and further bicyclic structures ([n.n.0] in the starting monomers, allowing added functionality.

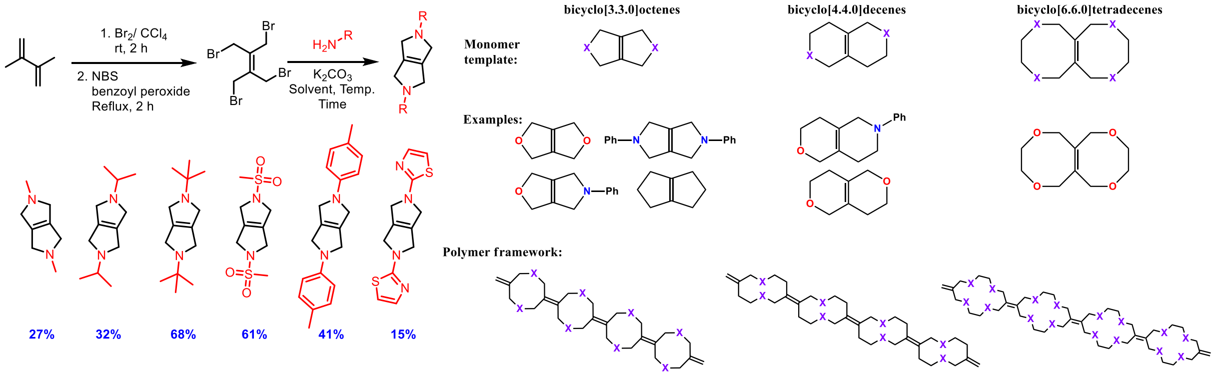


Figure 1. Novel tetrasubstituted alkenes made, and proposed polymer structures by TSO-ROMP.

Poster no. P_OOC_10

The Construction of Highly Substituted Piperidines via Dearomative Functionalization Reaction

Hao Ding,[a] Miao Hu,[a] William Desnoo,[b] Dean J. Tantillo*[b] Zackaria Nairoukh*[a]

[a]*Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, 9190401 Israel.* [b]*Department of Chemistry, University of California-Davis, Davis, California 95616, United States.*

E-mail: hao.ding@mail.huji.ac.il, djtantillo@ucdavis.edu, z.nairoukh@mail.huji.ac.il

Nitrogen heterocycles play a vital role in pharmaceuticals and natural products, with the six-membered aromatic and aliphatic architectures being commonly used.[1-2] While synthetic methods for aromatic *N*-heterocycles are well-established, the synthesis of their aliphatic functionalized analogues, particularly piperidine derivatives, poses a significant challenge (Figure 1).[3]

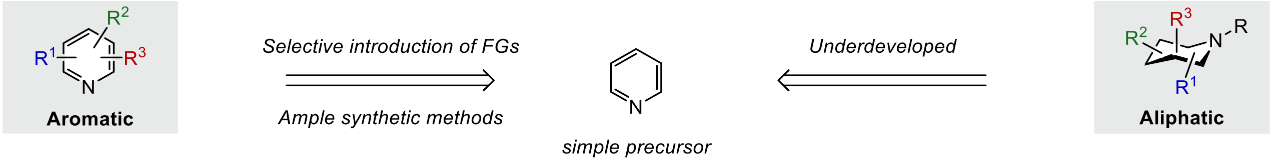


Figure 1: Important cores in drugs and natural products

In that regard, we propose a stepwise dearomative functionalization reaction as a transformative tool for the construction of highly decorated aliphatic *N*-heterocycles with diverse functional handles. We also discuss challenges related to site-selectivity, regio- and diastereoselectivity, and provide insights into the reaction mechanism through mechanistic studies and density functional theory computations (Figure 2).[4]

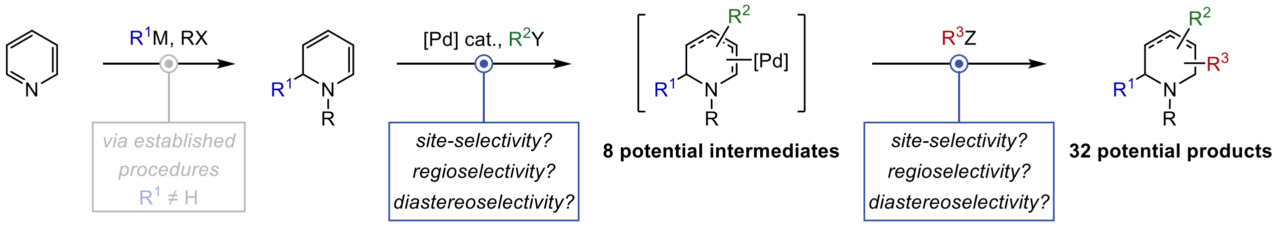


Figure 2: Dearomative functionalization of pyridine to deliver highly decorated piperidine derivatives

References:

1. a) Vitaku, E.; Smith, D. T.; Njardarson, J. T. Analysis of the structural diversity, substitution patterns, and frequency of nitrogen heterocycles among U.S. FDA approved pharmaceuticals. *J. Med. Chem.* **2014**, *57*, 10257-10274; b) Taylor, R. D.; MacCoss, M.; Lawson, A. D. G. Rings in drugs. *J. Med. Chem.* **2014**, *57*, 5845-5859.
2. O'Hagan, D. Pyrrole, pyrrodine, pyridine, piperidine and tropane alkaloids. *Nat. Prod. Rep.* **2000**, *17*, 435-446.
3. Campos, K. R.l Coleman, P. J.; Alvarez, J. C.; Dreher, S. D.; Garbaccio, R. M.; Terrett, N. K.; Tillyer, R. D.; Truppo, M. D.; Parmee, E. R. The importance of synthetic chemistry in the pharmaceutical industry. *Science*, **2019**, *363*, eaat0805.
4. Angew. Chem.Int. Ed.2023,62, e20231510

Poster no. P_OOC_11

Zinc complexes of ‘salalen’-like ligands in ring-opening polymerization catalysis of rac-Lactide

Inbar Zaltsman, Sophia Lipstman, Moshe Kol*

School of Chemistry, Faculty of Exact Sciences , Tel Aviv University 6997801, Israel

Email: inbarz@mail.tau.ac.il

Lipstman@tauex.tau.ac.il

Moshekol@tauex.tau.ac.il

Poly(lactic acid) (PLA) is a biocompostable aliphatic polyester produced by the catalytic ring-opening polymerization (ROP) of lactide (LA), the dilactone of lactic acid. Zinc-based catalysts are particularly appealing because zinc is a common, non-toxic metal, however, such catalysts are typically either non-stereoselective or heteroselective. Our previous work involved zinc complexes of sequential tetradentate-monoanionic {ONNN}-ligands featuring *sp*^{3}-hybridized internal donors, showcasing high activities and relatively high isoselectivities ($P_m \leq 0.83$). Previously, we observed significant alterations in activity and stereoselectivity by substituting one of the two internal amine donors with an imine donor in tetradentate dianionic {ONNO}-type ligands. In the current study, we aimed to explore if a similar impact would occur with the monoanionic ligands, and thereby introduced the {ONNN} ‘salalen’-like ligands. We synthesized a range of ligands comprising imine and amine internal donors, combined with pyridine and phenolate peripheral donors, which led to well-defined zinc complexes as single stereoisomers. Clear structure-activity relationships were revealed, that enabled the introduction of highly active and stereoselective catalysts. The most notable catalyst of this new family polymerized 92% of 300 equiv of *rac*-LA at within 13 minutes at 0 °C with an exceptionally high degree of isotacticity (P_m=0.93), which is the highest ever described for zinc catalysts.

Poster no. P_OOC_12

Iterative synthesis of stereodefined polyacetals and their domino Coates Claisen rearrangement

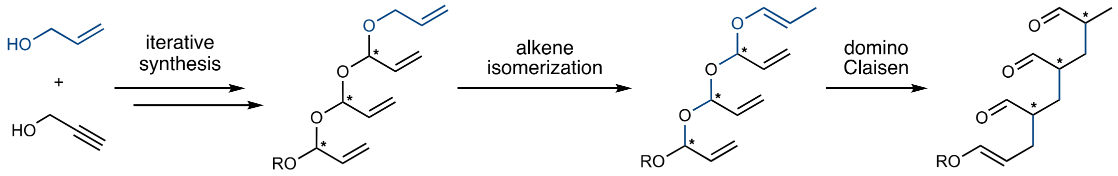
Itai Massad*[a] and Ilan Marek[a]

[a] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology.*

E-mail: im580@cam.ac.uk

Iterative synthetic strategies can dramatically simplify the preparation of complex organic molecules and thereby facilitate studies into their properties and applications. A convincing example is the evolution of polypeptide synthesis into a routine automated task, enabling the de novo synthesis of proteins and in turn tremendously advancing the field of chemical biology. Iterative syntheses of elusive molecular backbones are particularly exciting, as they enable forays into unknown structure and reactivity.

We describe an efficient and completely stereocontrolled iterative synthesis of previously unknown acyclic polyacetals, formally derived from acrolein. In addition to their novel structure, these polyacetals undergo a domino-Coates-Claisen rearrangement which transforms C–O bonds into C–C bonds, entirely rearranging the iteratively assembled molecular backbone.



Poster no. P_OOC_13

Well-Defined Ligand Effects in Cobalt(I) $PC_{NHC}P$ Pincer Complexes Control the Stereoselectivity (E and Z) in Allyl Ether Isomerization

Katarzyna Młodzikowska-Pieńko,*[a] Subhash Garhwal,[a] Sakthi Raje,[a] Tofayel Sheikh Mohammed,[a] Ron Rafaeli,[a] Natalia Fridman,[a] Linda J. W. Shimon,[b] Renana Gershoni-Poranne,[a] and Graham de Ruiter[a]

[a] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Technion City, 3200008 Haifa, Israel,*

[b] *Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, 7610001, Israel Department, Institution,*

E-mail: kasiamp@campus.technion.ac.il

The ongoing attempt to offer more sustainable prospects for future generations has triggered a resurgence in utilizing earth-abundant metals for homogenous catalysis.[1] Their usefulness is a result of their high natural abundance, low-toxicity, and typically high-spin electronic structure, which result in unique reactivities that their heavier congeners do not enjoy.[2–4] Recently, several catalytic species were developed for olefin isomerization based on earth-abundant metals, a field that was previously dominated by metals such as ruthenium, palladium or iridium.[1] However, the origin of their selectivity is often underexplored,[5] in particular for cobalt-based catalysts for alkene isomerization.

In this work, we investigate the selectivity control in allyl ether isomerization. In-depth mechanistic and computational studies reveal the role of an empty coordination site at the Co center, as well as interesting ligand effects (N_2 vs Me), which together explain the observed selectivity.

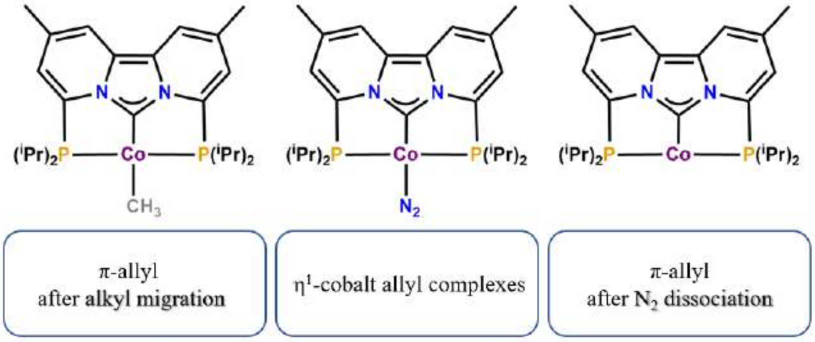


Figure 1: Cobalt-based catalysts for alkene isomerization investigated in presented study.

Acknowledgements: Research was supported the Israel Science Foundation (ISF) under a personal (574/20) and equipment (579/20) grant. G.de.R. is an Azrieli young faculty fellow and a Horev Fellow supported by the Taub Foundation. K.M.P. is grateful to the Azrieli Foundation for financial support through a postdoctoral fellowship. R.G.P. is a Branco Weiss Fellow and a Horev Fellow.

References:

1. Chirila, A. *et al.* Front Matter. *Non-Noble Metal Catalysis* i–xix, **2019**.
2. Hu, M. & Ge, S. Versatile cobalt-catalyzed regioselective chain-walking double hydroboration of 1,n-dienes to access gem-bis(boryl)alkanes. *Nat. Commun.* **2020**, 765,11.
3. You-Yun, Z. & Christopher, U. Catalytic reductive [4 + 1]-cycloadditions of vinylidenes and dienes. *Science* **2019**, 363, 857–862.
4. M, T. A. *et al.* Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes. *Science* **2012**, 353, 567–570.
5. Chen, C., Dugan, T. R., Brennessel, W. W., Weix, D. J. & Holland, P. L. Z-Selective Alkene Isomerization by High-Spin Cobalt(II) Complexes. *J. Am. Chem. Soc.* **2014**, 136, 945–955.

Poster no. P_OOC_14

Stereospecific nucleophilic substitution at quaternary carbon stereocenters via nonclassical carbocation

Kaushalendra Patel [a] and Ilan Marek *[b]

[a] Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel [b] Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel.

E-mail: k.patel@campus.technion.ac.il

Stereospecific nucleophilic substitution is a powerful tool for the preparation of diastereo- and enantiomerically enriched compounds. All nucleophilic displacements proceed at either a primary, secondary, or tertiary carbon stereocenters. What about nucleophilic substitution at a quaternary carbon center?

The stereospecific nucleophilic substitution at quaternary carbon stereocenter is a contra-intuitive transformation as it requires the cleavage of a C-C σ bond. The exergonic nature imbedded into a cyclopropyl ring offered a unique solution to this problem leading to a new approach to construct challenging acyclic structures possessing adjacent stereodefined tertiary and quaternary carbon stereocenters. The exploration of different sources of β-cyclopropyl carbocations and carbon nucleophiles add great values to this chemistry and allow a rapid access to molecular complexity and diversity.

A deep understanding of the mechanism through the formation of a cyclopropylcarbinyl (CPC) cation intermediate combined with our experimental studies have contributed to the advances and will further stimulate the discovery of additional fascinating transformations in acyclic systems.

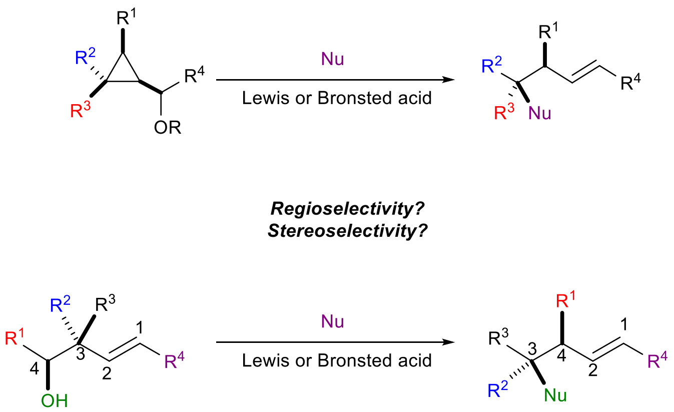


Figure 1: Nucleophilic substitution at quaternary carbon stereocenters in cyclic and acyclic system

Acknowledgements: We thank the Israel Science Foundation and the European Union's Horizon 2020 research and innovation program for financial support.

References:

1. **Patel, K.**; Lanke, V.; Marek, I., *J. Am. Chem. Soc.* **2022**, *144*, 7066-7071.
2. Chen, X.;# **Patel, K.**;# Marek, I., *Angew. Chem. Int. Ed.* **2023**, *62*, e202212425.
3. Chen, X.; **Patel, K.**; Marek, I., *Chem* **2023**, *9*, 266-279.
4. **Patel, K.**; Oginetz, L.; Marek, I., *Org. Lett.* **2023**, *25*, 8474−8477.
5. Larmore, S. P.; Champagne P. A., *J. Org. Chem.* **2023**, *88*, 6947-6954.

Poster no. P_OOC_15

Novel Naphthotriazinium Ligand Presents L/Z Type Coordination Duality and Facilitates Water Inverted Polarity Cooperative Activation

Liav Leiboviz[a] and Mark Gandelman[a]

[a] *Schulich Faculty of chemistry, Technion – Israel institute of technology, Haifa 320000.*

E-mail: liavl@campus.technion.ac.il

Ever since their discovery by Arduengo in 1991[1], N-Heterocyclic carbenes (NHC's) have made a great impact in the field of organo-metallic chemistry. Employed as strong coordinative ligands to transition metals, NHC based organo-metallic complexes were found to be extremely useful in catalytic reactions.

With increasing popularity of NHC, new derivatives and analogues were synthesized and studied. N-Heterocyclic Nitrenium (NHN) is an analogue of NHC where the carbene carbon is replaced by nitrogen cationic species. In 2011[2], our group presented the first example of a stable tri-dentate phosphine pincer NHN ligand which was successfully coordinated to various transition metals. Our experimental and computational studies suggest that 6-membered triazinium cations are better Lewis acids compared to their 5-membered nitrenium counterparts. Such systems could be highly beneficial in catalysis. Design, synthesis and studies of metal complexes based on triazenium is a major goal of our research. We hereby present a novel synthesis of pincer-type naphthotriazinium ligand and its coordination complexes of rhodium, iridium, palladium and nickel. Interestingly, unlike the complexes with our 5-membered nitrenium ligand, our new system can act as either L-type or Z-type ligand (fig.1). Moreover, when coordinated to iridium, this ligand helps facilitate an inverted polarity cooperative activation of water (fig.2).

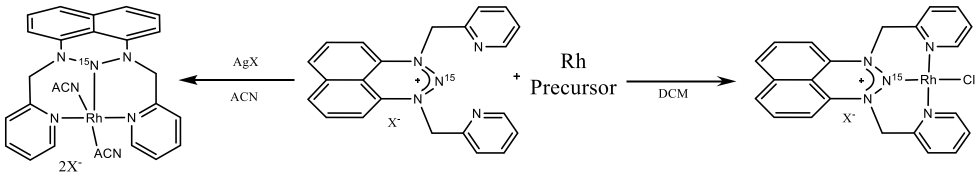


Figure 1: L/Z type Coordination duality

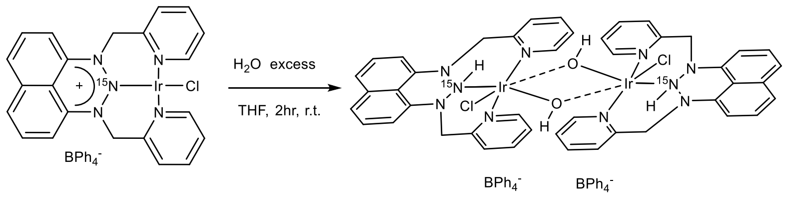


Figure 2: Water inverted polarity cooperative activation

References:

1. **Arduengo, A. J.; Harlow, R. L.; Kline, M., A stable crystalline carbene", *J. Am. Chem. Soc.* 1991, *113* (1), 361-363.**

2. **Tulchinsky, Y.; Iron, M. A.; Botoshansky, M.; Gandelman, M., Nitrenium ions as ligands for transition metals", *Nat. Chem.* 2011, *3* (7), 525-531.**

Poster no. P_OOC_16

EN ROUTE TOWARDS DERACEMIZATION IN ACYCLIC SYSTEMS VIA STEREO-CORRECTIVE CHAIN-WALKING

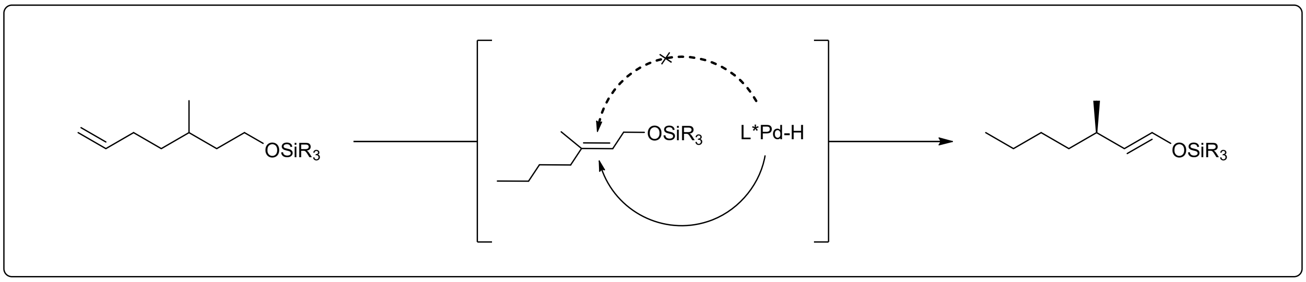
Lucas Segura[a*], **Ilan Marek**[a*]

[a]*Mallat Family Laboratory of Organic Chemistry, Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa, 32000 Israel.*

E-mail: **lucas.segura.pro@gmail.com; chilanm@technion.ac.il**

We report the first steps towards chain-walking deracemization in acyclic systems. To achieve this, a catalytic process would need to isomerize olefins to a termination site past tertiary carbon centers. Furthermore, preferential coordination of the catalyst to one face of a trisubstituted olefin will be pivotal to generate stereogenic information during the hydride migratory insertion step. Lastly, the consistent de-coordination of the catalyst from the olefin without compromising conversion will be crucial to avoid the classical stereoretention observed in highly associative isomerization mechanisms. Herein, we present our progress in determining optimal ligand design for a reliable, dissociative, palladium-catalyzed olefin isomerization on citronellol derivatives.

Stereo-corrective alkene isomerization



Poster no. P_OOC_17

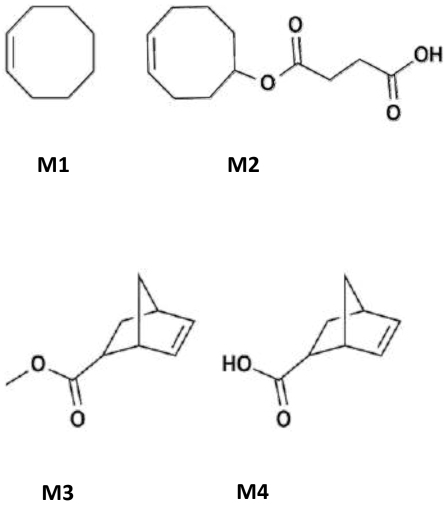
The Ultimate Recycling Process for Cross-Linked Polymers

Mai Fraim, Noy B. Nechmad, Yuval Vidavsky, N. Gabriel Lemcoff

[a] Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel. [b] Space Environment Department, Soreq NRC, Yavne 81800, Israel.

E-mail: (maif@post.bgu.ac.il, lemcoff@bgu.ac.il)

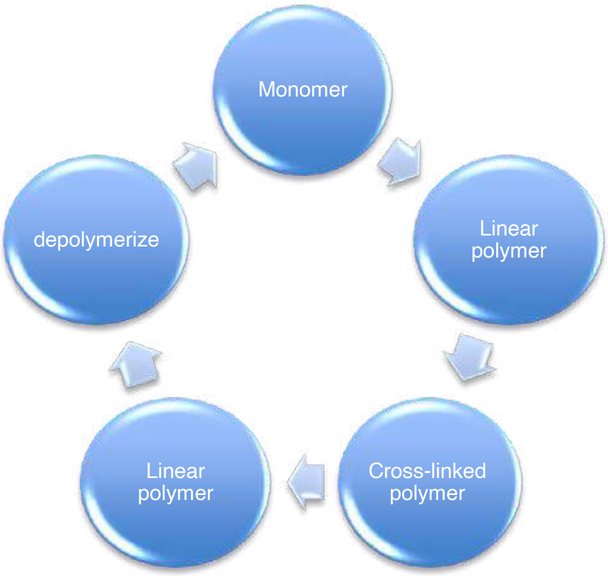
Our goal in this project is to recycle tough cross-linked polymers. The polymers will be made by ring-opening metathesis polymerization (ROMP) using functionalized monomers (Figure 1) creating the corresponding linear polymers. It has been shown[1] that carboxylic acids can coordinate to metal centers, such as copper or nickel, to create coordinatively cross-linked polymers. These coordination bonds can be broken, leading back to the original linear polymer. In our research group, we are studying depolymerization processes of ROMP-derived polymers.[2] Thus, after the metal cross-links are removed, we plan to depolymerize the remaining linear polymer by using Ruthenium-based catalysts bearing iodine as anionic ligands. This full cycle (Figure 2), if achieved, would be the ultimate recycling process for cross-linked materials. Herein, we describe the synthesis of the monomers **M2** and **M3** which in conjunction with available monomers **M1** and **M4** were chosen to produce the desired copolymers for this recycling project. Additionally, we show the synthesis of the linear copolymer in different ratios of carboxylic acid-containing monomers to study its effect on the metal-crosslinked polymeric networks.



M1 **M2**

M3 **M4**

Figure 1. Monomer's structure


Monomer

Linear polymer

Cross-linked polymer

Linear polymer

depolymerize

Figure 2. Proposed recycling process

References:

1. Vidavsky, Y., bae, S., Meredith Zilberstein, N., Modulating Metallopolymer Mechanical Properties by Controlling Metal Ligand Crosslinking, Journal of Polymer Science, 2018
2. Nechmad, N. B., Phatake, R., Ivry, E., Poater, A. and Lemcoff, N. G., Unprecedented Selectivity of Ruthenium Iodide Benzylidenes in Olefin Metathesis Reactions, Angew. Chem. Int. Ed. , 2020

Poster no. P_OOC_18

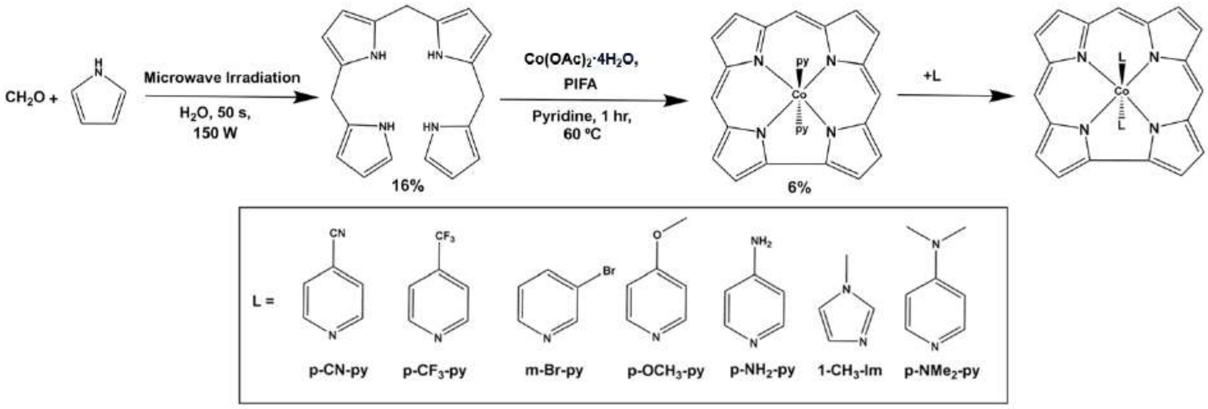
Fundamental Studies on Cobalt(III) Complexes of the Parent Corrole

Marcelo Fernandez-Dela-Mora,[a] Irena Saltsman,[a] and Zeev Gross[a]

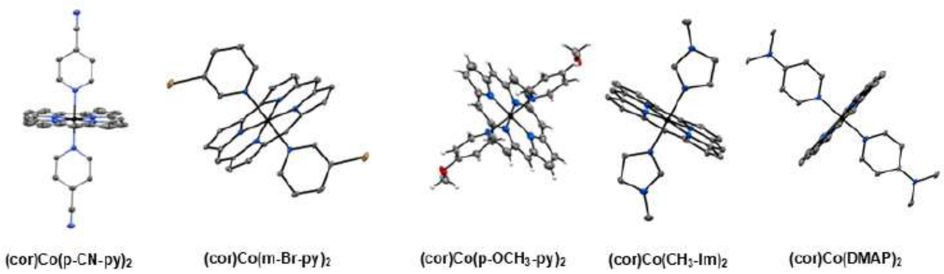
[a] *Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel.*

E-mail: chr10zg@tx.technion.ac.il; marcelo@campus.technion.ac.il; chira@technion.ac.il

Corrole, an 18π-electron conjugated version of the nonaromatic corrin, was initially reported in 1964.[1] Despite the large initial interest in this N_4 macrocycle, corrole chemistry remained underdeveloped until 1999 when the hitherto formidable synthetic challenges were resolved by introducing triarylcorroles obtainable through one-pot methodologies.[2] A plethora of studies have shown the versatility of the corresponding metal complexes in many fields including medical imaging, cancer treatment, and catalysis related to clean energy.[3] The Gross group has now (in 2021) introduced the parent corrole,[4] more than half a century after the report of the first corrole. In continuation of this significant milestone, this study describes the synthesis and characterization of cobalt(III) complexes of the parent corrole in which the coordination sphere is completed by both electron-poor and electron-rich pyridines. Also uncovered are their fundamental characteristics including X-ray structures, ^{1}H-NMR chemical shifts, and photophysical properties. One surprising result was that the weakest binding pyridine-based ligand (Scheme 1, L = para-cyanopyridine) displayed the shortest Co-N bond length (Scheme 2, leftmost structure).



Scheme 1: The pathway to cobalt(III) complexes of the parent corrole, (cor)Co$(L)_2$, with seven different ligands (L) in the two axial positions.



Scheme 2: The X-ray structures of the five complexes introduced in this investigation.

References:

1. A. W. Johnson and I. T. Kay, *Proc. Chem. Soc.*, **1964**, 89.
2. Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed.,* **1999**, 38, 1427.
3. Atif Mahammed and Zeev Gross, *Journal of the American Chemical Society* **2023** *145* (23), 12429-12445.
4. Kumar A., Yadav P., Majdoub M., Saltsman I., Fridman N., Kumar S., Mahammed A., Gross Z., *Angew. Chem. Int. Ed.* **2021**, *60*, 25097-25103.

Poster no. P_OOC_19

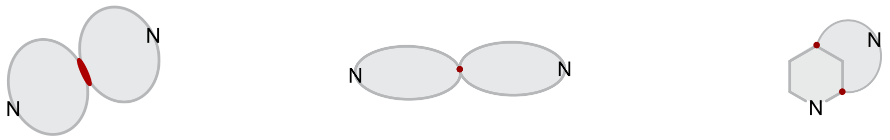
Formation of *N,N*-Spiro Heterocycles by Carbometalation Dearomatization Reaction

Mohamed Agbaria, Nwar Egbaria, Zackaria Nairoukh

Institute of Chemistry, The Hebrew University of Jerusalem

E-mail: mohamed.agbaria1@mail.huji.ac.il, nwar.egbaria@mail.huji.ac.il, z.nairoukh@mail.huji.ac.il

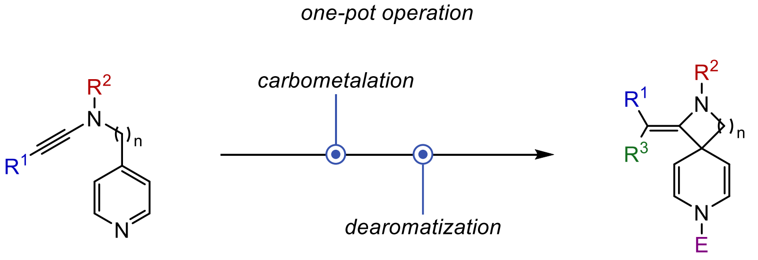
Aliphatic heterobicyclic compounds play a crucial role in pharmaceuticals due to their unique physicochemical and physiological properties.[1] Among various structures, *N*,*N*-spiro bicycles are particularly relevant, owing to their properties such as stability and flexibility (**Figure 1**).[1-4] However, their formation poses a challenging issue, typically requiring careful preparation of starting materials through tedious multistep synthesis, which is considered a major drawback. Furthermore, the formation of *N*,*N*-spiro bicycles is hindered by harsh reaction conditions and limited functional group tolerance, thereby limiting their applications in medicinal chemistry.



Fused N,N-bicyclic *Spiro N,N-bicyclic* *Bridge N,N-bicyclic*

Figure 1. Different type of *N*,*N*-bicycles.

To overcome these challenges, we have developed a direct method based on a carbometalation dearomatization reaction sequence (**Scheme 1**). This method facilitates the formation of *N*,*N*-spiro bicycles in a highly regio- and stereoselective manner. The strategy involves copper-catalyzed carbomagnesiation and subsequent intramolecular nucleophilic attack to furnish the targeted molecules, which carry a variety of functional handles that could potentially impact the output of drug discovery efforts.



Features

- *one-pot operation*
- *available precursors*
- *>25 examples*
- *complex architectures*

Scheme 1. General methodology for the formation *N*,*N*-spiro bicycles

References:

1. Marson, C. M. New and unusual scaffolds in medicinal chemistry. *Chem. Soc. Rev.* **2011**, *40*, 5514.
2. Nájera C.; Sansano, J. M.; Yusa, M. 1,3-Dipolar cycloadditions of azomethine imines. *Org. Biomol. Chem.* **2015**, *13*, 8596.
3. Zheng, Y.; Tice, C. M.; singh, S. B. The use of spirocyclic scaffold In drug discove. *Bioorg. Med. Chem. Lett.* **2014**, *24*, 3673.
4. Bérubé, G. An overview of molecular hybrids in drug discovery. *Expert Opin Drug Discov.* **2016**, *11*, 281.

Poster no. P_OOC_20

Brook Rearrangement as Trigger for Dearomatization Reaction: Synthesis of Non-Aromatic N-Heterocycles

Institute of Chemistry, The Hebrew University of Jerusalem

E-mail: mohamed.agbaria1@mail.huji.ac.il, z.nairoukh@mail.huji.ac.il

The Brook rearrangement involved intramolecular [1,2]-anionic migration of silyl groups from carbon to oxygen atoms.[1] Typically, these rearrangements need basic reaction conditions and occur via a pentacoordinate silicon intermediate.(**Figure 1**).[2-3] Their potency is typically mirrored in the subsequent relay process, which creates carbon-carbon (C-C) bonds by in situ functionalization of the carbanionic intermediate with appropriate electrophiles.[4-5] This is also a powerful approach for creating complex compounds.

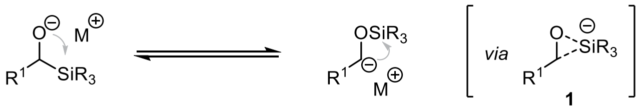
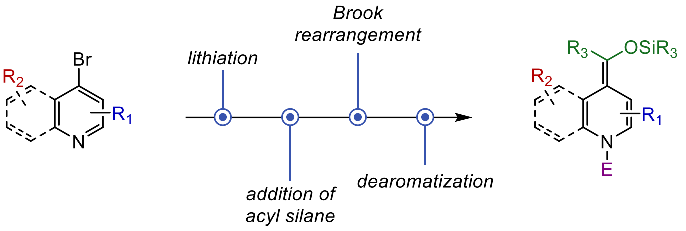


Figure 1. [1,2]-Brook rearrangement

In this study, we developed a four-step one-pot reaction that includes lithiation, nucleophilic addition, Brook rearrangement, and dearomatization reactions to allow the formation of non-aromatic *N*-heterocycles with functional capabilities from readily available precursors (**Scheme 1**).[6] Subsequent functionalization procedures allow access to a variety of complex structures.



Features

- *one-pot operation*
- *available precursors*
- *>30 examples*
- *complex architectures*

Scheme 1. one-pot process to access non-aromatic N-heterocycles

References:

1. Brook, A. G. Isomerism of Some α-Hydroxysilanes to Silyl Ethers. *J. Am. Chem. Soc.* **1958**, *80*, 1886–1889.
2. Jiang, X.-L.;. Bailey W. F. Facile Retro-[1,4]-Brook Rearrangement of a [(2-Siloxycyclopentyl)methyl]lithium Species. *Organometallics* **1995**, *14*, 5704–5707.
3. Kawashima, T.; Naganuma, K.; Okazaki, R. Generation and Decomposition of a Pentacoordinate Spirobis[1,2-oxasiletanide]. *Organometallics* **1998**, *17*, 367–372.
4. Smirnov, P.; Mathew, J.; Nijs, A.; Katan, E.; Karni, M.; Bolm, C.; Apeloig, Y.; Marek, I. One-Pot Zinc-Promoted Asymmetric Alkynylation/Brook-Type Rearrangement/Ene–Allene Cyclization: Highly Selective Formation of Three New Bonds and Two Stereocenters in Acyclic Systems. *Angew. Chem. Int. Ed.* **2013**, *52*, 13717–13721.
5. Eppe, G.; Didier, D.; Marek, I. Stereocontrolled Formation of Several Carbon–Carbon Bonds in Acyclic Systems. *Chem. Rev.* **2015**, *115*, 9175–9206.
6. Mondal, R.; **Agbaria, M**.; Cohen, O.; Nairoukh, Z. Rearrangement as Trigger for Dearomatization Reaction: Synthesis of Non-Aromatic N-Heterocycles. *Chem. Eur. J.* **2024**, *30*, e2023035.

Poster no. P_OOC_21

Push-Pull Bimanes: Bright Opportunities for Fluorescent Sensors

Nathaniel Chennattuparambil Roy[a], Joy Karmakar[b] and Flavio Grynszpan[a]*

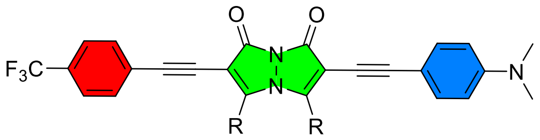
[a] *Dept. of Chemical Sciences, Ariel University, Ariel, Israel.* [b] *Dept. of Pediatrics, School of Medicine, U. of California, San Francisco, CA, US.*

E-mail: flaviog@ariel.ac.il

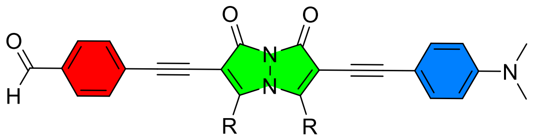
Organic π-conjugated molecules bearing electron-donor (D) and -acceptor (A) groups and exhibiting intramolecular charge transfer (ICT) properties are commonly referred to as push–pull systems.[1] Push-pull chromophores are of a dipole nature and present a vivid coloration, electrochemical responses, and crystalline structure. Nonlinear optical (NLO) characteristics, originate from the intermolecular interaction between the D and A components. Push-pull chromophores are versatile and have found applications in diverse fields such as anion sensors, fluorescence imaging, nonlinear optics, and organic solar cells.[2]

In the past, our group focused on the synthesis and investigation of novel bimane derivatives as highly sensitive fluorescent sensors for different analytes.[3-5] Recently, we introduced the fluorescent bimane core as π-conjugating spacer connecting D and A moieties leading to "push-pull bimanes".

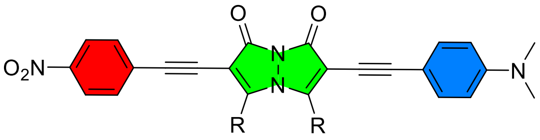
We synthesized and examined two series of push-pull bimane chromophores (**1-8**) combining a *N,N*-dimethylamine group as donor with four different acceptor groups (-CHO, -CF_3, -NO_2, -CH=C(CN)$_2$).



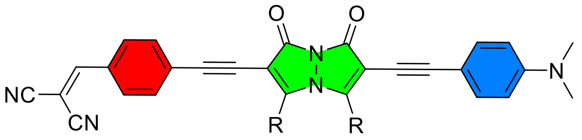
1. R = Me
2. R = Ph



3. R = Me
4. R = Ph



5. R = Me
6. R = Ph



7. R = Me
8. R = Ph

The photophysical properties of these novel bimanes were investigated. They absorb light in the range 448 to 505 nm and emit in the range 547 to 688 nm in a solvent dependent manner. Interstingly, when exposed to hydrazine, probe **8** undergoes distinctive spectral changes observable to the naked-eye. The reaction of hydrazine with the dicyanovinyl group produces the corresponding hydrazone thwarting the ICT and leading to noticeable blue shifts in both its absorption and fluorescence spectra. The study of the colorimetric and fluorometric detection of hydrazine by **8**, as a molecular sensor, will be presented.

References:

(1) Gompper, R.; Wagner, H. -U. Donor-Acceptor-Substituted Cyclic π-Electron Systems-Probes for Theories and Building Blocks for New Materials, *Angew. Chem. Int. Ed.* **1988**, *27(11)*,1437–1455.
(2) Bureš, F. Fundamental Aspects of Property Tuning in Push-Pull Molecules. *RSC Adv.* **2014**, *4*, 58826–58851
(3) Karmakar, J.; Pramanik, A.; Joseph, V.; Marks, V.; Grynszpan, F.; Levine, M. A Dipodal Bimane–Ditriazole–DiCu(II) Complex Serves as an Ultrasensitive Water Sensor. *Chem. Commun.* **2022**, *58 (16)*, 2690–2693.
(4) Pramanik, A.; Karmakar, J.; Grynszpan, F.; Levine, M. Highly Sensitive Water Detection Through Reversible Fluorescence Changes in a syn-Bimane Based Boronic Acid Derivative. *Front. Chem.* **2022**, *9*, 782481.
(5) Pramanik, A.; Karmakar, J.; Grynzspan, F.; Levine, M. Facile Iodine Detection via Fluorescence Quenching of β-Cyclodextrin:Bimane-Ditriazole Inclusion Complexes. *Isr. J. Chem.* **2021**, *61 (3–4)*, 253–260.

Poster no. P_OOC_22

Plasmonic visible–near infrared photothermal activation of olefin metathesis enabling photoresponsive materials

Nir Lemcoff*[a] & Yossi Weizmann [a], [b], [c]

[a] *Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel.*

[b] *Goldman Sonnenfeldt School of Sustainability and Climate Change, Ben-Gurion University of the Negev, Beer-Sheva, Israel.*

[c] *Ilse Katz Institute for Nanotechnology Science, Ben-Gurion University of the Negev, Beer-Sheva, Israel.*

E-mail: nirlem@post.bgu.ac.il

Light-induced catalysis and thermoplasmonics are emerging fields with the potential to create promising avenues for innovative research. Recent advancements in light-induced olefin metathesis have resulted in novel applications within polymer and material science. However, further improvements in reaction scope and efficiency are still needed. In this work, we detail the activation of latent ruthenium-based olefin metathesis catalysts using the photothermal response of plasmonic gold nanobipyramids (AuBPs). The ability to synthetically control the size of AuBPs in a straightforward manner allows for the generation of tunable localized surface plasmon resonance bands. This tunability enables catalyst initiation at a selected wavelength in the low-energy visible and near infrared regions. We successfully applied this approach to several olefin metathesis reactions including the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene, resulting in plasmonic polymer composites characterized by exceptional photoresponsive and mechanical properties. Importantly, the plasmonic photothermal method demonstrated significantly higher efficiency compared to conventional heating in all tested metathesis processes. This work may serve as a steppingstone towards the development of a broad range of photoinduced olefin metathesis processes and, more generally, photoinduced latent organic reactions by direct photothermal activation of thermally latent catalysts.

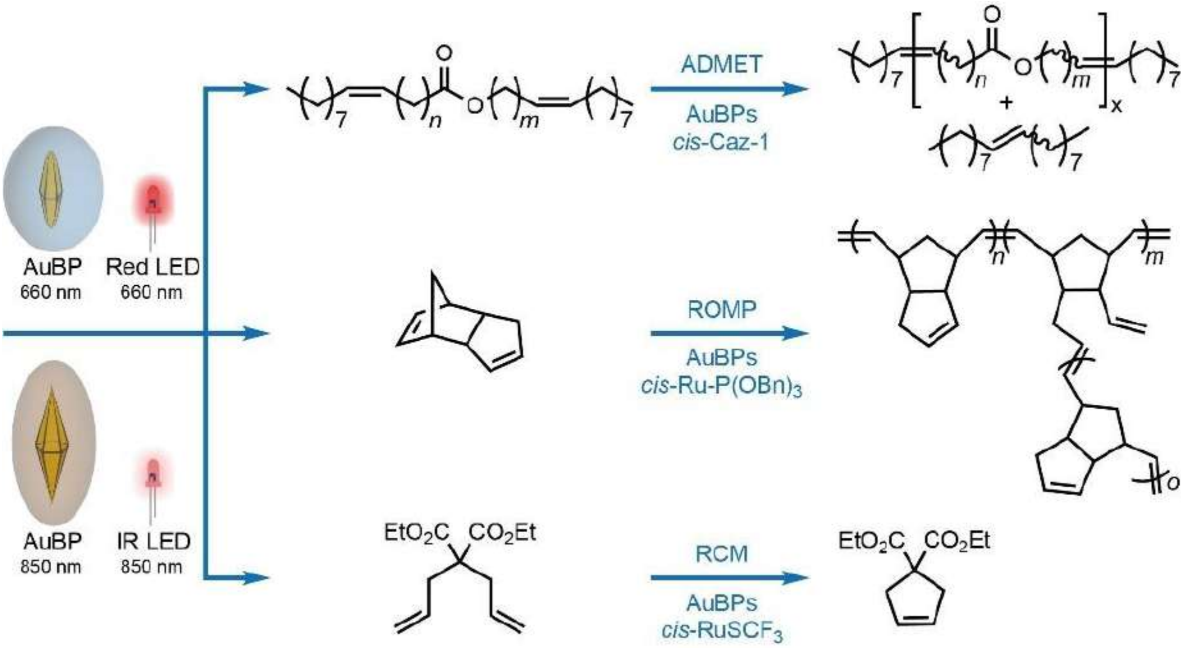


Figure 1: Thermoplasmonic activation was shown to enable efficient catalyst activation with low energy visible and infrared light.

References:

1. Nir Lemcoff, Noy B. Nechmad, Or Eivgi, Elad Yehezkel, Ofir Shelonchik, Ravindra S. Phatake, Doron Yesodi, Anna Vaisman, Aritra Biswas, N. Gabriel Lemcoff and Yossi Weizmann. Plasmonic visible–near infrared photothermal activation of olefin metathesis enabling photoresponsive materials. *Nat. Chem.* **15**, 475–482, (2023)

Poster no. P_OOC_23

Synthesis of Polysubstituted Housane

Noam Orbach, Rahul Suresh, Ilan Marek*

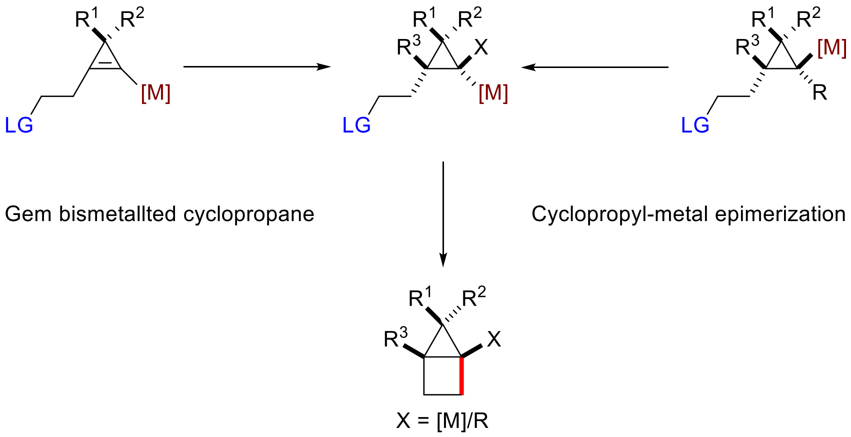
Chemistry department, Technion - Israel Institute of Technology

noam.orbach@campus.technion.ac.il

Bicyclo[2.1.0]pentane (housane) was first synthesized by Criegee and Rimmelin in 1956.[1] Since then, there were few methods for their synthesis,[2-3] but they lacked diversity in substitutions pattern and control over stereochemistry. Recently, our research group synthesized polysubstituted spiropentanes using carbometallation reactions of cyclopropenes.[4] We sought to utilize carbometallation reactions of cyclopropenes as the key step in accessing stereodefined polysubstituted housanes.

The direct approach for carbometallation-cyclization involves carbometallation of cyclopropene bearing a leaving group followed by 1,4-cyclization. However, a major challenge with this approach is accessing a leaving group that is in a favorable position (syn) with the nucleophilic metalated carbon. To address this, we came up with two strategies. The first involves carbometallation of the cyclopropene, followed by epimerization of the cyclopropyl metal to position the nucleophile in a favorable syn orientation with the leaving group, enabling cyclization. The second approach entails using a gem-bismetallated cyclopropane, which is achieved by lithiating the cyclopropene and then performing an ene-type reaction with allyl zinc bromide5. Subsequent cyclization allows the formation of the metalated housane which can be further functionalized

Approaches in accessing polysubstituted bicyclo[2.1.0]pentane (Housane)



References:

1. R. Criegee, A. Rimmelin. *Chem. Ber*, **1957**, *90*, 414.
2. M. Jung, V. N. Lindsay. *J. Am. Chem. Soc*. **2022**, *144*, 4764.
3. V. V. Semeno, V. O. Vasylchenko, B. V. Vashchenko, D. O. Lutsenko, R. T. Iminov, O. B. Volovenko, O. O. Grygorenko. *J. Org. Chem*. **2020**, *85*, 2321.
4. Y. Cohen, D. Toledano, I. Marek. *J. Am. Chem. Soc.* **2022**, *144*, 16732.
5. A. Levin, I. Marek. *Chem. Commun*, **2008**, 4300.

Poster no. P_OOC_24

Unlocking Polymer Design: The Power of Sulfur-Chelated Ruthenium Diiodo Catalysts

Noy B. Nechmad, [a] and N. Gabriel Lemcoff*[a]

[a] *Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel*

E-mail: (nechmad@post.bgu.ac.il, lemcoff@bgu.ac.il)

The development of new ruthenium benzylidene complexes bearing iodide ligands has led to the discovery of catalysts with unique selectivities, opening up valuable opportunities for industrial and academic applications. This work presents a detailed study of the synthesis, characterization, and catalytic properties of two such complexes, **Ru-S-Ph-I** and **Ru-S-CF$_3$-I**.[1-3]

A remarkable observation was made with **Ru-S-Ph-I**: when mixed with neat dicyclopentadiene (DCPD), the most reactive and widely used ROMP monomer, the liquid mixture remained unaffected even after prolonged periods. This highlights the remarkable latency of this complex towards this important industrial monomer. Intriguingly, addition of (Bu)$_4$NCl, even after a week's standing, immediately activated the complex by facilitating anionic ligand exchange, forming **Ru-S-Ph-Cl** in situ and initiating polymerization of the mixture. Anionic ligand exchange could also be triggered by the addition of photo-active chloride-releasing Cl-BODIPY, enabling an efficient Photoinduced ROMP (PROMP) sequence using visible light. Given its unusual reactivity, **Ru-S-Ph-I** was successfully employed in the recycling and repurposing of polyolefin polymers. The catalyst effectively depolymerized 1,4-cis-polybutadiene into small cyclic molecules, including the highly strained 1,5-cyclooctadiene, which serves as a valuable monomer.

A simple modification of the catalyst by replacing the sulfur substituent from phenyl to trifluoromethyl resulted in a dramatic change in reactivity. While DCPD readily polymerizes with conventional Ru catalysts, **Ru-S-CF$_3$-I** exhibited an exceptional ability to selectively ring-open DCPD and its derivatives to produce valuable 1,3-divinyl-hexahydropentalenes (DVHP) through a ring-opening metathesis reaction, bypassing the expected polymerization process. DVHP is a crucial intermediate in the development of epoxy compounds for high glass transition temperature thermosets, UV coatings, and in the semiconductors packaging industry. The significance of these compounds is underscored by a patent filed by Dow Global Technologies LLC on their synthesis. Notably, the iodide catalyst afforded high yields in short reaction times without the need for a large excess of either reagent, representing a significant improvement over previous methods.

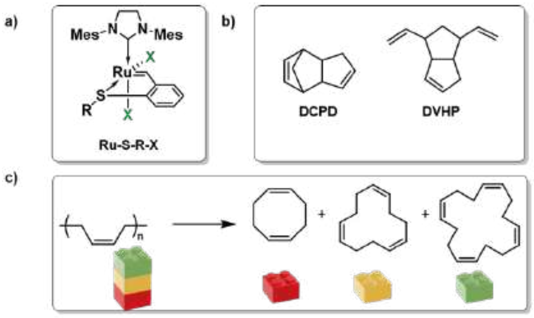


Figure 1: a) Ruthenium sulfur-chelated complexe, R=Ph/CF3; X=chloride/iodide. b) The stracture of DCPD and DVHP. c) Reaction scheme for the depolymerization of polybutadiene.

References:

1. Elisa Ivry†, Noy B. Nechmad†, Mark Baranov, Israel Goldberg, and N. Gabriel Lemcoff, Influence of Anionic Ligand Exchange in Latent Sulfur-Chelated Ruthenium Precatalysts, *Inorg. Chem.* **2018**, 57, 15592.
2. Noy B. Nechmad, Ravindra Phatake, Elisa Ivry, Albert Poater, and N. Gabriel Lemcoff, Unprecedented Selectivity of Ruthenium Iodide Benzylidenes in Olefin Metathesis Reactions, *Angew. Chem. Int. Edit.* **2020**, 59, 3539.
3. Noy B. Nechmad†, Victoria Kobernik†, Naziha Tarannam, Ravindra Phatake, Or Eivgi, Sebastian Kozuch and N. Gabriel Lemcoff, *Angew. Chem. Int. Ed.* **2021**, 60, 6372.

Poster no. P_OOC_25

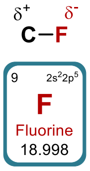
Understanding the Conformational Behavior of Fluorinated Aliphatic SHeterocycles

Nwar Egbaria,[a] Mohamed Agbaria,[a] and Zackaria Nairoukh[a]

Institute of Chemistry, The Hebrew University of Jerusalem

E-mail: nwar.egbaria@mail.huji.ac.il, mohamed.agbaria1@mail.huji.ac.il, z.nairoukh@mail.huji.ac.il

The introduction of fluorine atoms into molecules and materials across many fields of academic and industrial research is now commonplace, owing to their unique properties and effects.[1] Specifically, the incorporation of fluorine into drug lead candidates has been recognized as a powerful strategy for enhancing their pharmacokinetic and physicochemical properties.[2]

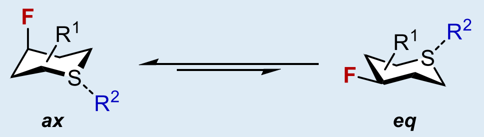


Impact of fluorine substitution in drugs

- physicochemical and pharmacokinetic properties
- metabolic stability
- membrane permeability
- drug potency
- conformation

In addition to their recognized properties, fluorine substitution can influence the conformational behavior of aliphatic cyclic and acyclic systems.[3] Previously, we observed this effect in fluorinated piperidines, where the axial conformation was predominant and primarily stabilized due to hyperconjugation interactions.[4] This observation prompted us to investigate whether similar behavior could be observed in other aliphatic heterocycles, such as tetrahydrothiopyran derivatives.

To address this question, we prepared a set fluorinated tetrahydrothiopyran derivatives using deoxy-fluorination protocols. The conformational behavior of these compounds was analyzed by NMR spectroscopy, revealing a selective adoption of axial structures. X-Ray analyses confirmed the consistency of our findings in solution. Additionally, computational studies showed that the conformational behavior is influenced by the interplay of different forces, including electrostatic interactions and hyperconjugation (**Scheme 1**).



The origin of axial-F preference

- hyperconjugation
- charge-dipole interaction
- dipole-dipole interaction
- steric repulsion

Scheme 1: The conformational preferences of fluorinated S-heterocycles systems

References:

1. Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. Fluorine in medicinal chemistry. *Chem. Soc. Rev.* **2008**, *37*, 320. (b) Lowe, P. T.; O'Hagan, D. A role for fluorine in flavours, fragrances and pheromones. *J. Fluor. Chem.* **2020**, *230*, 109420.
2. Gillis, E. P.; Eastman, K. J.; Hill, M. D.; Donnelly, D. J.; Meanwell, N. A. Applications of Fluorine in Medicinal Chemistry *J. Med. Chem.* **2015**, *58*, 8315.
3. Mondal, R.; Agbaria, M.; Nairoukh, Z. Fluorinated Rings: Conformation and Application. *Chem. Eur. J.* **2021**, *27*, 7193.
4. Nairoukh, Z.; Strieth-Kalthoff, F.; Bergander, K.; Glorius, F. Understanding the Conformational Behavior of Fluorinated Piperidines: The Origin of the Axial-F Preference. *Chem. Eur. J.* **2020**, *26*, 6141.
5. Egbaria, N.; Agbaria, M.; Nairoukh, Z. Understanding the conformational behavior of fluorinated aliphatic *S*-heterocycles. *Manuscript under preparation*.

Poster no. P_OOC_26

Chiral Guided Growth of Crystals-on-Crystals: Predictable Morphologies with Local Functionalization

Ofir Eisenberg, Qiang Wen, Maria Chiara di Gregorio, Linda J. W. Shimon, Lothar Houben, Ifat Kaplan-Ashiri,

Tali Dadosh, Yoseph Addadi, Michal Lahav,* and Milko E. van der Boom*

Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Herzl 234, Rehovot, Israel

E-mail: ofir.eisenberg@weizmann.ac.il, michal.lahav@weizmann.ac.il, milko.vanderboom@weizmann.ac.il

Metal-organic frameworks (MOFs) are a promising class of porous, crystalline materials with diverse potential applications. The intensive research of MOFs has led to an emerging family of hybrid crystals constructed by the conjugation of two or more different MOF units. Such hybrid crystals mainly consist of a core-shell structure, in which a guest MOFs is grown on a pre-synthesized host MOF, isotropically. Herein, we designed a unique MOF-on-MOF by combining two crystal structures resulting in a dumbbell-shaped morphology. The dumbbell's cups have been formed by epitaxial growth on the bases of the dumbbell's rod, due to a common (001) facet. These crystals maintain their original morphologies and crystal structures in the MOF-on-MOF and their chiral channels are perfectly aligned along their long axis. Extensive single-crystal X-ray studies and reconstruction of the grain boundary between the two structures confirmed that there is chirality transfer from the rod to the cups. The two crystal structures have chiral channels with different nano-size diameters and hydrophobicity. We were able to utilize this difference in hydrophobicity and selectively confine aligned arrays of different chromophores to the rod and cup regions resulting in selective optical functionalization of these unique micro-scale objects.

Poster no. P_OOC_27

Chemical Engineering of Artificial Transcription Factors

Omer Harel and Muhammad Jbara*

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, 69978 Israel

*Correspondence to: jbaram@tauex.tau.ac.il

Transcription factors (TFs) play a pivotal role in numerous cellular processes, acting as molecular switches that govern the conversion of genes into functional products. For example, Myc and Max TFs form dynamic complexes that bind specific DNA sequences, influencing approximately 15% of the genome. Dysregulation of the Myc-Max TFs is implicated in various human cancers, highlighting their therapeutic potential. Here we leveraged chemical protein synthesis to tackle this system by engineering artificial TFs with defined modifications.[1],[2] We combined chemoselective protein ligations and organometallic palladium reagents[3] to produce a focused library of DNA-binding mini-proteins aimed to target the Myc/Max system.

[1] **O. Harel** and M. Jbara, 'Posttranslational Chemical Mutagenesis Methods to Insert Posttranslational Modifications into Recombinant Proteins', *Molecules 2022, Vol. 27, Page 4389*, vol. 27, no. 14, p. 4389, Jul. 2022.

[2] **O. Harel** and M. Jbara, 'Chemical Synthesis of Bioactive Proteins', *Angewandte Chemie International Edition*, vol. 62, no. 13, p. e202217716, Mar. 2023.

[3] X. Lin, R. V. Nithun, R. Samanta, **O. Harel**, and M. Jbara, 'Enabling Peptide Ligation at Aromatic Junction Mimics via Native Chemical Ligation and Palladium-Mediated S-Arylation', *Org Lett*, vol. 25, no. 25, pp. 4715–4719, Jun. 2023.

Poster no. P_OOC_28

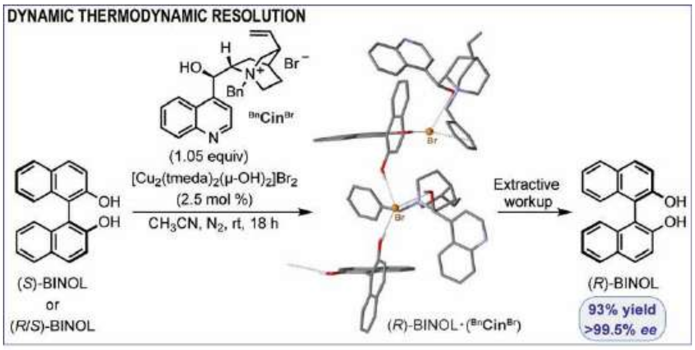
Dynamic Thermodynamic Resolution of Racemic 1,1’-Binaphthyl-2,2’-diol (BINOL).

Omer Shaashua,[a] Dennis Pollok,[b] Alina Dyadyuk,[a] Alexander I. Shames,[c] Siegfried R. Waldvogel,*,[b] Doron Pappo*,[a]

[a] *Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.*
[b]*Department of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany*
[c]*Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva 8410501, Israel*

E-mail: pappod@bgu.ac.il

1,1’-Binaphthyl-2,2’-diol (BINOL) represents an axially chiral molecule extensively utilized in various fields of chemistry[1]. Its significance arises from its role as a fundamental chiral building block in ligand and organocatalyst synthesis for asymmetric transformations[2], alongside its application in molecular recognition[3] and metal-organic frameworks[4]. While the synthesis of racemic BINOL is established, obtaining optically pure (R)- or (S)-BINOL presents challenges addressed through three primary methodologies: enantioselective oxidative coupling, resolution with chiral derivatizing agents (CDA), and chemical or enzymatic kinetic resolution[5]. Enantioselective oxidative coupling offers direct access to optically pure BINOL but incurs high costs and purification steps. Conversely, resolution methods offer simplicity but are constrained by a theoretical yield limit of 50%. To mitigate these limitations, an electron-borrowing dynamic thermodynamic resolution system was developed to achieve 100% theoretical yield in the production of (R)-BINOL from racemic mixtures. This poster elucidates the implementation of this system in the dynamic thermodynamic resolution of BINOLs, highlighting its efficacy in generating large quantities of enantiopure BINOLs.



Scheme 1: Dynamic thermodynamic resolution of BINOL.

References:

(1) Wencel-Delord, J.; Panossian, A.; Leroux, F. R.; Colobert, F. Recent Advances and New Concepts for the Synthesis of Axially Stereoenriched Biaryls. *Chem. Soc. Rev.* **2015**, *44* (11), 3418–3430. https://doi.org/10.1039/C5CS00012B.
(2) Shibasaki, M.; Matsunaga, S. Design and Application of Linked-BINOL Chiral Ligands in Bifunctional Asymmetric Catalysis. *Chem. Soc. Rev.* **2006**, *35* (3), 269. https://doi.org/10.1039/b506346a.
(3) Yu, F.; Chen, Y.; Jiang, H.; Wang, X. Recent Advances of BINOL-Based Sensors for Enantioselective Fluorescence Recognition. *The Analyst* **2020**, *145* (21), 6769–6812. https://doi.org/10.1039/D0AN01225D.
(4) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. A Series of Isoreticular Chiral Metal–Organic Frameworks as a Tunable Platform for Asymmetric Catalysis. *Nat. Chem.* **2010**, *2* (10), 838–846. https://doi.org/10.1038/nchem.738.
(5) Brunel, J. M. BINOL: A Versatile Chiral Reagent. *Chem. Rev.* **2005**, *105* (3), 857–898. https://doi.org/10.1021/cr040079g.

Poster no. P_OOC_29

Subtle Polymer Dynamics Revealed by Fluorescence Lifetime Imaging Microscopy

Or Eivgi[a,b] and Suzanne A. Blum*[a]

[a] *Department of Chemistry, University of California, Irvine, Irvine California, 92697-2025 United States*

[b] *Current affiliation: Institute for Molecular Systems Engineering and Advanced Materials, Universität Heidelberg, Im neuenheimer Feld 225, Heidelberg, 69120, Germany*

E-mail: or.eivgi@uni-heidelberg.de

Fluorescence lifetime imaging microscopy (FLIM) is an emerging analytical technique to investigate chemical processes, providing access to unique granular mechanistic information with excellent spatial resolution. Here, FLIM was developed to investigate the dynamics of ring-opening-metathesis-polymerization- (ROMP-) based polymeric materials. By designing ROMP-functionalized viscosity-sensitive fluorescent molecular rotors that change their fluorescence lifetime based on the viscosity of their polymeric microenvironment, simultaneous imaging of changing physical parameters and catalytic activity in living polymers was achieved for the first time.[1] These data show that catalytic turnover decreases with reaction progress due to decreased molecular diffusion caused by the increasing polymer viscosity, rather than by chemical decomposition of the catalyst. Moreover, it was demonstrated that these microenvironment viscosity changes during polymerization are monomer-dependent, accelerated by crosslinking, and variable in the rate of change between different particles and subparticle regions of the same sample. Together, these data provide a physical mechanism for irregular reaction kinetics observed for single Grubbs catalysts that may impact molecular weight polydispersity on the bulk scale. The sensitivity of these viscosity-sensitive fluorescent molecular rotors also uncovered and quantitatively elucidated previously undisclosed differential block-selective responses toward solvation changes upon addition of DMSO and THF to self-assembled ROMP-based amphiphilic block copolymers (Figure 1).[2] The method provided unique information on block-selective solvent-triggered assembly and disassembly mechanisms that are also influenced by material morphology and method of preparation[3], revealing behaviors invisible to or with superior sensitivity to traditional spectroscopic and imaging methods.

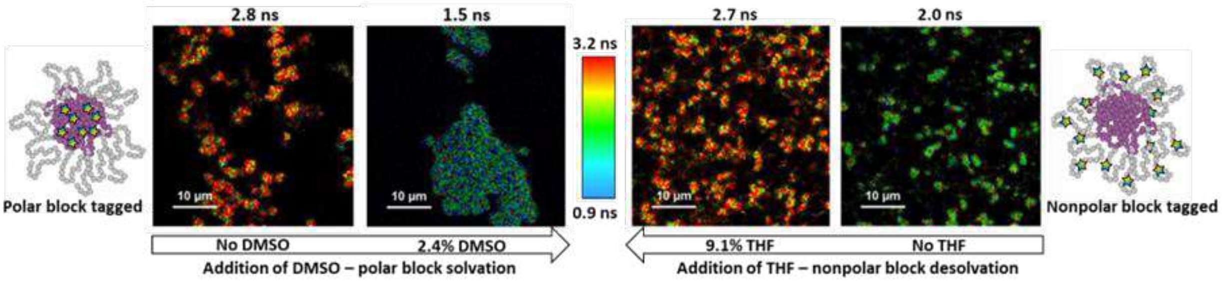


Figure 1. Block-selective solvation of the polar block upon addition of a good solvent (DMSO) and block-selective desolvation of the nonpolar block upon addition of anti-solvent (THF).

References:

1. Eivgi, O.; Blum S. A. Real Time Viscosity-Catalytic activity Relationships in the Microscale *J. Am. Chem. Soc.* **2022**, 144, 13574–13585.

2. Eivgi, O.; Ravenscroft, A. C.; Blum, S. A. Imaging Block-Selective Copolymer Solvation. *J. Am. Chem. Soc.* **2023**, 145, 2058–2063.

3. López, P. A.; Eivgi, O.; Blum, S. A. Nature of Self-Assembly Revealed by Individual-Polymer-Block Solvation. Submitted

Poster no. P_OOC_30

Synthesis of Stereodefined Polysubstituted Bicyclo[1.1.0]butanes

Rahul Suresh, Noam Orbach, Ilan Marek*
Technion-Israel Institute of Technology, Technion City, Haifa
E-mail: rahul.suresh9@gmail.com

Bicyclo[1.1.0]butane (BCB), the smallest fused ring carbocycle has fascinated chemists because of the unusual bonding1 and reactivity. The central C-C bond of BCBs behaves like a pseudo-double bond reacting with nucleophiles,[2,5] electrophiles,[6-8] radicals[9] and carbenes.[7] The “strain release” of BCBs has been used to access intricate molecular frameworks[2,3] and label peptides.[4] However, these functionalizations were limited by the availability of polysubstituted BCBs. The available ones are either electronically biased or with few substituents.[2,5,7,9]

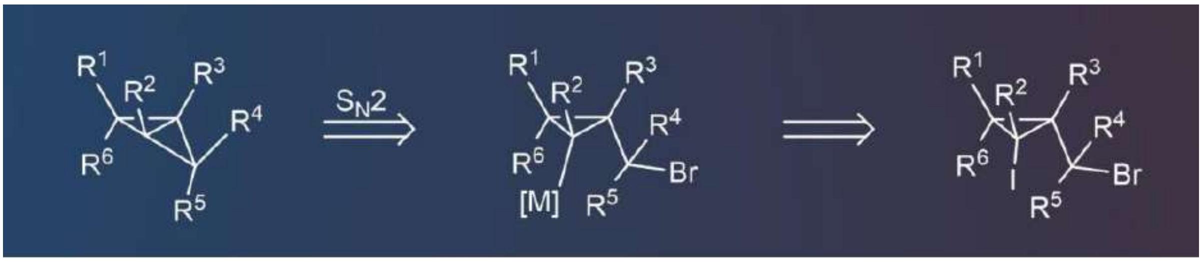


Figure 1: Synthesis of Polysubstiuted BCBs.

(Bromomethyl)-iodocyclopropanes undergoes lithium-iodine exchange to generate the lithiated cyclopropanes which undergoes an intramolecular S_N2 reaction to furnish diastereoand enantioenriched polysubstituted BCBs.[10] The former can be accessed easily from carbometallation reactions of cyclopropenes.[11] This methodology will allow easy, reliable, and efficient route for the synthesis of diastereo- and enantioenriched polysubstituted BCBs.

References:

1. M. Pomerantz, E. W. Abrahamson, *J. Am. Chem. Soc*. **1996**, *88*, 3970.
2. R. Panish, S. R. Chintala, D. T. Boruta, Y. Fang, M. T. Taylor, J. M. Fox, *J. Am. Chem. Soc*. **2013**, *135*, 9283.
3. A. Fawcett, T. Biberger, V. K. Aggarwal, *Nat. Chem*. **2019**, *11*, 117.
4. P. S. Baran et al. *J. Am. Chem. Soc*. **2017**, *139*, 3209-3226.
5. Y. Gaoni, A. TomažIč, *J. Org. Chem.* **1985**, *50*, 2948.
6. W. Von, J. F. Coburn, *Tetrahedron Lett*. **1965** , *6*, 991.
7. R. E. McNamee, A. L. Thompson, E. A. Anderson, *J. Am. Chem. Soc.* **2021**, *143*, 21246.
8. R. E. McNamee, N. Frank, K. Christensen, F. Duarte, E. A. Anderson, Taming non-classical carbocations to control small ring reactivity, *ChemRxiv,* **2023**, doi:10.26434/chemrxiv-2023-zgdq8.
9. K. B. Wiberg, R. P. Ciula, *J. Am. Chem. Soc*. **1959,** *81*, 5261.
10. A. I. D’yachenko, S. V Zotova, O. V Bragin, N. M. Abramova, A. Nesmeyanova, N. D. Zelinskii, *Izv. Akad. Nauk.* **1985**, 2043.
11. Y. Cohen, I. Marek, *Acc. Chem. Res.* **2022**, *55*, 2848.

Poster no. P_OOC_31

ortho-Selective Oxidative Coupling of Phenols by Hydroxo Multicopper(II) Clusters

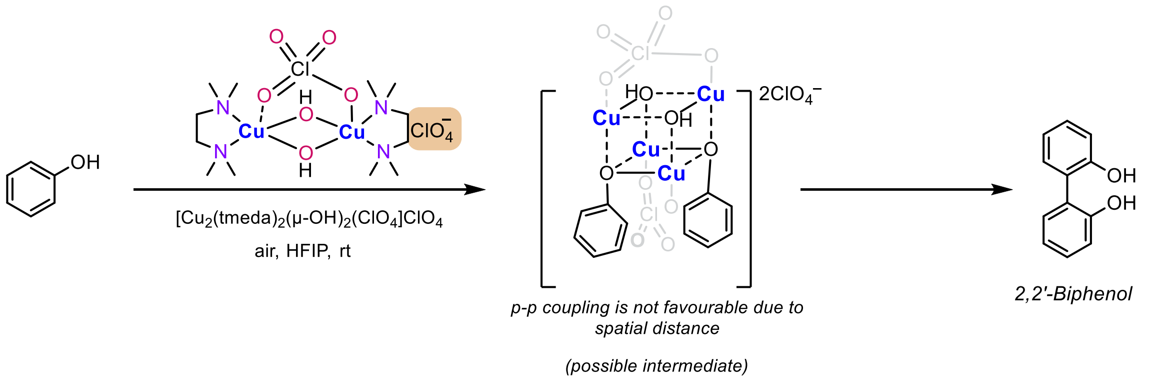
Ratnadeep Bera[a], Lina Kertzman[a], Anna Libman[a], Mor Ben Lulu[a] and Doron Pappo *[a]

[a] *Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.*

E-mail: pappod@bgu.ac.il

Oxidative coupling reactions offer a powerful strategy in forging carbon-carbon and carbon-heteroatom bonds.[1] The oxidative coupling of simple phenols poses a considerable challenge, given the presence of multiple reactive sites leading to the formation of a mixture of biphenols and biaryl-ether regioisomers.[2]

Our group has recently introduced novel $[Cu^{II}_n(tmeda)_n(\mu\text{-}OH)_n](Y)_n$ ($^{NN}\mathbf{Cu_2}^{Y}$, NN = bidentate nitrogen ligand, Y = OTf or ClO_4, n = 2 or 4) clusters as selective catalysts for aerobic oxidative phenol macrocyclization (OxPM) of tethered diphenols in 1,1,1,3,3,3-hexafluoroisopropan-2-ol (HFIP).[3]
The poster presents the application of these multicopper clusters for the unprecedented ortho-selective oxidative homocoupling of phenols, affording 2,2'-biphenol compounds in a high degree of regioselectivity. The method's generality is demonstrated through the preparation of different 2,2'-biphenols. Additionally, we showcase the regioselective homocoupling of tyrosine and coumarin derivatives.



$[Cu_2(tmeda)_2(\mu\text{-}OH)_2(ClO_4]ClO_4$
air, HFIP, rt

p-p coupling is not favourable due to spatial distance

(possible intermediate)

2,2'-Biphenol

Scheme 1: Oxidative coupling of phenol.

References:

(1) Wu, J.; Kozlowski, M. C. Catalytic Oxidative Coupling of Phenols and Related Compounds. *ACS Catal* **2022**, *12* (11), 6532–6549. https://doi.org/10.1021/acscatal.2c00318.
(2) Kang, H.; Lee, Y. E.; Reddy, P. V. G.; Dey, S.; Allen, S. E.; Niederer, K. A.; Sung, P.; Hewitt, K.; Torruellas, C.; Herling, M. R.; Kozlowski, M. C. Asymmetric Oxidative Coupling of Phenols and Hydroxycarbazoles. *Org Lett* **2017**, *19* (20), 5505–5508. https://doi.org/10.1021/acs.orglett.7b02552.
(3) Libman, A.; Ben-Lulu, M.; Gaster, E.; Bera, R.; Shames, A. I.; Shaashua, O.; Vershinin, V.; Torubaev, Y.; Pappo, D. Multicopper Clusters Enable Oxidative Phenol Macrocyclization (OxPM) of Peptides. *J Am Chem Soc* **2023**, *145* (38), 21002–21011. https://doi.org/10.1021/jacs.3c06978.

Poster no. P_OOC_32

A Journey to the Land of Polycyclic Aromatic Systems

Renana Gershoni-Poranne

Technion—Israel Institute of Technology, Technion City, Haifa 32000 Israel
rporanne@technion.ac.il

Polycyclic aromatic systems (PASs) are among the most prevalent and impactful classes of compounds in the natural and man-made world. Though aromatic systems have captured the fascination of chemists for almost two centuries, a general conceptual framework for understanding and predicting the structure-property relationships of polycyclic systems remains elusive. Yet, the structure-property relationships of PBHs have both conceptual and practical implications and understanding them can enable design of new functional compounds. We address this gap using a combination of computational chemistry and data science tools.

We first interrogated polybenzenoid hydrocarbons using a combination of traditional computational techniques, including characterization of their aromatic character in the S_0 and T_1 states (described with the NICS metric), their spin density in the T_1 state, and their S_0—T_1 energy gaps. Regularities were revealed that allowed for simple and intuitive design guidelines to be defined.[1]

To verify these guidelines in a data-driven manner, we generated a new database – the COMPAS Project[2] and developed two types of molecular representation to enable machine- and deep-learning models to train on the new data: a) a text-based representation[3] and b) a graph-based representation.[4]

In addition to their predictive ability, we demonstrate the interpretability of the models that is achieved when using these representations. The extracted insight in some cases confirms well-known “rules of thumb” and in other cases disproves common wisdom and sheds new light on this classical family of compounds.

Finally, we implemented a generative model that design novel PASs with targeted properties in an effective and efficient manner, demonstrating the first inverse design of PASs.[5]

(1) Markert, G.; Paenurk, E.; Gershoni-Poranne, R. Prediction of Spin Density, Baird-Antiaromaticity, and Singlet–Triplet Energy Gap in Triplet-State Polybenzenoid Systems from Simple Structural Motifs. *Chem. Eur. J.* **2021**, *27*, 1–14. https://doi.org/10.1002/chem.202100464.
(2) Wahab, A.; Pfuderer, L.; Paenurk, E.; Gershoni-Poranne, R. The COMPAS Project: A Computational Database of Polycyclic Aromatic Systems. Phase 1: Cata-Condensed Polybenzenoid Hydrocarbons. *J. Chem. Inf. Model.* **2022**, *62* (16), 3704. https://doi.org/10.1021/acs.jcim.2c00503.
(3) Fite, S.; Wahab, A.; Paenurk, E.; Gross, Z.; Gershoni-Poranne, R. Text-Based Representations with Interpretable Machine Learning Reveal Structure-Property Relationships of Polybenzenoid Hydrocarbons. *Journal of Physical Organic Chemistry* **2022**, e4458. https://doi.org/10.1002/poc.4458.
(4) Weiss, T.; Wahab, A.; Bronstein, A. M.; Gershoni-Poranne, R. Interpretable Deep-Learning Unveils Structure-Property Relationships in Polybenzenoid Hydrocarbons. **2022**. https://doi.org/10.26434/chemrxiv-2022-krng1.
(5) Weiss, T.; Cosmo, L.; Yanes, E. M.; Chakraborty, S.; Bronstein, A. M.; Gershoni-Poranne, R. Guided Diffusion for Inverse Molecular Design. ChemRxiv April 5, 2023. https://doi.org/10.26434/chemrxiv-2023-z8ltp.

Poster no. P_OOC_33

The First Planar, Not Twisted, Distannene – A Structural Alkene Analog. Synthesis, Isolation and X-ray Crystallography Characterization

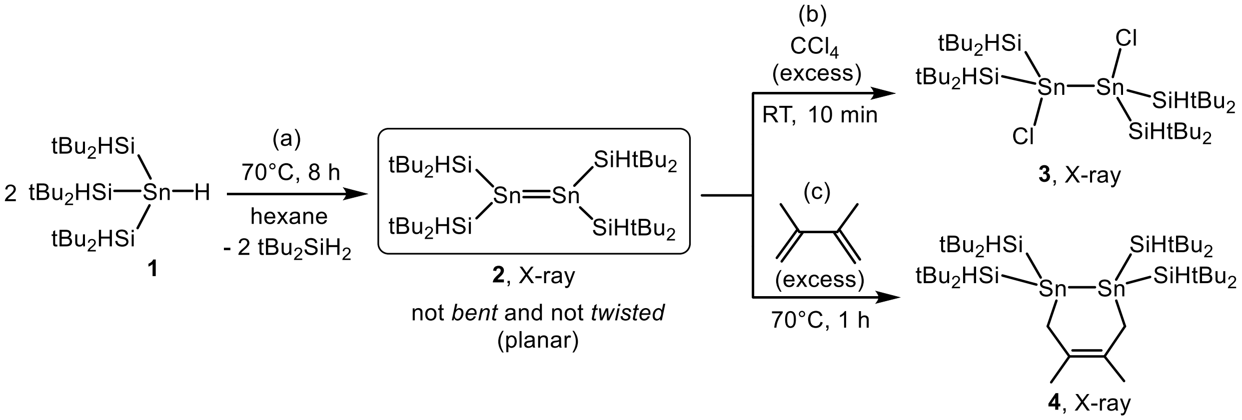
Roman Bashkurov,[a] Natalia Fridman,[a] Dmitry Bravo-Zhivotovskii,*[a] and Yitzhak Apeloig*[a]

[a]*Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*

E-mail: chrbrzh@technion.ac.il; apeloig@technion.ac.il

The tetrasilyl-substituted distannene, $(tBu_2HSi)_2Sn{=}Sn(SiHtBu_2)_2$ (**2**), was synthesized by mild thermolysis at 70°C of tris(di-t-butyl-hydridosilyl)stannane **1** in hexane (Scheme, step a). The X-ray structure of **2** (Figure) reveals several unique unusual structural properties: (1) the shortest Sn=Sn double bond (2.599 Å) among all acyclic distannenes; (2) a nearly planar geometry around both Sn atoms ($\Sigma\measuredangle Sn = 359.87°$); (3) a non-twisted Sn=Sn double bond. ***Thus, compound 2 represents the first example of a distannene featuring structural properties similar to those of a classical alkene***.

Reactions of **2** with carbon tetrachloride and 2,3-dimethylbuta-1,3-diene to give 1,2-dichlorodistannane **3** (Scheme, path b) and the [2+4] cycloadduct **4** (Scheme, path c), respectively, are characteristic for a Sn=Sn double bond.



Scheme. Synthesis of distannene **2** and its reactions with CCl_4 and 2,3-dimethylbuta-1,3-diene.

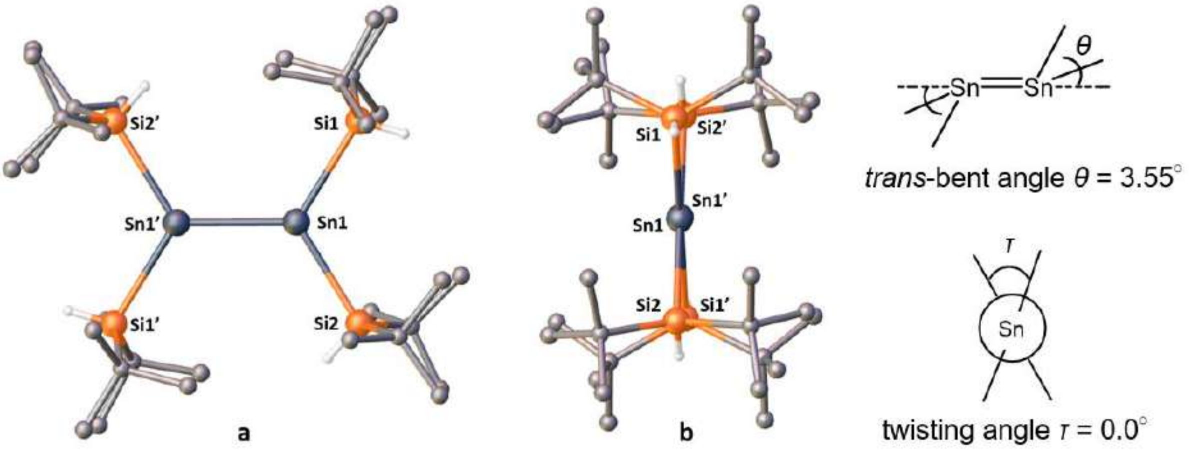


Figure. Olex2 drawing of the X-ray crystallographic molecular structure of distannene **2**; top view (**a**) and side view (**b**). Hydrogen atoms are omitted for clarity, except the hydrogens attached to the silyl groups. Selected structural parameters: r(Sn1-Sn1') = 2.599 Å, $\Sigma\measuredangle Sn = 359.87°$, ∡Si1-Sn1-Sn1'-Si1' = 180°.

References:

1. R. Bashkurov, N. Fridman, D. Bravo-Zhivotovskii, Y. Apeloig, *Chem. Eur. J.* **2023**, e202302678.

Poster no. P_OOC-34

Rational Design and Fabrication of Block Copolymer Templated Hafnium Oxide Nanostructure

Ruoke Cai[a], Inbal Weisbord[a], Shaked Caspi[b], Lilach Naamat[], Lior Kornblum[b], Alon Grinberg Dana[a], and Tamar Segal-Peretz*[a]

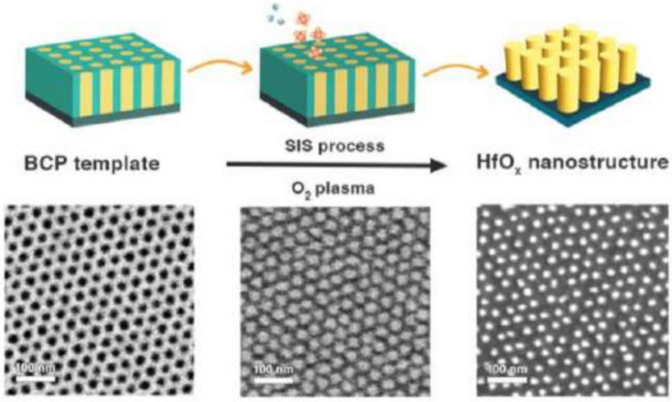
[a] The Wolfson Department of Chemical Engineering, Technion, Haifa 3200003, Israel

[b] The Andrew and Erna Viterbi Faculty of Electrical and Computer Engineering, Technion, Haifa 3200003, Israel

E-mail: tamarps@technion.ac.il

Hafnium oxide (HfO2) is an attractive material for optoelectronic applications and high-κ dielectrics in semiconductor devices due to its advantageous properties- high dielectric constant, wide band gap, and high stability. However, hafnium oxide nanostructure fabrication currently relies on complex nanofabrication processes. Sequential infiltration synthesis (SIS)- a method derived from atomic layer deposition (ALD), in which vapor phase precursors diffuse into polymers and react with them to form hybrid material, can provide a simple and cost-effective alternative for these processes. [1]

In this study, we expand the SIS library with the development of hafnium oxide SIS and demonstrate HfOx nanostructure fabrication via SIS within block copolymer (BCP) templates. Insights into the infiltration behavior of tetrakis(dimethylamino)hafnium (TDMAHf), the Hf precursor, in various homopolymers, were obtained by in situ quartz crystal microgravimetry (QCM) measurements. These insights guided us to judiciously choose BCP systems for HfOx nanofabrication, where polystyrene-block-poly(epoxyisoprene) (PS-b-EPI) and HfOx SIS at 95 °C showed exceptional selective growth of HfOx in the EPI domains. Density functional theory (DFT) calculations supported the experimental observation that TDMAHf exhibits higher reactivity with the EPI domain compared to the PS domain. Detailed investigation of the templated HfOx nanostructures using scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) further validates the presence and distribution of Hf and O elements, as well as two oxidation states of the oxide. Our work presents the first report of HfOx SIS in BCPs, providing a method for HfOx nanostructure fabrication with tuned morphology and precise control over the HfOx growth. Furthermore, it contributes to the growing SIS library and its new avenues for functional nanomaterials with customizable properties fabrication.



Scheme or Figure 1: Schematic illustration of the HfOx nanostructure fabrication process through selective SIS growth in self-assembled BCP templates

Acknowledgements: We thank the ICS for financial support.

References: 1. Peng, Q.; Tseng, Y.-C.; Darling, S. B.; Elam, J. W. A Route to Nanoscopic Materials via Sequential Infiltration Synthesis on Block Copolymer Templates. *ACS Nano* **2011**, 5 (6), 4600–4606.

Poster no. P_OOC_35

Deciphering the chemistry of B, N-substituted polybenzenoid hydrocarbons: A computational study

Sabyasachi Chakraborty, Itay Almog, and Renana Gershoni-Poranne*

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel

E-mail: (rporanne@technion.ac.il)

ata-condensed polybenzenoid hydrocarbons consist of multiple fused benzene units where adjacent subunits share o atoms. These molecules find applications across various fields, benefiting from their broad optoelectronic operties. Modifying their electronic features can be achieved through substitutions and/or extensions of the pi-system specific patterns. An under-explored method involves exchanging two carbon atoms with an isoelectronic boron and rogen pair, offering the potential for diverse chemical spaces with unique optoelectronic properties. Despite its omise, a comprehensive conceptual and quantitative framework that rationalizes these structure-property lationships is lacking. In this study, we computationally model a representative subset of the chemical space of B and substituted polybenzenoid systems, encompassing approximately 20,000 molecules, at the CAM-B3LYP/def2-/P//CAM-B3LYP/def2-TZVPD level. Our investigation focuses on understanding the impact of B, N substitution on rious computationally accessed molecular properties. Additionally, we assess the effectiveness of a regression model at utilizes readily accessible chemical bonding features to predict molecular properties obtained at the DFT level. Our al is to decipher the influence of B, N substitution on cc-PBHs, shedding light on design principles that could guide e construction of novel functional molecules.

knowledgments: We thank Technion – Israel Institute of Technology, the Branco Weiss Fellowship (awarded to R. G. P), and H Zurich's Euler cluster.

Poster no. P_OOC_36

Synthesis of Diastereoenriched AllylBoronic Esters via 1,2-Metalate Rearrangement

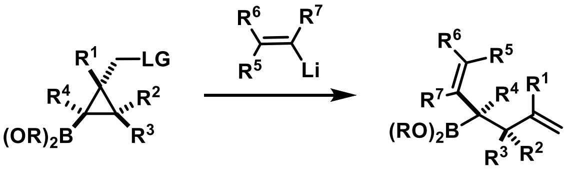
S. Di Silvio[a] and I. Marek*[b]

[a,b] Technion – Israel Institute of Technology, Technion City , Haifa

E-mail: sergio-di@campus.technion.ac.il
E-mail: chilam@campus.technion.ac.il

Allyl boronates are useful chemicals for forming C-C bonds through reactions with carbonyl compounds.[1] The reaction proceeds through a chair-like transition state (TS), allowing for control over double bond geometry and stereochemistry of the product.[2] Over the decades, chemists have developed several strategies to synthesize stereodefined allyl boronates, but most of them do not include α-disubstituted stereoenriched highly functionalized compounds.

We developed a methodology involving diastereoenriched polysubstituted borylated cyclopropanes,[3] which can be successfully ring-opened *via* 1,2-metalate rearrangement using organolithium reagents to obtain stereodefined acyclic allyl boronic esters.



Scheme 1. Stereoselective Synthesis of Allyl Boronic Esters.

References:

1. R.W. Hoffmann, *Pure Appl.Chem.*, **1988**, *60*, 123
2. R.W. Hoffmann, H. Zeiss, *Angew. Chem. Int. Ed.*, **1979**, *18*, 306
3. A. U. Augustin, S. Di Silvio, I. Marek, *J. Am. Chem. Soc.* **2022**, *144,* 36, 16298.

Poster no. P_OOC_37

A fluorescent PNA-merocyanine probe used for the detection of HER2 Uterine Serous Carcinoma (USC) cancer mRNA marker in cancerous cell extract

Alon Amir[a], Shirly Zisman-Martinez[a], Natalie Pariente-Cohen, Bilha Fischer

[a] Both authors contributed equally to this work

a *Department of Chemistry, Bar-Ilan University, Ramat Gan 5290002, Israel*

E-mail: agwalon@gmail.com, shirlyzisman@gmail.com, nataliepc1@gmail.com, Bilha.Fischer@biu.ac.il

Fluorescent guided surgery (FGS) is an intraoperative technique that allows the surgeon to visualize cancerous tissues during a surgical procedure. Here we developed a PNA-merocyanine dye conjugate as hybridization FGS probe for the detection of HER2 Uterine Serous Carcinoma (USC) mRNA marker. For this purpose, we first synthesized a push-pull dye: ((E)N,N-dimethyl-4-(2-(pyridine-4-yl)vinyl)aniline) and then attached it via a 6-carbon spacer to uracil at C5-position (λex 460 nm, λem 610 nm, in PBS buffer). We observed a 2.5-fold enhancement of the dye's emission intensity in highly viscous glycerol versus that in water. This observation implies that the conformational flexibility of the dye is restricted in viscous medium and hence may be used for the construction of a turn-on probe based on the intercalation of the PNA-conjugated-dye within a PNA-mRNA duplex. Next, we synthesized a 17-mer PNA-dye probe which is complementary to part of HER2 mRNA marker. PNA was selected, rather than an oligonucleotide probe, due to its higher stability in cells, and higher affinity to complementary RNA. The probe incorporates uracil-dye PNA monomer (U-dye) at position 11 (3'-CTGTTAGGAG**U-dye**CTTGAG-5'). Hybridization of this probe with the complementary RNA resulted in a 2-fold enhancement of emission intensity. When the probe was added to total RNA extract from ZR7530 cells expressing high levels of HER2 mRNA, emission was enhanced 2.5-fold vs. that of PNA-dye probe in PBS buffer. The hybrid was photostable for at least 200 min. In conclusion, PNA-merocyanine-dye probe may be potentially useful as FGS tool for USC cancer operations.

Poster no. P_OOC_38

Carbometallation of 1-Halocyclopropenes

Tal Weissbrod, Alin Asraf and Ilan Marek*

Schulich Faculty of Chemistry, Technion—Israel Institute of Technology, Haifa, 32000 Israel.

E-mail: chilanm@technion.ac.il

The carbometallation of cyclopropenes is a powerful tool for constructing polysubstituted cyclopropanes. Controlling the regio- and diastereoselectivity of this transformation has been a main subject of our group's research, leading to substantial advances and paving the way to a general synthesis of stereodefined fully substituted cyclopropanes.[1] These strained systems bearing multiple carbon stereocenters serve as key precursors for complex stereodefined acyclic molecules, through a wide array of selective C-C bond cleavage transformations.[2]

In continuation of our research efforts to explore and induce stereocontrol in carbometallations, we wished to study the effects of incorporating a halogen atom on the cyclopropene double bond. In addition to testing the stereoselectivity in these systems, the significance of this research stems from the reactivities of the two possible regioisomeric intermediates, each features a metal and a halogen in either a 1,1 or a 1,2 arrangement.

The copper-catalyzed carbomagnesiation of chloro- or bromocyclopropenyl esters resulted in two different products- a diastereopure halocyclopropane derived from the formed carbenoid, and a substitution product derived from the regioisomeric intermediate, that undergoes β-halide elimination (**Figure 1a**). Meticulous substrate design enabled complete divergency as both products could be obtained in high selectivities. Surprisingly, a small alteration from halocyclopropenyl *esters* to the reduced halocyclopropenyl *methanols* uncovered a new product, showcasing a third reactivity pathway of the halocyclopropyl metal species. In this transformation, the carbenoid undergoes a Doering-Moore-Skattebøl rearrangement[3] to yield allenes (**Figure 1b**). The diversity of products, accessible by judicious choice of substrate, highlights the synthetic potential of the carbometallation of halocyclopropenes.

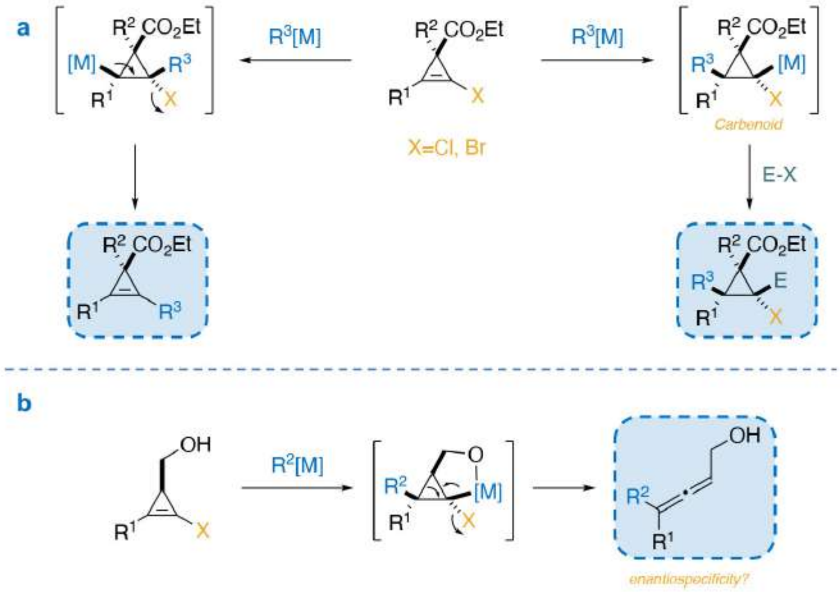


Figure 1: a) Carbometallation of halocyclopropenyl esters. b) Allene formation through a sequence of carbometallation of halocyclopropenyl methanols and Doering-Moore-Skattebøl rearrangement.

References:
1. Cohen, Y., Marek, I., *Acc. Chem. Res.* **2022**, 55, 2848−286.
2. Cohen, Y., Cohen, A., Marek, I., *Chem. Rev.* 2021, 121, 1, 140−161
3. Doering, W.v.E., LaFlamme, P.M., *Tetrahedron*, **1958**, 2, 75.

Poster no. P_OOC_39

Ring Opening of Borylated Cyclopropanes: Beyond 1,2-Metalate Rearrangement

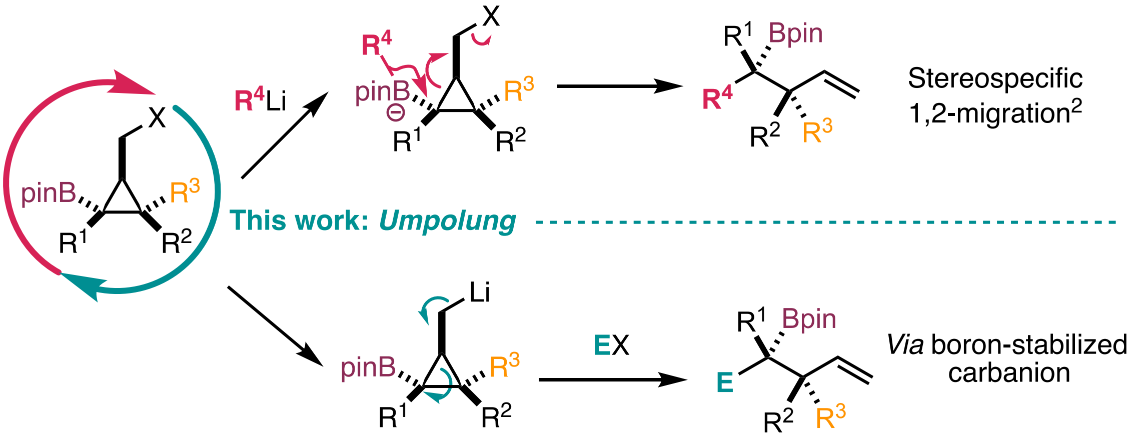
Tereza Pavlickova[a] and Ilan Marek*[a]

[a] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Technion City, Haifa, 3200009, Israel*

E-mail: chilanm@technion.ac.il

Controlled construction of congested stereogenic centers within acyclic systems represents an acute challenge in stereoselective organic synthesis. The main obstacle is conformational flexibility of these organic frameworks compared to cyclic systems. An elegant solution to this problem involves introduction of stereocenters to cyclopropanes as highly strained carbocycles and subsequent selective ring opening.[1]

Previously, we reported synthesis and 1,2-metalate rearrangement-mediated ring opening of polysubstituted borylated cyclopropanes by various alkyl-, aryl- and alkynyllithium reagents.[2] Here, we present a selective lithium-halogen exchange-mediated ring fragmentation of cyclopropyl pinacolboranes (**Scheme 1**). Thus generated boron-stabilized carbanions react with various electrophiles to give acyclic borylated products with high levels of diastereoselectivity. This strategy represents an original way to access and functionalize these elusive intermediates within densely substituted frameworks.



Scheme 1

Acknowledgements: This research was supported by the European Union's Horizon 2020 research and innovation program under grant agreement no. 786976.

References:

1. Cohen, Y.; Cohen, A.; Marek, I. Creating Stereocenters within Acyclic Systems by C–C Bond Cleavage of Cyclopropanes. *Chem. Rev.* **2021**, *121*, 140-161.

2. a) Augustin, A. U.; Di Silvio, S.; Marek, I. Borylated Cyclopropanes as Spring-Loaded Entities: Access to Vicinal Tertiary and Quaternary Carbon Stereocenters in Acyclic Systems. *J. Am. Chem. Soc.* **2022**, *144*, 16298-16302. b) Pavlíčková, T.; Stöckl, Y.; Marek, I. Synthesis and Functionalization of Tertiary Propargylic Boronic Esters by Alkynyllithium-Mediated 1,2-Metalate Rearrangement of Borylated Cyclopropanes. *Org. Lett.* **2022**, *24*, 8901-8906.

Poster no. P_OOC_40

Photocatalysis for Halide to Halogen Conversion Using Porphyrinoid Dimers and Monomers

Tomer Ianovici[a], Atif Mahammed[a], Sankar Prasad Rath*[b], Zeev Gross*[a]

[a] Schulich Faculty of Chemistry, Technion- Israel Institute of Technology, Haifa, Israel. [b]Department of Chemistry, Indian Institute of Technology Kanpur, India.

E-mail: ianovici@campus.technion.ac.il; chatif@technion.ac.il; sankarrath04@gmail.com; chr10zg@technion.ac.il.

Photocatalysis is a change in the rate of a chemical reaction or its initiation under the action of UV, visible, or infrared radiation.[1] The photocatalyst absorbs light and can donate/accept electrons to/from the substrates. Porphyrins and to a lesser extent corroles have been extensively investigated in recent years for such purposes since they have unique and promising optical and electronic properties.[2]

In this research, monomeric and dimeric corrole and porphyrin metal complexes (selected examples are shown in Figure 1a, 1b), were examined for the light-induced conversion of bromide (Br^-) to bromine (Br_2), and subsequently bromination of phenol. We used HPLC (shown in Figure 1c) to determine which photocatalysts gave the highest yield in the reaction by using low-loading concentrations of the examined photocatalysts, visible light energy sources (400 nm and 410 nm LED lamps), and short time of irradiation (2h and 3h respectively). The main advantage of the dimers is their utility for catalyzing the reaction at long wavelength (600 nm) irradiation.

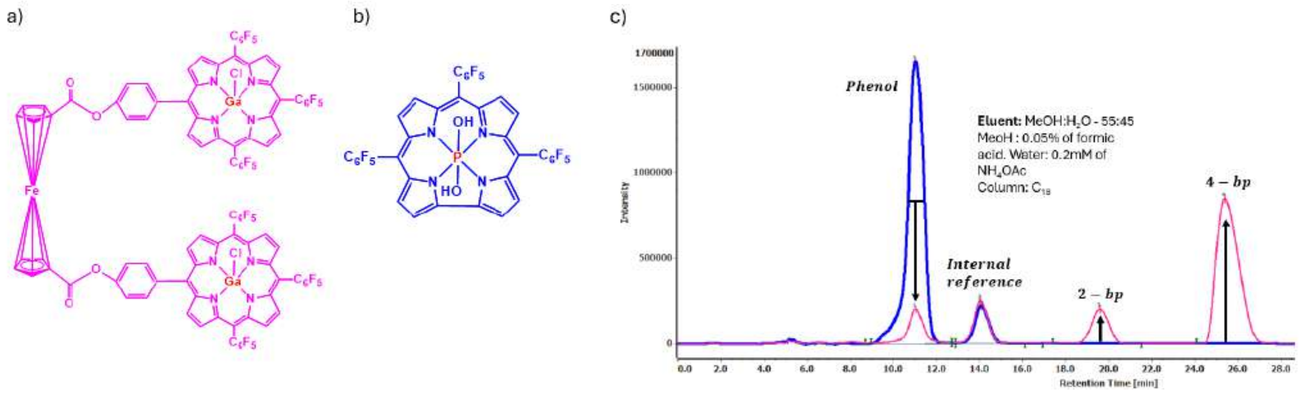


Figure 1: Chemical structures of a) Gallium porphyrin dimer, b) 2-hydroxy phosphorous corrole, and c) HPLC data for bromination of phenol by aq. HBr, using the depicted porphyrin dimer as a photocatalyst. 2-bp and 4-bp are 2- and 4- bromophenol, respectively; the blue and red traces represent the reaction times of 0 and 3 hours respectively.

Acknowledgements: India - Israel joint project, sponsored by the Ministry of Science, Technology and Space.

References:

1. Michelin, C.; Hoffmann, N. Photosensitization and Photocatalysis—Perspectives in Organic Synthesis. *ACS Catal.* **2018**, *8*, 12046–12055.
2. Zhan, X.; Kim, D.; Ullah, Z.; Lee, W.; Gross, Z.; Churchill, D. G. Photophysics of Corroles and Closely Related Systems for Emergent Solar Energy, Medicinal, and Materials Science Applications. *Coor. Chem. Rev.* **2023**, *495*, 215363.

Poster no. P_OOC_41

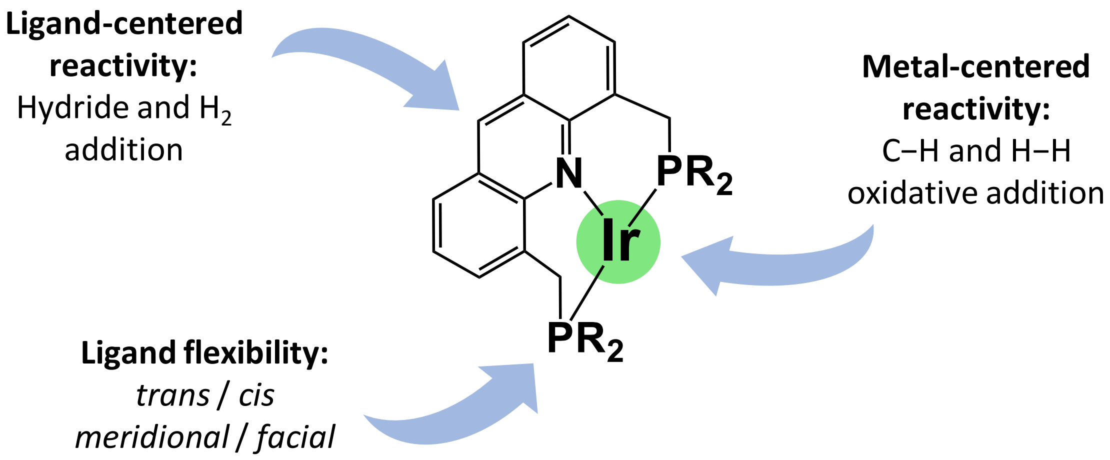
Iridium complexes of acridine-based PNP-type pincer ligands: Synthesis, structure and reactivity

Yarden Lavi,[a] Michael Montag,[a],* Yael Diskin-Posner,[b] Liat Avram,[b] Linda J.W. Shimon,[b] Yehoshoa Ben-David,[a] David Milstein[a],*

[a] *Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot, Israel.*
[b] *Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel*

E-mail: michael.montag@alumni.weizmann.ac.il (M. Montag), david.milstein@weizmann.ac.il (D. Milstein)

Acridine-based PNP-type pincer ligands (AcrPNP) have previously been used for the construction of a small number of Ru(II), Mn(I) and Ir(III) complexes, with most attention being given to the catalytically-active ruthenium complexes.[1–4] In the present work, we significantly expand the scope of known AcrPNP complexes by introducing a series of new Ir(I) and Ir(III) complexes. These were synthesized from two AcrPNP ligands differing in their P-substituents (^{i}Pr *vs* Ph), in conjunction with various Ir(I)-olefin precursors, through different sequences of reactions that include intramolecular C–H activations and additions of H_2 and $NaBEt_3H$. The new iridium complexes, with their observed structures and reactivities, reflect the unique properties of the acridine-based PNP ligands, i.e., their inherent structural flexibility and ability to support both metal-centered reactivity (C–H and H–H oxidative addition) and ligand-centered reactivity (hydride- and H_2-induced dearomatization). These attributes provide us with valuable tools for future development of catalytic systems.



Ligand-centered reactivity:
Hydride and H_2 addition

Metal-centered reactivity:
C–H and H–H oxidative addition

Ligand flexibility:
trans / cis
meridional / facial

References:

(1) Gunanathan, C.; Milstein, D. Selective Synthesis of Primary Amines Directly from Alcohols and Ammonia. *Angew. Chem. Int. Ed.* **2008**, *47* (45), 8661–8664. https://doi.org/10.1002/anie.200803229.
(2) Kar, S.; Milstein, D. Sustainable Catalysis with Fluxional Acridine-Based PNP Pincer Complexes. *Chem. Commun.* **2022**, *58* (23), 3731–3746. https://doi.org/10.1039/D2CC00247G.
(3) Daw, P.; Kumar, A.; Oren, D.; Espinosa-Jalapa, N. A.; Srimani, D.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Carmieli, R.; Ben-David, Y.; Milstein, D. Redox Noninnocent Nature of Acridine-Based Pincer Complexes of 3d Metals and C–C Bond Formation. *Organometallics* **2020**, *39* (2), 279–285. https://doi.org/10.1021/acs.organomet.9b00607.
(4) Li, W.; Xie, J. H.; Lin, H.; Zhou, Q. L. Highly Efficient Hydrogenation of Biomass-Derived Levulinic Acid to γ-Valerolactone Catalyzed by Iridium Pincer Complexes. *Green Chem.* **2012**, *14* (9), 2388–2390. https://doi.org/10.1039/c2gc35650c.

Poster no. P_OOC_42

Synthesis of the First Germenyl Lithiums and Germenyl Radicals

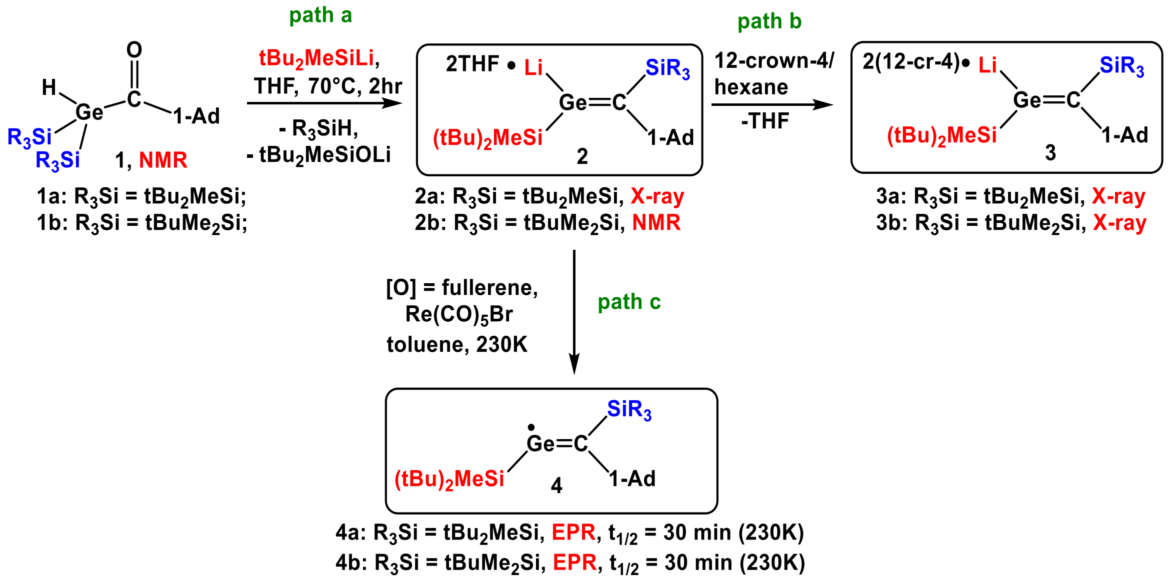
Yulia Goldshtein, Yuri Glagovsky, Natalia Fridman, Boris Tumanskii, Dmitry Bravo-Zhivotovskii,* Yitzhak Apeloig*

Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

E-mail: sjgold@campus.technion.ac.il; chrbrzh@technion.ac.il; apeloig@technion.ac.il

The heavier analogs of vinyl lithium $R_2E{=}E'R{-}Li$ (E,E'= C, Si, Ge, Sn), featuring multiple bonds between heavier Group 14 elements, attract growing attention.[1] Vinyl lithiums are widely used in organic synthesis.

The only known silenyl lithiums ($R_2C{=}SiR{-}Li$) were synthesized and isolated by our group.[2] Herein, we report the synthesis of the first stable germenyl anions, ($R_2C{=}GeR{-}Li$) **2** and **3**, via metalation of the corresponding acyl germanes (Scheme, path a, b). **2a** and **3a,b** were isolated and characterized by NMR spectroscopy and X-ray diffraction analysis ($r_{avr}(C{=}Ge) = 1.871$ Å).[3] Oxidation of **2a** or **2b** (toluene, 230K) produces the first germenyl radicals ($R_2C{=}Ge{\bullet}{-}R$) **4a** or **4b**, respectively, (Scheme, path c), which were characterized by EPR spectroscopy at 230K (g = 2.029, $a_{avr}(^{73}Ge)$ is 55.0G for **4a** and 60.2G for **4b**), and by DFT calculations. Radicals **4** have a strongly bent geometry at the Ge atom.[3] Analogous silenyl radicals were previously reported.[4]



Scheme. Synthesis of germenyl lithiums **2** and **3** (path a, b) and their oxidation radical products (path c).

References:

1. a) Präsang, C.; Scheschkewitz, D. Chem. Soc. Rev. 2016, 45 (4), 900-921; b) Nieder, D.; Klemmer, L.; Kaiser, Y.; Huch, V.; Scheschkewitz, D., *Organometallics* **2018**, *37 (5)*, 632-635; c) Majhi, P. K.; Huch, V.; Scheschkewitz, D. *Angew. Chem. Inter. Ed.* **2021**, *60 (1)*, 242-246.

2. a) Zborovsky, L.; Dobrovetsky, R.; Botoshansky, M.; Bravo-Zhivotovskii, D.; Apeloig, Y., *J. Am. Chem. Soc.* **2012**, *134 (44)*, 18229-18232; b) Pinchuk, D.; Mathew, J.; Kaushansky, A.; Bravo-Zhivotovskii, D.; Apeloig, Y. *Angew. Chem. Inter. Ed.* **2016**, *55 (35)*, 10258-10262.

3. Y. Goldshtein, Y. Glagovsky, B. Tumanskii, N. Fridman, D. Bravo-Zhivotovskii, Y. Apeloig, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202452; *Angew. Chem.* **2022**, *134*, e202202452.

4. D. Pinchuk, Y. Kratish, J. Mathew, L. Zborovsky, D. Bravo-Zhivotovskii, B. Tumanskii, Y. Apeloig, *Angew. Chem. Int. Ed.* **2019**, *58*, 7435-7439.

Poster no. P_OOC_44

Calochorturils: tangentially desymmetrized cavitands

Sadhna Shah,[a] Venkata subbarao Ganga,[a] Ofer Reany[b,*] Ehud Keinan[a,*]
[a]The Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel
[b]Department of Natural Sciences, The Open University of Israel, Ra'anana, Israel

Chiral molecular hosts are helpful for the stereoselective recognition of chiral guest molecules, chiral asymmetric catalysis, solid phases for separation of racemic mixtures, and other applications. Desymmetrization of achiral bowl-shaped scaffolds, such as corannulene, Sumanene, cyclotriveratrylene (CTV), and tribenzotriquinacene, can be achieved either by enantiomerically pure substituents of by preferred directionality of achiral substituents to form clockwise or counterclockwise directionality (P or M chirality). Substituting every repeating unit in CTV with two achiral groups, R1 and R2, in a directional manner (Figure 1), thus converting the symmetrical bowl to an asymmetrical one with preferred directionality. When R1 > R2, one can envision two significantly different modes of substitution: radial orientation of the side chains or tangential orientation (Figure 1). We predicted that the helicity in the first case would be smaller than the latter. The maximal effect of tangential substitution on the helicity is reminiscent of a water wheel or a propeller-shaped receptor.

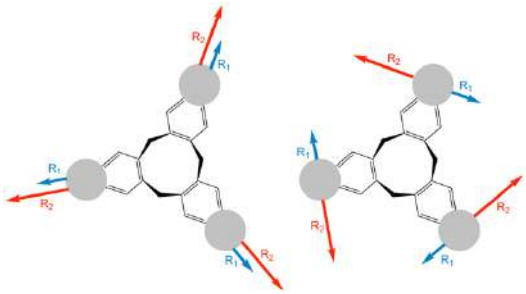


Figure 1. Radial (left) vs. tangential (right) desymmetrization of bowl-shaped molecules.

Here we report on a new family of synthetic receptors, Calochorturil (CT), reminiscent of the C_{3h} symmetric Calochortus flower (Figure 2). A highly regioselective synthesis of the CT skeleton streamlined the synthesis of various analogs, allowing for HPLC resolution of its enantiomers and elucidation of the energy barrier for the bowl-bowl inversion (racemization). Drivatization with phenylmethyl-L-proline allowed for chromatographic separation of diastereomers. Further synthesis of cage compounds was achieved by capping with 1,4,7- triazacyclononane (Figure 2D) and other methods. Applications for enantioselective binding and chiral metal complexes are currently underway in our laboratories.

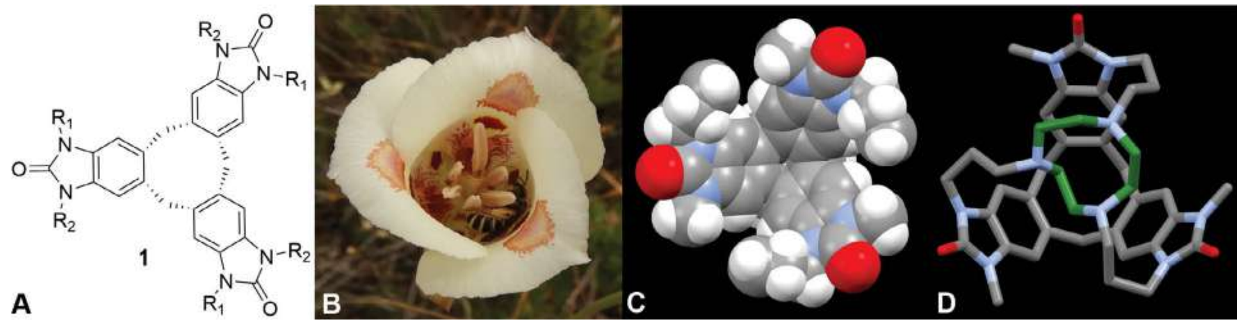


Figure 2. A. General structure of calochorturil (CT), **1**, looking down at its concave face. B. Calochortus venustus flower (a California species of the lily family, photo by Anana). C Crystal structure of **1**, R_1=Me, R_2=allyl. D. Crystal structure of a capped CT using triaza-crown ether with its carbon atoms shown in green.

Poster no. P_OOC_43

Synthesis of the first isolated Group 14 heavy enolate in both the keto and enol forms

Yuri Glagovsky, Yulia Goldshtein, Natalia Fridman, Dmitry Bravo-Zhivotovskii*, Yitzhak Apeloig*[a]

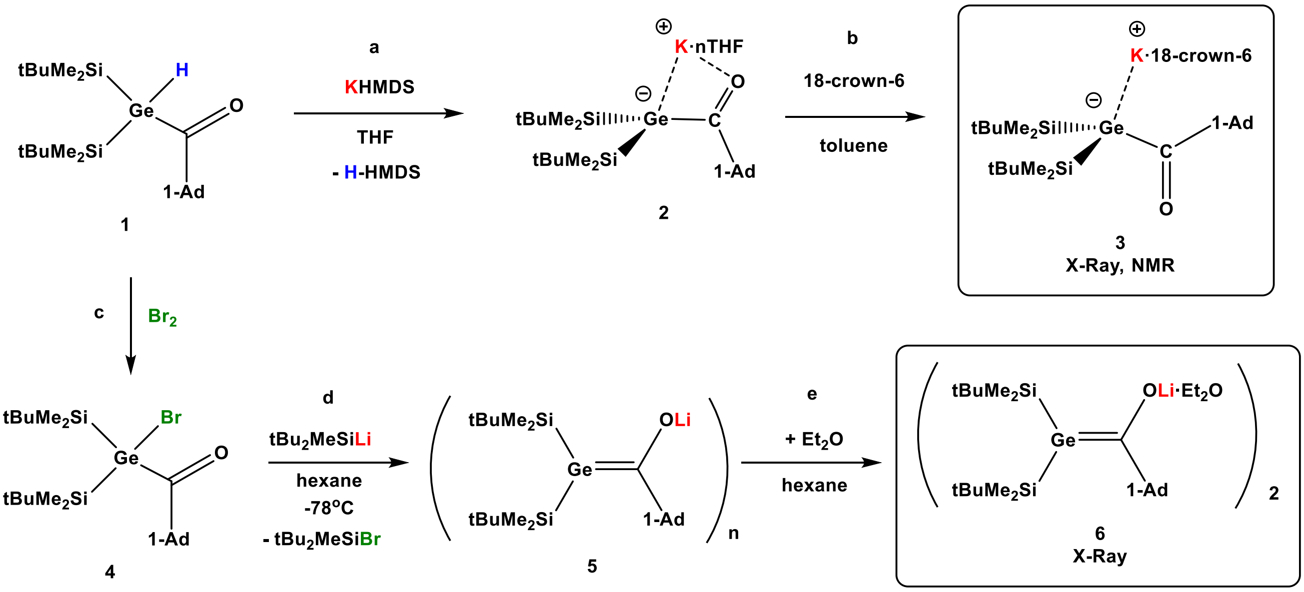
[a] *Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*

E-mail: apeloig@technion.ac.il, chrbrzh@technion.ac.il

Enolates are compounds containing an E=C-OM moiety (M = metal). They can exist as keto (M-E-C=O) and enol (E=C-OM) tautomers. While organic enolates (E=C) are widely used in industry and academic research, the chemistry of "heavy" enolates (E=Si, Ge, Sn) remains challenging, and only a few examples were published.[1][2] Contrary to organic enolates, most known heavy enolates exist as the keto tautomers. Only two examples of enol-form silenolates were published.[3] **Germenolates and stannenolates in enol form have not been reported.**

We now report the synthesis and isolation of the **first enol-form germenolate 6**. Moreover, we demonstrate that this germenolate can exist as the keto (**3**) or the enol (**6**) tautomer, depending on the solvent.

Reaction of bromo-acylgermane **4** in hexane at -78°C produces unsolvated germenolate **5** (Scheme 1, step d), which crystallizes upon addition of Et_2O as **enol-germenolate 6**, while reaction of acylgermane **1** with KHMDS in THF at r.t. yields **keto-germenolate 2** (Scheme 1, step a), which crystallizes as **keto-germenolate 3** after addition of 18-crown-6 ether. The differences between X-ray geometries of **3** and **6** are discussed. Synthesis of the lithium analogue of the potassium keto-germenolate **2** was previously reported by us, but crystals suitable for X-Ray were not obtained.[4]



Scheme 1: Synthesis of keto-germenolate **3** and enol-germenolate **6**

References:

[1] I. S. Biltueva, D. A. Bravo-Zhivotovskii, I. D. Kalikhman, V. Y. Vitkovskii, S. G. Shevchenko, N. S. Vyazankin, M. G. Voronkov, *J. Organomet. Chem.* **1989**, *368*, 163–165.

[2] M. Haas, *Chem. - A Eur. J.* **2019**, *25*, 15218–15227.

[3] R. Dobrovetsky, L. Zborovsky, D. Sheberla, M. Botoshansky, D. Bravo-Zhivotovskii, Y. Apeloig, *Angew. Chemie Int. Ed.* **2010**, *49*, 4084–4087.

[4] Y. Goldshtein, Y. Glagovsky, B. Tumanskii, N. Fridman, D. Bravo-Zhivotovskii, Y. Apeloig*, Angew. Chemie Int. Ed.* **2022**, *61*, e202202452.

Physical Chemistry

Poster no. P_PC_01

Investigating the mechanism of CO_2 hydrogenation on ceria surfaces using simultaneous X-ray photoelectron spectroscopy (XPS) and grazing incidence resonant X-ray scattering (GIXS)

Adva Ben-Yaacov[1], Roey Ben-David[1], Lorentz Falling[2], Maximilian Jaugstetter[2]
Slavomir Nemsak[2] and Baran Eren[1]*

[1]Department of Chemical and Biological Physics, Weizmann Institute of Science, 234 Herzl Street, 76100 Rehovot, Israel,

[2]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Email: Adva.ben-yaacov@weizmann.ac.il, Baran.Eren@weizmann.ac.il

Ceria catalysts present a great potential for the selective hydrogenation of alkynes to alkenes and the hydrogenation of CO_2 to methanol [1]. Recent works suggest that the type of surface and subsurface hydrogen may play an important role, affecting both the activity and the selectivity of hydrogenation reactions. Interaction with hydrogen typically follow two routes: formation of hydroxyls or formation of hydride and a proton, although other pathways are possible. Hydrides are stabilized by oxidizing the cerium atoms next to the oxygen vacancies [2-4].

Using simultaneous X-ray photoelectron spectroscopy (XPS) and grazing incidence resonant X-ray scattering (GIXS) measurements at ambient conditions, we aim to understand both the structural and chemical changes occurring during reduction, oxidation, and interaction with hydrogen and CO_2. We are able to detect differences in the scattering images of our ceria sample under different conditions, and thus provide evidence of volume changes in the different conditions, such as shrinking of the material upon reduction and expansion of it in the presence of H_2. We additionally observed changes when CO_2 is added. Those results will be the key for understanding the mechanism of CO_2 hydrogenation.

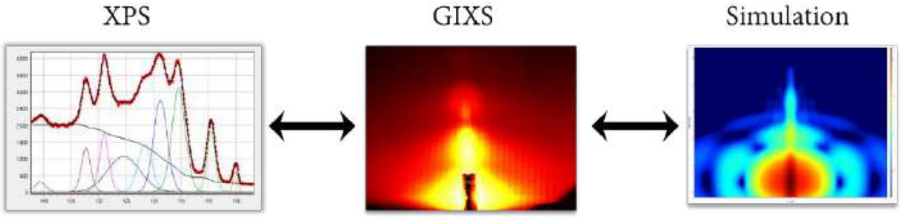


Fig. 1: *Schematic representation of the experiment process combining chemical information from XPS, structural information from GIXS and simulation of GIXS images with XPS as an input.*

[1] J. A. R. Jesús Graciani, K. Mudiyanselage, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. Fernández Sanz and J. A. Rodrigues, Science,345, 546 (2014).
[2] Z. Li, K. Werner, L. Chen , A. Jia, K. Qian, J. Q. Zhong , R. You, L. Wu, L. Zhang, H. Pan, X. P. Wu, X. Q. Gong, S. Shaikhutdinov, W. Huang, H. J. Freund, Chem. - A Eur. J., 27, 16, 5268, (2021).
[3] D. Schweke, L. Shelly, R. Ben David, A. Danon, N. Kostirya, and S. Hayun. J. Phys. Chem. C, 124, 11, 6180, (2020).

[4] Adva Ben-Yaacov, Lorenz J Falling, Roey Ben David, Smadar Attia, Miguel A Andrés, Slavomír Nemšák, Baran Eren , *J Phys Chem Lett*. 2023 Aug 24; 14(33):7354-7360

Poster no. P_PC_02

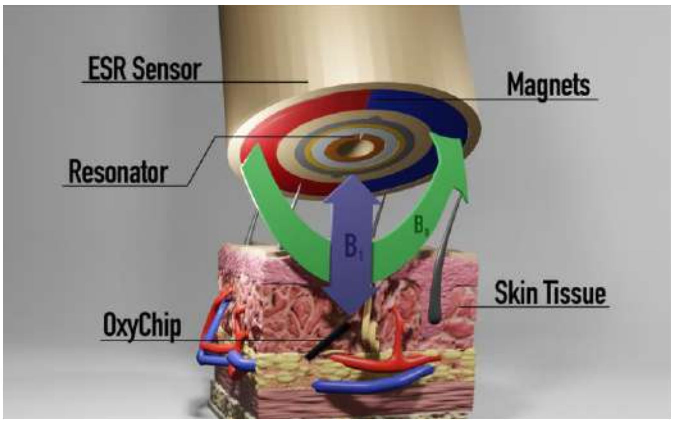
Magnetic Resonance – from spectroscopic tools to practical technological devices

Aharon Blank[a]*

[a] *Schulich Faculty of Chemistry, Technion- Israel Institute of Technology, 3200003, Haifa, Israel*

E-mail: ab359@technion.ac.il

Magnetic resonance is a well-established field, historically utilized mainly in spectroscopy and medical imaging. However, from its early days, it has also served as a foundation for practical technological devices, including microwave sources and amplifiers. This duality continues today, with new technological advancements in magnetic resonance enhancing its capabilities in both spectroscopy and medicine. Additionally, these advancements enable the creation of innovative devices and instruments, such as sensitive sensors, advanced amplifiers, and even quantum computers. In this talk, I will focus on developments emerging from the magnetic resonance laboratory at the Technion. These developments mostly aim to enhance the spectroscopic capabilities of magnetic resonance, enabling sensitive detection and imaging of a small number of electron spins, such as in microfluidics and micro-single crystals [1-3]. Additionally, our developments also seek to provide small diagnostic medical tools without resorting to the use of large and bulky magnets [4-5] (see Figure). Finally, we apply these new capabilities and tools to develop unique microwave devices for a plethora of physical and engineering applications that can enable low-noise amplification of microwave signals [6], refrigerate microwave cavities [7], and generate coherent, stable microwave signals.



Compact (20 mm in size) electron spin resonance probe for sensing oxygen inside skin tissue

Acknowledgements: We thank the ISF, NIH, and Israel Innovation Authority for financial support.

References:

1. Artzi, Y., Twig, Y., and Blank, A., "Induction-detection electron spin resonance with spin sensitivity of a few tens of spins," Applied Physics Letters 106, (2015) 084104.
2. Dayan, N., Ishay, Y., Artzi, Y., Cristea, D., Reijerse, E., Kuppusamy, P., and Blank, A., “Advanced Surface Resonators for Electron Spin Resonance of Single Microcrystals,” Review of Scientific Instruments 89, (2018) 124707.
3. Dayan, N., Ishay, Y., Artzi, Y., Cristea, D., Driesschaert, B., and Blank, A. “Electron Spin resonance microfluidics with subnanoliter liquid samples,“ Journal of Magnetic Resonance Open, (2020) 100005.
4. Cristea, D., Wolfson, H., Ahmad R., Twig Y., Kuppusamy P., and Blank, A. “Compact electron spin resonance skin oximeter: Properties and initial clinical results,“ Magnetic Resonance in Medicine, 85, (2021). 2915-2925.
5. Wolfson, H., Ahmad, R., Twig, Y., Williams, B. and Blank, A., "A magnetic resonance probehead for evaluating the level of ionizing radiation absorbed in human teeth," Health Physics Journal 108, (2015) 326-35.
6. Sherman, A., Zgadzai, O., Koren, B., Peretz, I., Laster, E., and Blank, A., "Diamond-based microwave quantum amplifier," Science Advances, 8, (2022) eade6527
7. Blank, A., Sherman, A., Koren, B., and Zgadzai, O., “An anti-maser for mode cooling of a microwave cavity,” Journal of Applied Physics – Accepted for publication

Poster no. P_PC_03

Characterization of Plasmonic nanocavities under 2-photon microscopy and their coupling to molecular excited states

Alon Krause, Adi Salomon

Abstract:
This research involves the creation of strongly coupled plasmonic-molecular systems, which can modify molecular properties and reactions. The proposed system is composed of plasmonic nanocavities, milled in a thin metal layer, and thin films of dye molecules. A characterization of various nanocavity structures and of dye molecules of different chemical natures will be done. Once both components have been characterized on their own, a combined system will be fabricated and measured for the strength of the coupling it produces. Second Harmonic Generation (SHG) measurements can utilize the unique properties of plasmonic nanocavities and produce clear and selective results in these measurements. A successful fabrication of the described coupled system allows for future experiments focusing on the modification of molecular properties such as fluorescence rate and on influencing chemical reaction rates and selectivity.

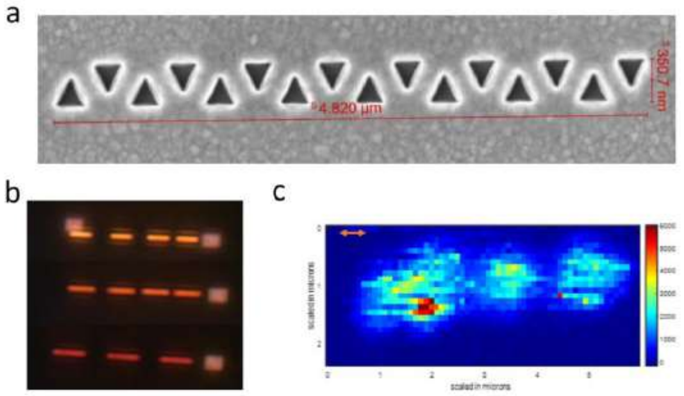


Figure 1- A Zig-Zag hole formation, examined for plasmonic activity. (a)- HRSEM image of a formation, milled by FIB on a 200nm layer of Ag on glass. (b)-Optical microscopy image of the transmitted light from formations with differently spaced triangle units, showing a change in color. (c)- 2-photon scan of a formation (5mW, 940nm, 90^{o}polrisation), showing different regions of activity on a single formation in a node-anti node formation.

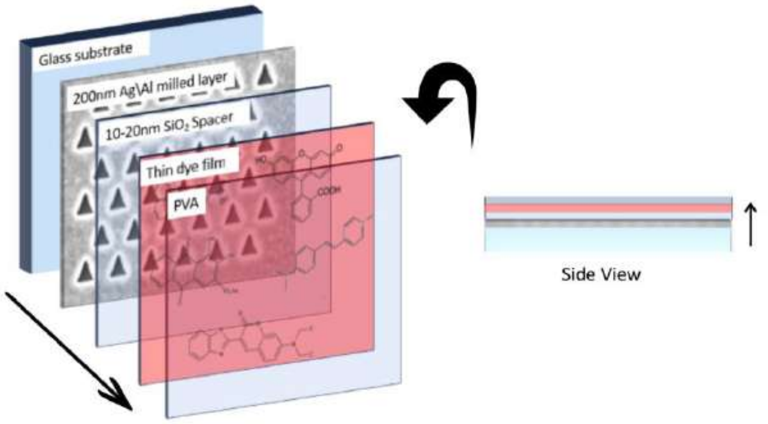


Figure 2- An illustration of the resulted hybrid system

Poster no. P_PC-04

Optimization of sample formulations for high-field DNP

Amit Israelstam[a], Orit Nir Arad[a], Nurit Manukovsky[a], and Ilia Kaminker*[a]

[a] *School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv, Israel.*

E-mail: Iliakam@tauex.tau.ac.il

Solid-state nuclear magnetic resonance (ssNMR) spectroscopy is a powerful, versatile, analytical technique for the investigation of the structure, dynamics, and interactions in a wide range of systems. However, its applications to dilute systems, e.g. surface defects or biomolecules at their native concentrations, remain challenging due to its intrinsic low sensitivity. This limitation has stimulated the development of dynamic nuclear polarization (DNP). This approach enables a ssNMR sensitivity increase by orders of magnitude, allowing the characterisation of a wide range of systems previously inaccessible to ssNMR. The sensitivity increase is achieved by introducing suitable paramagnetic species and using microwave irradiation to transfer the high polarization of the unpaired electron spins to the nuclear spins investigated.

DNP sample formulation strongly affects the achievable NMR signal enhancement. The common formulation consists of embedding the substrate of interest in a radical-containing medium known to form a glassy matrix at cryogenic temperatures ($\leq 100\ K$). The purpose of the matrix is to allow for the dissolution of the polarizing agents and the target and for the propagation of the hyperpolarization from the electron spins to the target nuclei. The choice of the matrix affects the aggregation/precipitation propensity of both the radicals and the target, thus strongly affecting the DNP efficiency.

In this project, we used different polymer matrices (polystyrene Mw $\sim 35{,}000\ \mathrm{g\,mol^{-1}}$, polystyrene Mw $\sim 280{,}000\ \mathrm{g\,mol^{-1}}$, ortho-terphenyl, and poly-l-lactic acid) and different polarizing agents (α,γ-Bisdiphenylene-β-phenylallyl (BDPA), (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), and 4-hydroxy-tempo-benzoate (4HTB)). Using a combination of x-band and high-field EPR spectroscopy, we investigated aggregation propensity and electron spin relaxation properties of polarizing agents/matrix combinations. For example, we find that while TEMPO radical in polystyrene matrix (Figure 1. A) is very dynamic, 4-hydroxy TEMPO benzoate radical in polystyrene matrix (Figure 1. B) is solid-like at room temperature, as shown in Figure 1.

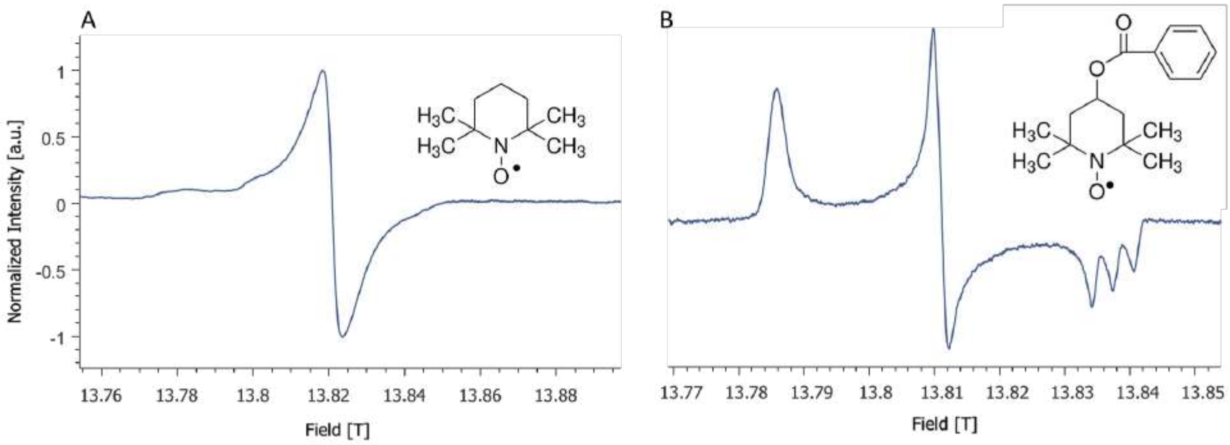


Figure 1: CW EPR field sweep at 388 GHz and RT of (A) 1 % w/w TEMPO in polystyrene and (B) 1 % w/w 4-hydroxy TEMPO benzoate in polystyrene.

Poster no. P_PC_05

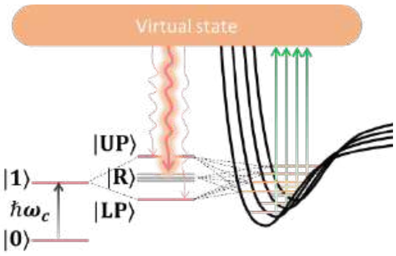
Searching for Elusive Spontaneous Raman Scattering from Vibrational Polaritons

Bar Cohn, [a] and Lev Chuntonov[a].

[a] *Schulich Faculty of Chemistry, Technion–Israel Institute of Technology, Haifa 3200003, Israel*

E-mail: scrcohn@campus.technion.ac.il,chunt@technion.ac.il

Vibrational strong coupling results from interaction between molecular vibrational excitations and the resonant mode of an infrared cavity, this interaction is presumed to hold the potential to non-conventionally influence ground-state chemical reactivity and various other chemical properties [1-2]. Strong coupling leads to the formation of hybrid states known as vibrational polaritons, which are readily observed in transmission measurements, and a manifold of dark reservoir states [3]. In contrast, Raman spectroscopy of vibrational polaritons is elusive and has recently been the focus of both theoretical and experimental investigations [4-7]. Because Raman measurements are frequently performed with high numerical aperture excitation/collection optics, angular dispersion of the strongly coupled system must be carefully considered [8]. In this study [9], we conducted experimental investigations focused on vibrational polaritons, specifically those associated with dispersive collective lattice resonances within infrared antenna arrays. While the transmission spectrum provided clear evidence of strong coupling to vibrational excitations, intriguingly, the Raman spectra did not exhibit signatures indicative of polaritonic transitions. However, our interpretation of these results, employing the Tavis-Cummings-Holstein model, suggested that the ratio of Raman transition strengths between reservoir and polariton states scales with the number of strongly coupled molecules (approximately 10^9 molecules per unit cell). Thus, the spountateous Raman scattering signal arising from scattering into the vibrational polaritons states is eclipsed by the signal of the reservoir states.



Scheme: Schematic illustration of spountateous Raman scattering from strongly coupled N- number of molecules to a photonic cavity represented by the energy postential and the $\bar{h}\omega_c$ transtion, respectively. The strong coupling results in the formation of the two lower ($|LP\rangle$) and upper ($|UP\rangle$) polariton states and N-1 reservoir states ($|R\rangle$). The spountateous Raman scattering from the virtual states to the polariton state is 1/N weaker than that to the reservoir state, thus the spountateous Raman scattering from vibrational polaritons is overshadowed by the reservoir states.

References:

1. A. Shalabney, J. George, J. Hutchison, G. Pupillo, C. Genet, and T. W. Ebbesen, “Coherent coupling of molecular resonators with a microcavity mode,” Nat. Commun. 6(1), 5981 (2015)
2. A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux, C. Genet, J. Moran, and T. W. Ebbesen, “Tilting a ground-state reactivity landscape by vibrational strong coupling,” Science 363(6427), 615 (2019).
3. B. Cohn, S. Sufrin, A. Basu, and L. Chuntonov, “Vibrational polaritons in disordered molecular ensembles,” J. Phys. Chem. Lett. 13, 8369 (2022).
4. A. Shalabney, J. George, H. Hiura, J. A. Hutchison, C. Genet, P. Hellwig, and T. W. Ebbesen, “Enhanced Raman scattering from vibro-polariton hybrid states,” Angew. Chem., Int. Ed. 54(27), 7971 (2015).
5. J. del Pino, J. Feist, and F. J. Garcia-Vidal, “Signatures of vibrational strong coupling in Raman scattering,” J. Phys. Chem. C 119(52), 29132 (2015)
6. A. Strashko and J. Keeling, “Raman scattering with strongly coupled vibronpolaritons,” Phys. Rev. A 94(2), 023843 (2016).
7. W. M. Takele, L. Piatkowski, F. Wackenhut, S. Gawinkowski, A. J. Meixner, and J. Waluk, “Scouting for strong light–matter coupling signatures in Raman spectra,” Phys. Chem. Chem. Phys. 23(31), 16837 (2021)
8. W. Ahn and B. S. Simpkins, “Raman scattering under strong vibration-cavity coupling,” J. Phys. Chem. C 125(1), 830 (2021).
9. Cohn, B.; Filippov, T.; Emanuel, B.; Chuntonov, L. Spontaneous Raman Scattering from Vibrational Polaritons is Obscured by Reservoir States. J. Chem. Phys. 2023, 159 (10).

Poster no. P_PC_06

Unravelling CO_2 Electroreduction by Supervised Regression-Assisted Operando Spectroscopy

Daniel Sinausia,[a] and Charlotte Vogt*[a]

[a] *Schulich Faculty of Chemistry, Technion – Israeli Institute of Technology, 3200003, Haifa Israel.*

E-mail: c.vogt@technion.ac.il

The average global concentration of carbon dioxide (CO_2) increased by 2020 by 149% since the pre-industrial era,[1] severely contributing to the climate crisis. Subsequently, the electrochemical CO_2 reduction reaction (CO2RR) has received considerable interest as a means to reduce the concentration of CO_2 in the atmosphere. In this context, copper (Cu) has arisen as a promising catalyst, as it is the only pure metal capable of reducing CO_2 into carbon-containing compounds that require more than two electron transfers (C_{2+} products). However, major challenges are still to be tackled, such as low selectivity control or poor Faradaic efficiencies. To face these challenges, novel experimentation techniques are required to comprehend the reaction mechanism, which can facilitate the control over these factors. Herein, we introduce the concept of Supervised Pulsed Speciation (SPS) and its application on the study of the cation effects during CO2RR.

Acknowledgements: The authors thank the German-Israeli Foundation for Scientific Research and Development (GIF) for financial support, and the Russell Berrie Nanotechnology Institute (RBNI) for their assistance during the development of the wafers employed for the ATR-FTIR experiments.

References:

1. IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)]. IPCC, Geneva, Switzerland, pp. 35-115, doi: 10.59327/IPCC/AR6-9789291691647

Poster no. P_PC_07

Pulsed EPR at 7 and 14 T of Optically Polarized NV Centers in Diamond

Eyal Laster,[a] Orit Nir-Arad,[a] Alex B Fialkov,[a] Nurit Manukovsky,[a] and Ilia Kaminker*[a]

[a] *School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel Aviv, Israel*

E-mail: iliakam@tauex.tau.ac.il

Nuclear Magnetic Resonance (NMR) is amongst the most powerful spectroscopy methods. However, NMR suffers from inherently low sensitivity due to the low spin polarization of nuclei. Dynamic Nuclear Polarization (DNP) is an efficient technique for enhancing NMR signals by transferring the high spin polarization of unpaired electrons to nuclei.

Paramagnetic defects in diamonds are studied as a promising platform for a variety of novel technologies in the fields of magnetic resonance, quantum computation, quantum sensing, and more. Two notable defects are the Nitrogen substitution center, called P1 center, and the negatively charged Nitrogen-Vacancy (NV) center. Both exhibit long coherence times at room temperature and proved to be efficient DNP agents. In NV centers, the electron spin and optical properties are coupled, thus they can be hyperpolarized to $|m_S = 0\rangle$ using light irradiation, much above thermal equilibrium.

We explore the use of NV centers for enhancing high-field NMR signals. The electron spin properties of NV centers are measured using high-field (7 and 14 T) Electron Paramagnetic Resonance (EPR), and the transfer of polarization is studied using DNP-enhanced ^{13}C NMR. We present the first 14 T pulsed EPR results on optically polarized NV centers as shown in Figure 1. We find that the optical NV polarizability is proportional to the mixing coefficients of the $|m_S = 0\rangle$ state.

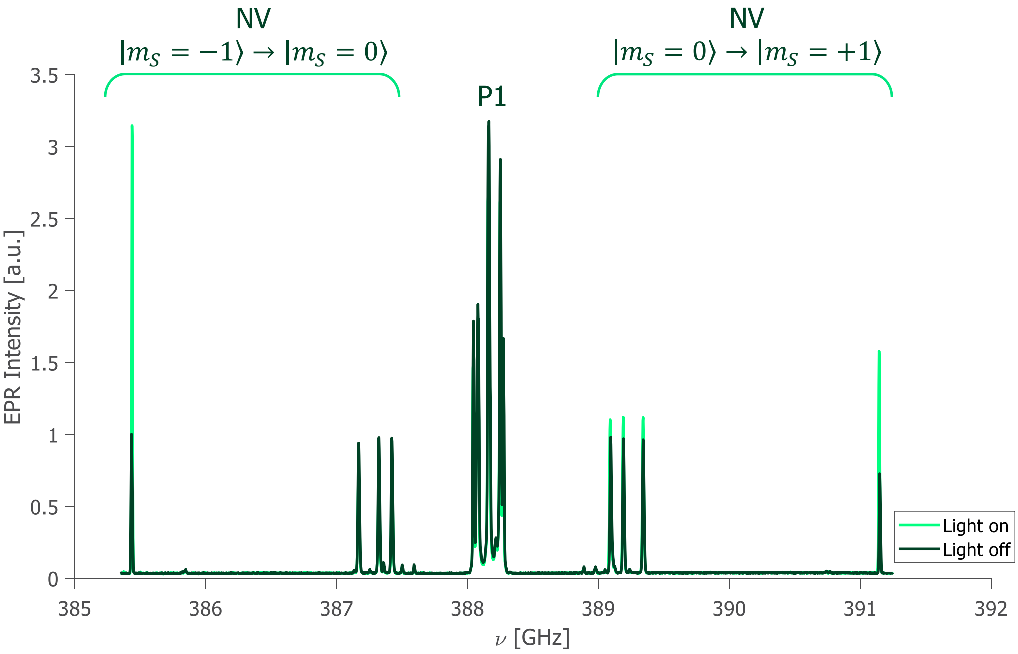


Figure 1: Echo-detected frequency sweep of diamond at 14 T

Poster no. P_PC_08

INVESTIGATION OF THE SURFACE TENSION-COMPOSITION BEHAVIOUR OF A NUMBER OF CHEMICAL SYSTEMS

FREDERICK U. AKHIGBE (CORRESPONDING AUTHOR)

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IBADAN,

IBADAN, NIGERIA.

E-MAIL: frederick.dsppp.akhigbe@gmail.com

MOHAMMED M. SULEIMAN, DEPARTMENT OF CHEMISTRY,

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGERIA.

ABSTRACT

The capillary rise method is used to study the change in surface tension as a function of concentration for aqueous solutions of n-butanol, Propan-2-01, sodium chloride, potassium chloride and aluminum sulphate. The data are interpreted in terms of the surface concentration using the Gibb's isotherm.

The "effective empty-layer thickness" of solutions of sodium chloride, potassium chloride and aluminum sulphate have been determined in this work to be -2.2 x 10^{-5}M, -1.5x10^{-4}M and -1.33 x 10^{-4}M, respectively. The surface concentrations of n-butanol and propan-2-0l, were found to be -3.064 x0^{-6} molm^{-2} and -1.599 x 10^{-6} molm-^{2}, respectively. The "effective cross-sectional area" per adsorbed molecule of n-butanol and propan-2-ol were also determined and found to have values of 54 Ȧ^{2} and 104 Ȧ^{2}, respectively.

The import of the use of surface tension measurements in facilitating the determination of such important quantities as "effective empty-layer thickness" of electrolyte solutions, surface concentration and "effective cross-sectional area" per adsorbed molecule of solutes cannot be over emphasized.

Keywords: surface tension, surface concentration, effective empty-layer thickness, effective cross-sectional area per adsorbed molecule.

Poster no. P_PC_09

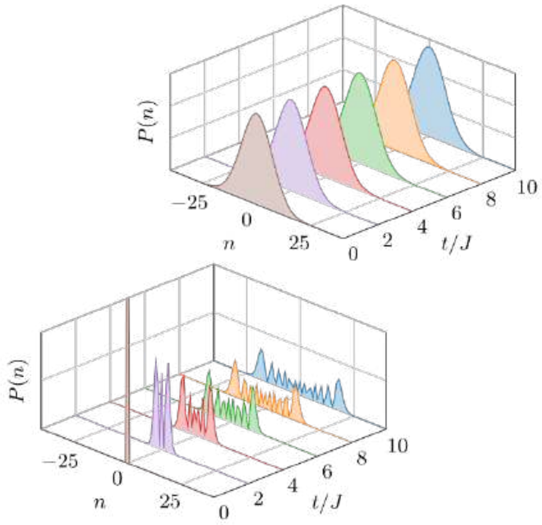
Coherent spatial control of wave packet dynamics on quantum lattices

Ilia Tutunnikov[a]*, Chern Chuang[b], Jianshu Cao[a]

[a] *Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA*
[b] *Department of Chemistry and Biochemistry, University of Nevada, 4505 S Maryland Pkwy, Las Vegas, Nevada 89154, USA*

* e-mail: iliat@mit.edu

Quantum lattices play a pivotal role in the burgeoning fields of quantum materials and information science. Novel experimental techniques now enable the preparation and monitoring of wave packet dynamics on quantum lattices with high spatiotemporal resolution. In this work, we present an analytical study of wave packet diffusivity and diffusion length in tight-binding quantum lattices subjected to stochastic noise. Our analysis highlights the crucial role of spatial coherence and predicts a series of novel phenomena: notably, noise can enhance the transient diffusivity and diffusion length of spatially extended initial states. We observe that both standing and traveling initial states, with large momentum, spread faster than localized initial states, and exhibit a noise-induced peak in transient diffusivity. Furthermore, we find that the differences in diffusivity and diffusion length between extended and localized initial states display a universal dependence on the initial state width. Time permitting, our presentation will also delve into the diffusivity in systems with static energy disorder. Preliminary analysis indicates that static energy disorder can increase the rate of transient wave packet expansion in sufficiently spatially extended initial states (when the initial width exceeds the lattice constant). Interestingly, this enhancement effect is qualitatively similar to the noise-induced effects. These findings suggest the potential for controlling wave packet dynamics through spatial manipulations, a prospect with significant implications for materials science and quantum technologies.



Scheme or Figure 1: Spreading of spatially localized vs extended initial states on a tight binding quantum lattice.

Acknowledgments: The work is supported by the NSF (Grants No. CHE1800301 and No. CHE2324300), and the MIT Sloan fund.

References:

1. I. Tutunnikov, C. Chuang, J. Cao, "Coherent spatial control of wave packet dynamics on quantum lattices", arXiv:2311.07254 [quant-ph], 2023.

Poster no. P_PC_10

Studying ion chemistry using an electrostatic ion trap.

Jehuda Mendelsohn (jehuda.mendelsohn@gmail.com)

Discipline: Molecular dynamics

School: Himmelfarb High School, Jerusalem

Mentor: Alon Bogot, Yael Abraham (yael.abraham@mail.huji.ac.il)

Lab: Professor Daniel Strasser (The Hebrew University of Jerusalem, Los Angeles 38)

Observations in telescopes that measure the emission and absorption of light in interstellar space show that it contains large organic molecules, and the question arises, how are they formed in space? On the surface of the earth there is heat that provides energy (activation energy) for the reactions that create complex organic molecules, but in space and high in the atmosphere, there is not enough energy because the temperatures are low compared to the temperature on Earth. In addition, there is a low pressure (vacuum) where the particle density is much smaller than on Earth. This reduces the chance of a reaction between two separate reactants.

The answer to the question above is that the molecules are formed from reactions by charged reactants that does not require activation energy and can occur even at low temperatures. As the molecules or atoms meet, they form a bond with each other independently of external energy. My research deals with these reactions - without initial energy.

The HEIBT system is a system for capturing positive and negative molecular ions and bringing them close so that a chemical reaction will occur to form neutral particles. The system is made up of several parts that generate, accelerate, focus and center the ions. Finally, the ions enter the ion trap which is a cylindrical body consisting of two sets of round electrodes. One internal set for the negative ions and an external set for the positive ions. Each set consists of two groups of 12 electrodes in each group. The collisions between the ions occur in the middle region where the positive and negative ions move. To avoid collisions with energy, it is necessary to accelerate them at an equal speed and that they will move in the same direction when they collide. The neutral molecule formed finally leaves the ion trap and reaches a camera that transfers the signal to the computer.

In addition, we used MATLAB software to create the simulations and compare these results to the results from the trap.

This research is innovative in that it explores a field that has not been widely studied as it requires the recreation of the conditions in space. In our laboratory we create a way to do it in a relatively cheap and simple way. In my research, I prepared an innovative simulation of the activity of the ion trap system, with the help of which it will be possible to develop the system in a better way. During the research, we discovered that the entire capture device could be redesigned so that it would be cheaper and easier to operate - by replacing the 10 electrodes with three electrodes so that the entire system would have only 20 electrodes instead of 48. Reducing the number of electrodes can reduce and simplify the system, thus encouraging more researchers to try to build a similar device and expand this field of research.

Acknowledgements: I would like to thank Professor Daniel Strasser and Alon Bogot for letting me research in their lab

References:

[1] Shahi A, Singh R, Ossia Y, Zajfman D, Heber O, Strasser D. Hybrid electrostatic ion beam trap (HEIBT): Design and simulation of ion-ion, ion-neutral, and ion-laser interactions. *Review of Scientific Instruments*. 2019;90(11). doi:10.1063/1.5114908

[2] Bogot, A., Lioubashevski, O., Heber, O., Zajfman, D., & Strasser, D. (2023). Simultaneous electrostatic trapping of merged cation & anion beams. *Physical Chemistry Chemical Physics*, *25*(37), 25701–25710. https://doi.org/10.1039/d3cp03633b

Poster no. P_PC_11

ULTRAVIOLET INTRACAVITY LASER ABSORPTION SPECTROSCOPY

Uri Zamir, [a] Maayan Cohen, [a] Illya Rozenberg, [a] Avi Lerer, [a] Yehoshua Kalisky, [b]

Amir Kaplan,[b] Igor Rahinov,*[c] Joshua H. Baraban*[a]

[a] *Department of Chemistry, Ben-Gurion University of the Negev* [b] *Department of Chemistry, IAEC* [c] *Department of Chemistry, Open University of Israel*

E-mail: igorra@openu.ac.il, jbaraban@bgu.ac.il

Intracavity Laser Absorption Spectroscopy (ICAS) provides an excellent solution for ultrasensitive, multiplexed, quan- titative detection of reactive species, but has traditionally been limited to the visible and infrared spectral regions by the requirement for direct broadband lasing media. We report the first realization of this technique in the ultraviolet (UV- ICAS), based on a home-built Ce:LiCAF laser that operates in the 280-316 nm range. Three key species were investigated using our prototype UV-ICAS spectrometer: formaldehyde, sulfur dioxide, and hydroxyl radical. Successful initial measurements of static gases (the formaldehyde $\tilde{A}\,^1A_2 - \tilde{X}\,^1A_1$ electronic transition and the sulfur dioxide $\tilde{X}\,^1B_2 - \tilde{B}\,^1A_1$ electronic transition) led us to record in situ the $A\,^2\Sigma^+ - X\,^2\Pi$ spectrum of hydroxyl radical in a butane flame. Comparison of the latter to a LIFBASE simulation allowed single shot extraction of the temperature of hydroxyl radicals in the flame, demonstrating the data acquisition efficiency of UV-ICAS. We will also discuss the technique's potential for novel ultrasensitive, high resolution, broadband spectroscopy.

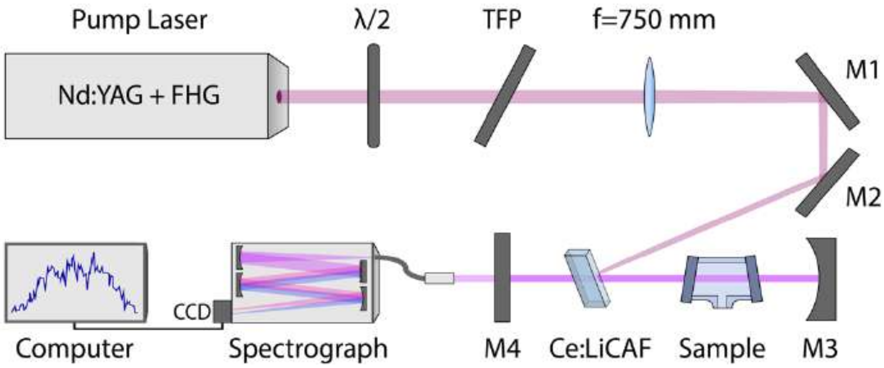


Figure 1: UV-ICAS system schematic.

Acknowledgements: We thank Prof. A. Ishaaya (BGU) for helpful discussions. This project has received funding from the Pazy Foundation (Grants 284 and 293), European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 848668), Israel Science Foundation, Israel, grant No. 194/20, and Israel Ministry of Energy (grant 3-18282/221-17-025).

References:

1. U. Zamir, M. Cohen, A. Lerer, Y. Kalisky, A. Kaplan, I. Rahinov, and J. H. Baraban. Ultraviolet Intracavity Laser Absorption Spectroscopy. *Sensors and Actuators B: Chemical,* 398:134173, 2023.

Poster no. P_PC_12

Color Coding of Axial Fluorophore Distance for Nanometrology

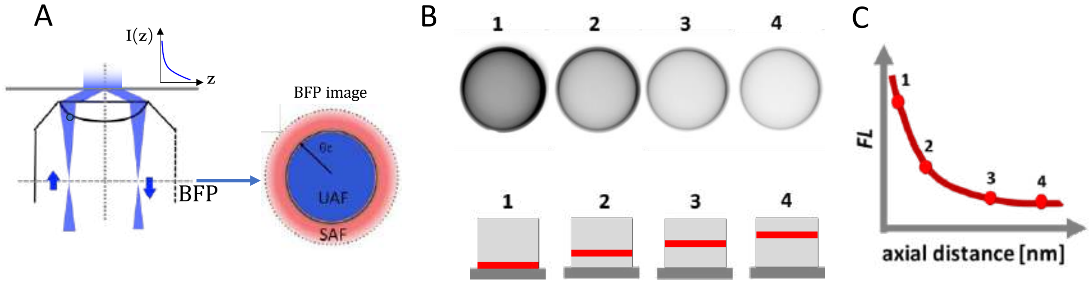
Ilya Olevsko Arad [1,2], Moshe Feldberg[1], Eti Teblum[1], Eswaran Lakshmanan[2], Yossi Abulafia[1], Hodaya Klimovsky[1,2], Paz Toledano[1,2] ,Omer Shavit[1,2,3], Gerardo Byk[2], Martin Oheim[3*], Adi Salomon[1,2*]✉

1. *Institute of Nanotechnology and Advanced Materials (BINA), Bar-Ilan University, Ramat-Gan, 52900 Israel;*
2. *Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52900 Israel;*
3. *Université de Paris, CNRS, SPPIN - Saints-Pères Paris Institute for the Neurosciences, F-75006 Paris, France*

E-mail: adi.salomon@biu.ac.il , martin.oheim@parisdescartes.fr

Evanescent-wave (EW) based fluorescence nanoscopy techniques (also known as critical angles super-resolution microscopy) have expanded optical imaging ability to reach the nanometer resolution range of the near field area. Those methods are a key for studying near-membrane processes in microbiology and neurobiology, but the quantitative interpretation of EW-excited images has been problematic.

In our present work we described the development and fabrication of multi-colors axial nano-ruler devices. Those calibration samples are made of thin fluorescent layer(s) located at a well-defined axial distance and imbedded in water-like optical environment. Ultra-thin and smooth fluorescent films were deposited using different emitters and a modified layer by layer (LBL) technique. Our test slide combines on a standard microscope coverslip substrate two flat, thin, uniform and brightly emitting fluorophore layers, separated by a nanometric transparent spacer layer having a refractive index close to a biological cell. As a proof-of-principle, we estimate the light confinement resulting from evanescent-wave excitation in total internal reflection fluorescence (TIRF) microscopy. Our test sample permits, even for the non-expert user, a facile axial metrology at the sub-100-nm scale, a critical requirement for axial super-resolution, as well as near-surface imaging, spectroscopy, and sensing. We have experimentally shown that our multi-color test samples, in conjunction with Back Focal Plane imaging (BFP) analysis (as outlined in Klimovsky, H. et al. 2023), generate a reliable calibration curve for TIRF , exhibiting emission patterns in strong agreement with theoretical expectations.



Construction of the axial calibration curve for EW microscopies. (A) An illustration depicting EW excitation and a Back Focal Plane image that showcases the separation into supercritical fluorescence (SAF) and under-critical fluorescence (UAF). (B) Back Focal Plane images (Inverted color) capturing axial series from fluorophores positioned at different axial

Poster no. P_PC_13

The Effect of Pre-Adsorbed Oxygen on the Growth of D_2O Multilayers on Cu(111)

Michelle Sykes Akerman and Baran Eren*

Department of Chemical and Biological Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

Email: michelle.akerman@weizmann.ac.il, baran.eren@weizmann.ac.il

Understanding water-surface interactions is important in various fields such as electrochemistry, atmospheric chemistry, and heterogenous catalysis. The adsorption of water molecules on a substrate is influenced by the substrate-water interaction as well as by hydrogen bonding interactions between neighboring water molecules. The properties of the substrate and its structure dictate the adsorption geometry of individual water molecules on the surface and the growth mechanism of the first layers of water. Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) can be used to study how the properties of the substrate affect the structure of multilayer crystalline water ice films grown under ultrahigh vacuum (UHV) conditions and at cryogenic temperatures. Pre-covering a Cu(111) surface with oxygen changes the substrate from hydrophobic to hydrophilic. Crystalline multilayer films of D_2O are grown on Cu(111) and Cu(111) + O_2 at 160 K under a constant flow of D_2O vapor. PM-IRRAS measurements show that the structure of D_2O ice grown on Cu(111) is different from D_2O ices grown on Cu(111) + O_2 (**Figure 1a-b**). The characteristic asymmetric (ν_1 ~2500 cm^{-1}) and symmetric (ν_3 ~2445 cm^{-1}) OD stretching peaks are observed for both films. The differences in the relative intensities of the asymmetric and symmetric OD stretching peaks reveal differences in the D_2O film structures. For D_2O multilayers grown on Cu(111), the asymmetric peak is more intense, indicating that the films are more disordered. In this case, the first layers of D_2O are probably comprised of domains of D_2O molecules adsorbed D-up and D-down. In contrast, D_2O multilayers grown on Cu(111) + O_2 initially show a more intense symmetric OD stretching peak, indicating that these films are more ordered. On this surface, there is a preference for the D_2O molecules to adsorb D-down, so that the D_2O molecules can hydrogen bond with the oxygen adsorbed on the Cu(111) surface.

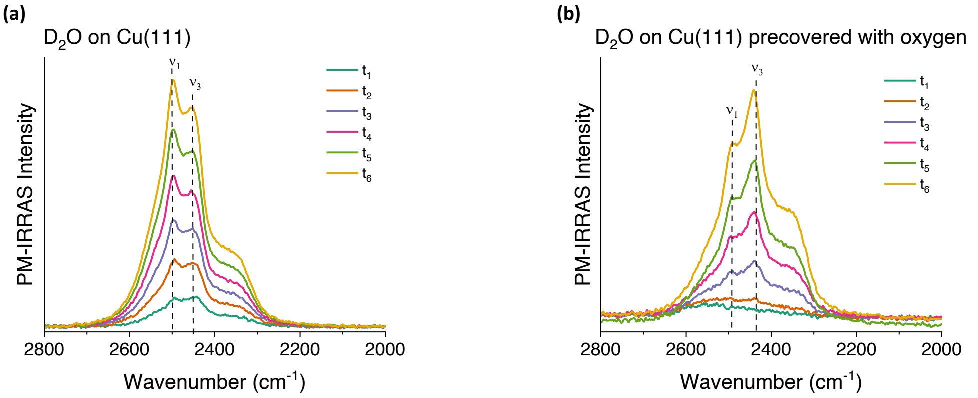


Figure 1a-b. PM-IRRAS Measurements of (a) First layers of D_2O on Cu(111) and (b) First layers of D_2O on Cu(111) + O_2

Poster no. P_PC_14

Operando NEXAFS characterization of Nickel nanoparticles during OER

Miguel A. Andrés,[a] Bat-Or Shalom,[a] Ashley R. Head,[b] Olga Brontvein,[c] Alex S.Walton,[d] Kacper Polus,[d] Boruch Z. Epstein,[e] Robert S. Weatherup,[e], Baran Eren,*[a]

[a] Dept. of Chemical and Biological Physics, Weizmann Institute of Science, 234 Herzl St, Rehovot (Israel). [b] Center for Functional Nanomaterials, Brookhaven National Lab., Upton (U.S.). [c] Chemical Research Support, Weizmann Institute of Science, 234 Herzl St, Rehovot (Israel). [d] Photon Science Institute, Univ. of Manchester, Oxford Road, Manchester (U.K.). [e] Dept. of Materials, University of Oxford, Parks Road, Oxford (U.K.).

E-mail: baran.eren@weizmann.ac.il

The increasingly rising population is putting massive pressure on global energy demand, with fossil fuels being one of the main pillars of the modern energy and economy sectors. Some reports have forecast that crude oil reserves could be outgrown within a few decades[1]. As a consequence, there is a rising interest in finding alternative energy sources that are able to provide high calorific values with ideally no carbon emissions[2]. Water electrolysis is a promising energy vector and a serious alternative to batteries, especially when combined with fuel cells for the on-site generation of electricity. This process involves two simultaneous reactions, the hydrogen evolution reaction (HER) in the cathode and the oxygen evolution reaction (OER) in the anode. However, the OER suffers from sluggish kinetics due to its 4-electron transfer process. Transition metals (e.g., Co, Ni, Fe) are an inexpensive alternative to precious metal catalysts (e.g., Pt). However, there are still open questions about their mechanism to catalyze the OER. Optimizing the OER electrocatalysts has to be a top priority for advancing this utmost important technology further.

Our group uses a very unique approach, where microelectrochemical reactors are capped with perforated silicon nitride grids containing a few layers of graphene. Graphene acts as a catalyst bed for the model catalyst NPs while it is transparent enough to allow access to spectroscopies using X-rays as a probe. In this contribution, we use X-Ray Photoelectron Spectroscopy (XPS) in conjunction with Near Edge X-Ray Absorption Fine Structure (NEXAFS) to investigate Ni NPs under *operando* conditions in alkaline media. While XPS gives access to the oxidation state, NEXAFS is also sensitive to the bonding environment, so it can provide information about the geometry, bonding distances and neighboring atoms. Our results confirm previous observations that Ni^{3+} and Ni^{2+} coexist during OER conditions[3]. Moreover, the presence of Fe from impurities or alloying greatly increases the activity of Ni NPs by promoting their oxidation. Theoretical modeling of NEXAFS data can also give insights about the different species involved in the reaction, such as α- and β-$Ni(OH)_2$ or γ-NiOOH. This tandem approach can be extended to other reactions as well, revealing insights into the working mechanism and efficiency of the electrocatalyst NPs.

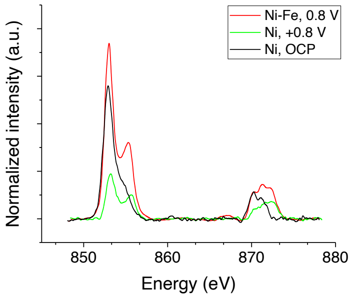


Figure 1: *Operando* NEXAFS obtained on a sample with Ni NPs at OCP and +0.8 V bias, and a Ni-Fe 81-19 % alloy at +0.8 V bias.

Acknowledgments: M.A.A. acknowledges the 'la Caixa' Foundation postdoctoral fellowship. The authors also acknowledge financial support from the following institutions and programs: U.S. – Israel Binational Science Foundation (BSF), the Ministry of Energy of Israel, the Weizmann-UK making Connections Program, the European Research Council (ERC).

References:

1. Owen, N. A.; Inderwildi, O. R.; King, D.A. The status of conventional world oil reserves—Hype or cause for concern?, *Energy Policy* **2010**, *38*(8), 4743-4749.
2. Stančin, H.; Mikulčić, H.; Wang, X.; Duić, N. A review on alternative fuels in future energy system, *Renew. Sust. Energ. Rev.* **2020**, *128*, 109927.
3. Joya, K. S.; Joya, Y. F.; Groot, H. J. M. Ni-based Electrocatalyst for Water Oxidation Developed In-Situ in A HCO3-/CO2 System at Near-Neutral pH. *Adv. Energy Mater.* **2014**, *4*, 1301929.

Poster no. P_PC_15

Investigating Radical Chemistry With Synchrotron Radiation

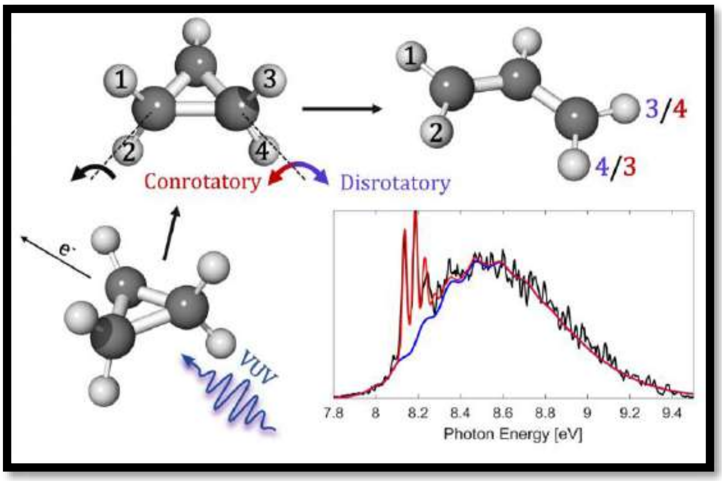
Nadav Genossar-Dan*[a] and Joshua H. Baraban[a]

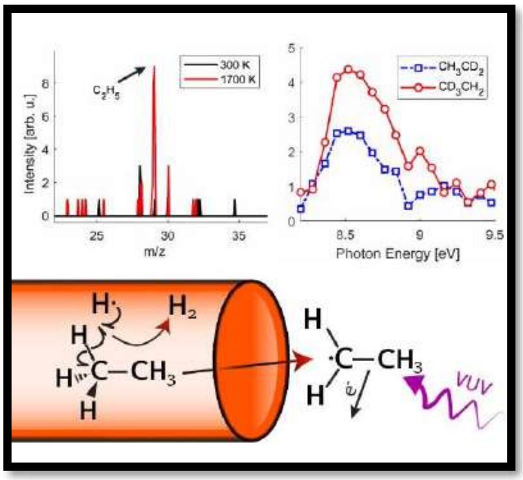
[a] *Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva, Israel.*

E-mail: nadavge@post.bgu.ac.il

Chemistry in extreme environments, such as pyrolysis, combustion, and astrochemical processes, is often driven by radicals. Particularly interesting examples include molecular growth by radical chain and ring-forming reactions. However, due to their high reactivity, the direct observation of these important intermediate species in reactive chemical systems requires the use of advanced spectroscopic tools with great sensitivity and selectivity.

In my talk, I will show how using tunable vacuum ultraviolet (VUV) radiation from synchrotron sources, coupled to a photoelectron-photoion coincidence (PEPICO) spectrometer, we are capable of detecting and characterizing previously unobserved radicals involved in even some of the simplest reactions, such as the pyrolysis of ethane and acrolein[1,2], the ring opening of cyclopropyl[3], and the radical Diels-Alder reaction between ethylene and allyl. Combined with advanced kinetic and spectroscopic simulations based on high accuracy *ab initio* quantum chemistry, our results shed new light upon the mechanisms of these reactions, and advance our understanding of radical chain reactions and pericyclic systems.





References:

1. Nadav Genossar-Dan, Sharona Atlas, Dana Fux, Shani Har Lavan, Uri Zamir, Illya Rozenberg, Thanh Lam Nguyen, Patrick Hemberger and Joshua H. Baraban. Direct Observation of the Ethyl Radical in the Pyrolysis of Ethane. *Angewandte Chemie International Edition*, e202305881, 2023.

2. Michael Muzika, Nadav Genossar-Dan, Dana Fux, Shani Har Lavan, Uri Zamir, Illya Rozenberg, Patrick Hemberger and Joshua H. Baraban. Radical intermediates and stable products in acrolein pyrolysis. *Environmental Chemistry Letters*, 2023.

3. Nadav Genossar, P. Bryan Changala, Bérenger Gans, J.-C. Loison, Sebastian Hartweg, Marie-Aline Martin-Drumel, Gustavo Garcia, John F. Stanton, Branko Ruscic, and Joshua H. Baraban. Ring Opening Dynamics of the Cyclopropyl Radical and Cation: The Transition State Nature of the Cyclopropyl Cation. *Journal of the American Chemical Society*, 144(40):18518-18525, 2022.

Poster no. P_PC-16

Improving the quality factors of plasmonic silver cavities for strong coupling with quantum emitters

Ora Bitton[1,*], Lothar Houben[1], Hagai Cohen[1], Sigal Keshet[1], Eran Mishuk[1], Alexander Vaskevich[2] and Gilad Haran[2]

(1) Chemical Research Support department, Faculty of Chemistry, Weizmann Institute of Science, Rehovot, Israel

(2) Department of Chemical and Biological Physics, Faculty of Chemistry, Weizmann Institute of Science, Rehovot, Israel

*Ora.Bitton@weizmann.ac.il

Silver is known as potentially the best plasmonic material with the naturally lowest ohmic losses and therefore are the most favorable for light-matter interaction. We previously showed that we can observe strong coupling (SC) in the limit of a single quantum emitter positioned within a plasmonic silver bowtie cavity[1-4]. Scattering spectra and electron energy loss spectroscopy (EELS), registered from individual bowties containing one to a few colloidal quantum dots (QDs) showed vacuum Rabi splitting, indicating that the SC regime was approached both in bright and dark plasmonic modes.

Damping reduction increases the quality factor of these cavities and therefore facilitating reaching the SC regime with QDs. One of the elements that has a large impact on the plasmon damping and that is very often ignored is the adhesion layer. Despite this, in-depth characterization of localized surface plasmons in lithographic silver nanostructures have not been fully characterized compared to gold. In this work we show that sub 1 nm thick of deposited Ti as an adhesion layer on SiO_2 substrate results in significant decrease of plasmon linewidth compared to no-adhesion layer bowties. The key for understanding the narrowing of plasmon linewidth is the formation of titanium dioxide (TiO_2) during deposition. In this work we aim to understand the mechanism behind the decrease in plasmon damping when TiO_2 adhesion layer is used, as opposed to plasmonic bowties sitting directly on SiO_2 substrate. Interestingly, the observed decrease in plasmon damping in the presence of TiO_2 adhesion layer is unique to bowtie structures and does not occur in the case of individual prisms, implying that the hotspot plays a crucial role in the mechanism behind this effect. In-depth analysis reveals that the bowties are characterized by a very unique geometry and this sheds light on which damping mechanism is responsible for the observed narrowing of plasmon linewidth.

[1] Santhosh, K., Bitton, O., Chuntonov, L. & Haran, G. *Vacuum Rabi splitting in a plasmonic cavity at the single quantum emitter limit*. Nature communications 7, 11823, (2016).

[2] Bitton, O. & Haran, G. *Plasmonic Cavities and Individual Quantum Emitters in the Strong Coupling Limit.* Acc. Chem. Res. 55, 12, 1659–1668 (2022).

[3] Bitton, O., Nath Gupta, S., Houben, L., Kvapil, M., Křápek, V., Šikola, T., Haran, G. *Vacuum Rabi splitting of a dark plasmonic cavity mode revealed by fast electrons*. Nature Communications 11, 487 (2020).

[4] Nath Gupta, S., Bitton, O., Neuman, T., Esteban, R., Chuntonov, L., Aizpurua, J., Haran, G. *Complex plasmon-exciton dynamics revealed through quantum dot light emission in a cavity.* Nature Communications 12, 1310 (2021).

Poster no. P_PC_17

Nitrogen Substitutions Clustering in Diamonds as Revealed by High-Field Electron Paramagnetic Resonance and Dynamic Nuclear Polarization

Orit Nir-Arad [a], David Shlomi[a], Eyal Laster[a], Nurit Manukovsky[a], Alexander Fialkov[a], Ilia Kaminker*[a]

[a] *School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv, Israel.*

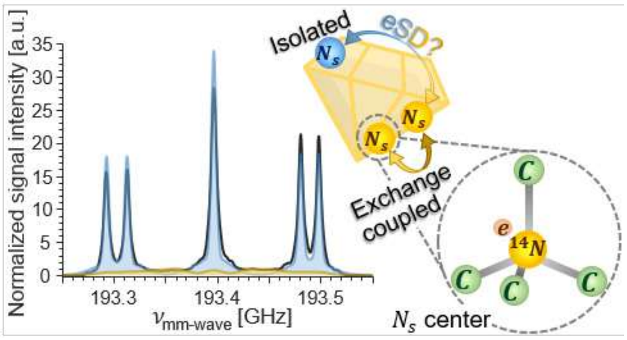
E-mail: iliakam@tauex.tau.ac.il

Dynamic Nuclear Polarization (DNP) was shown to enhance Nuclear Magnetic Resonance (NMR) signals by orders of magnitude, vastly expanding the range of NMR applications. For the largest benefits, DNP must be performed at high magnetic fields where the resolution and information content of NMR are maximal. Understanding DNP quantum mechanics requires knowledge about electron spin dynamics, available only through Electron Paramagnetic Resonance (EPR) experiments, such as electron-electron double resonance (ELDOR).[1-3] Since electron spin properties are field-dependent they must be performed at high fields characteristic of DNP. However, the required high-field EPR instrumentation is commercially unavailable, making the relevant data unobtainable.

Over the past five years, our group constructed a dual DNP/EPR spectrometer, operating at 13.8 and 6.9 T, capable of multinuclear static DNP, continuous wave EPR, pulsed EPR, and ELDOR. Using these new capabilities we investigated the DNP mechanisms in substitutional nitrogen centers in diamond (P1 centers). P1 centers were recently shown to provide efficient hyperpolarization at room temperature and 3.3 T with multiple DNP mechanisms contributing to the DNP lineshape.[4] We present the first hyperpolarization results using P1-DNP at 13.8 T and show that in this field too, P1-DNP is very efficient, and is mediated by multiple mechanisms in a complex interplay.

In order to rationalize our DNP results we performed EPR measurements at both 13.8 and 6.9 T. The resulting P1-EPR spectra revealed an unexpected broad signal with fast relaxation in between the sharp P1 peaks. Using simulations of the EPR line we could assign this broad signal to exchange-coupled P1 center clusters and quantify the ratios between them and the other populations of P1 centers in the diamond.[5] Using ELDOR experiments, we showed that all P1 populations interact which provides an efficient mechanism for electron-electron spectral diffusion (eSD). At 13.8 T eSD is even stronger due to a strong state mixing between the ^{14}N hyperfine levels.

This work shows the importance of the previously unnoticed P1 population for DNP and that EPR results acquired under DNP conditions are indispensable for the identification of the active DNP mechanisms.



References:

1. Hovav, Y.; Kaminker, I.; Shimon, D.; Feintuch, A.; Goldfarb, D.; Vega, S. The Electron Depolarization during Dynamic Nuclear Polarization: Measurements and Simulations. *Phys. Chem. Chem. Phys.* **2014**, *17* (1), 226–244.
2. Hovav, Y.; Shimon, D.; Kaminker, I.; Feintuch, A.; Goldfarb, D.; Vega, S. Effects of the Electron Polarization on Dynamic Nuclear Polarization in Solids. *Phys. Chem. Chem. Phys.* **2015**, *17* (8), 6053–6065.
3. Shimon, D.; Kaminker, I. A Transition from Solid Effect to Indirect Cross Effect with Broadband Microwave Irradiation. *Phys. Chem. Chem. Phys.* **2022**, *24* (12), 7311–7322.
4. Shimon, D.; Cantwell, K. A.; Joseph, L.; Williams, E. Q.; Peng, Z.; Takahashi, S.; Ramanathan, C. Large Room Temperature Bulk DNP of 13C via P1 Centers in Diamond. *J. Phys. Chem. C* **2022**, *126* (41), 17777–17787.
5. Nir-Arad, O.; Shlomi, D. H.; Manukovsky, N.; Laster, E.; Kaminker, I. Nitrogen Substitutions Aggregation and Clustering in Diamonds as Revealed by High-Field Electron Paramagnetic Resonance. *J. Am. Chem. Soc.* **2023**.

Poster no. P-PC_18

Multinuclear NMR diffusion measurements of isotopic effects on selfdiffusion of water and aqueous ions

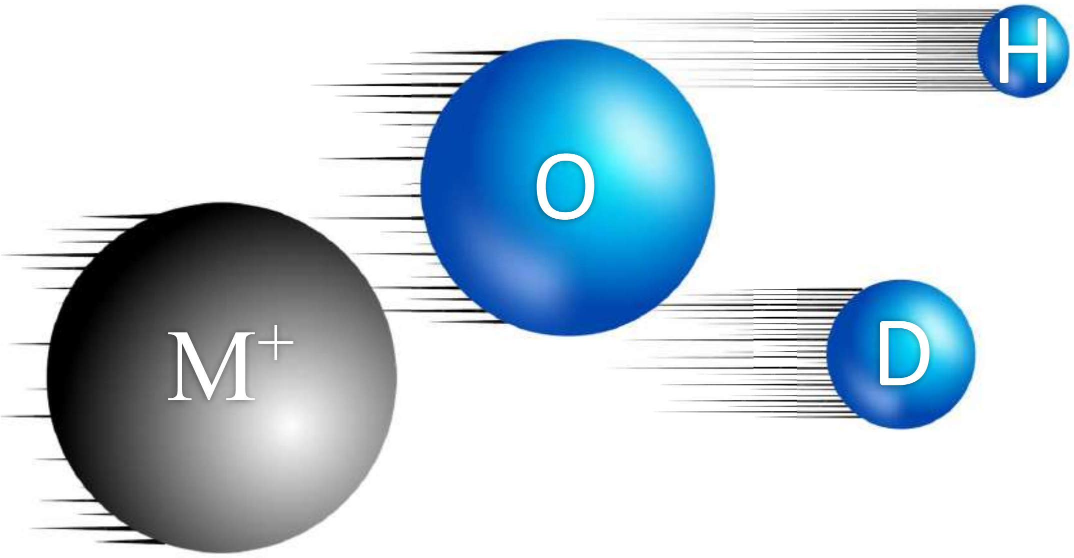
Roy E. Hoffman

The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.

E-mail: royh63@gmail.com

NMR measurements of the diffusion rate of water vary depending on which nucleus is measured. This is due to exchange of protons on the NMR timescale which means that they move at a different rate than that of oxygen. For the first time, the NMR diffusion of $^{17}0$ is measured and is found to be different from the diffusion rate of protons. The gradient strength for diffusion measurements is often calibrated to that of protons in water or residual protons in D_2O which are, in turn, referenced to optical measurements. If different parts of the water molecule diffuse at different rates, then such calibration is invalid.

The diffusion rates of protons and deuterons are compared and discussed. The diffusion rates of aqueous ions in water and the influence of deuteration are measured.



Poster no. P-PC_19

Atomic composition analysis in 4D-STEM

Shahar Seifer[a], Lothar Houben[b], Michael Elbaum[a]

[a] *Chemical and Biological Physics, Weizmann Institute of Science, Israel.* [b] *Chemical Support Unit, Weizmann Institute of Science, Israel.*

E-mail: Shahar.seifer@weizmann.ac.il, Michael.Elbaum@weizmann.ac.il

4-dimensional Scanning Transmission Electron Microscopy (4D-STEM) uses a fast camera to record a 2D diffraction image per scan position (see Fig.1). It is well developed as a tool for mapping phases of crystalline structures. In amorphous materials, we can extract the angular distribution for electron scattering, both elastic and inelastic, by the sample. The elastic cross section is related to the Coulomb potential of the nuclei, and theoretical calculations are available. For inelastic scattering, we extend calculations of Inokuti that were applied so far in stopping power predictions. The oscillator strength of discrete electronic transitions can be related to the probability of Plasmon generation, which is the leading cause of inelastic cross section. Plasmons interact with the probing electron and we are able to observe the Lorentzian angular distribution in momentum transfer. We used a pixelated detector mounted behind an energy filter to monitor the separate contributions of elastic and inelastic scattering for amorphous carbon, silica, and vitrified water. We find that for light atoms the separation in energy loss emerges naturally between small and large scattering angles. We define specific scattering coefficients from the measurement that enable characterize the intrinsic material properties, and compare the results to our theoretical predictions. Thus, we are able to show that a fingerprint of the material composition can be identified at the nanoscale based on analysis of the 4D-STEM data. Such approach is applicable also in 3D tomographic reconstruction of a tilt series for biological samples.

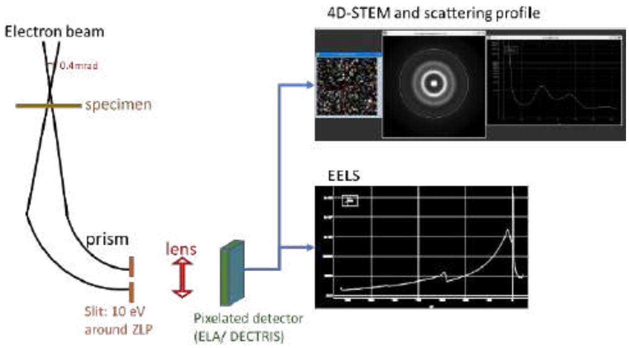


Figure 1: Setup of 4D-STEM with energy-loss filter in a transmission electron microscope

References:

1. Shahar Seifer, Lothar Houben, Michael Elbaum, Ultramicroscopy 2024 (https://doi.org/10.1016/j.ultramic.2024.113936)

Poster no. P_PC_20

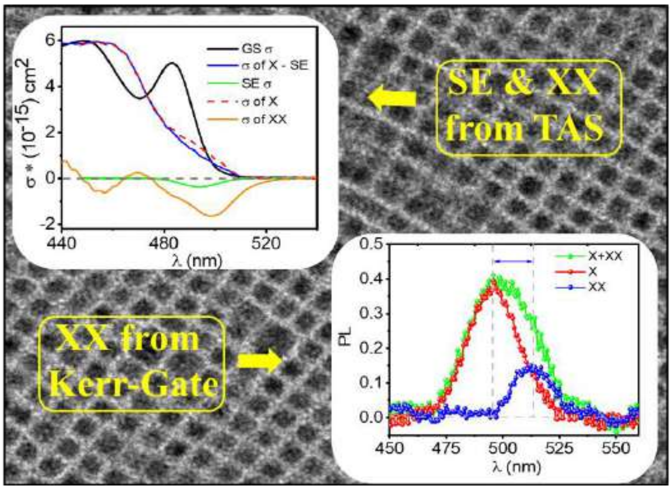
Time-resolved emission vs pump-push-probe in quantum confined $CsPbBr_3$ nanocrystals: Finding towards bi-exciton interaction and stimulated emission.

*Apurba De, Soumyadip Bhunia, Tal Binyamin, Lioz Etgar and Sanford Ruhman**
Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem-91904, Israel
**Corresponding author: sandy@mail.huji.ac.il*

Abstract

Quantum-confined $CsPbBr_3$ nanocrystals exhibit unique photophysical properties including particle size-dependent brightness of the lowest-lying exciton state and appearance of unusual photoinduced absorption bands in relaxed mono-exciton transient absorption. Given recent studies that contest this, similar samples are revisited here by comparing time-resolved fluorescence and wavelength-dependent three-pulse "spectator exciton" experiments.[1] It involves a comparison of identical pump-probe sequences, once on unexcited NCs, and then on a sample that has been uniformly excited with one cold exciton per particle – the spectator. The latter can be generated by high intensity above BE excitation which initially generates a distribution of multi-exciton states.

Results clarify the long-term debate regarding bi-exciton interaction, which is indeed strongly attractive. Hot exciton cooling following recombination of several excitons is found to be prolonged from less than one to several picoseconds, slower even than bi-exciton recombination itself. Using the 3-pulse "spectator exciton" method we have determined the cross section for stimulated emission from the relaxed single excitons in QC $CsPbBr_3$ NCs, even in overlapping continued absorption at the BE (Scheme 1).[2] The degeneracy and selection rules concerning BE states from this measure, as well as all cross-sections will be represented.



Scheme 1: Single-exciton, bi-exciton, stimulated emission cross sections in a quantum confined $CsPbBr_3$ NCs

Acknowledgements: S.B. thank the S.A. Schonbrunn Fund for financial support.

References:

1 T. Ghosh, J. Dehnel, M. Fabian, E. Lifshitz, R. Baer and S. Ruhman, Spin Blockades to Relaxation of Hot Multiexcitons in Nanocrystals *J. Phys. Chem. Lett.*, 2019, **10**, 2341–2348.

2 A. De, S. Bhunia, T. Binyamin, L. Etgar and S. Ruhman, Time resolved emission vs multi-pulse pump-probe in quantum confined $CsPbBr_3$ nanocrystals: Revised bi-exciton interaction estimates, and direct measurement of stimulated emission cross sections. *(Manuscript under preparation)*.

Poster no. P_PC_21

Drunk Membranes: Phospholipids under High Concentrations of Ethanol and Methanol

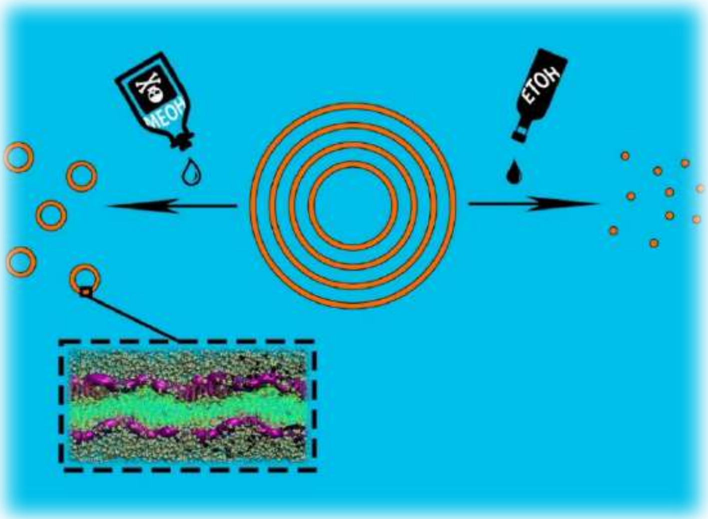
Yehonatan Levy[1], Uri Raviv[1], Dganit Danino[2] and Daniel Harries[1]

1 Institute of Chemistry, The Fritz Haber Research Center, The Hebrew University, Jerusalem 9190401, Israel; 2 Technion, Haifa, Israel 32000

Author's e-mail: yehon.levy@mail.huji.ac.il

Alcohol is known to impact the structure of lipid bilayers, but most studies of ethanol and methanol have focused on low concentrations of alcohol. Here, we focus on the impact of ethanol and methanol on DMPC (1,2-Dimyristoyl-sn-glycero-3-phosphocholine) over a wide range of alcohol concentrations.

We employ small-angle X-ray scattering (SAXS), cryo-electron microscopy, and molecular dynamic (MD) simulations to determine changes in the lipid's structure. We find that at low to moderate concentrations, alcohol increases the distance between DMPC layers, due to an increase in the repulsive undulation force. Structurally, membrane softening is due to alcohols acting similar to a surfactant, concentrating in the headgroup region. At even higher alcohol concentrations, we find a lipid unbinding transition, and thereafter a transition into smaller micellar structures. Our study links the molecular interactions between lipid assemblies and alcohol that lead to rich structural transitions.



Poster no. P_PC_22

Coherent Control of Ultrafast Molecule Making

Moran Geva,[a] Arie Landau,[a] and Zohar Amitay*[a]

[a] *Schulich Faculty of Chemistry, Technion-IIT, Haifa 32000, Israel.*

E-mail: amitayz@technion.ac.il

One of the holy grails in the field of quantum coherent control is the yet-to-be-realized coherent control of binary chemical photoreactions. The operating principle is to use shaped femtosecond pulses to control and actively drive binary chemical reaction along its full desired path from the initial state of the reactants to the final state of the desired products. This is actually one of the dreams that led, more than thirty years ago, to the birth of the coherent control concept. Its realization at high temperatures, which are typical of chemical reactions, will enable a novel type of photochemistry. The first part of the scheme is a coherently controlled ultrafast making of a molecular intermediate from the pair of free colliding reactants via a photo-excitation at short internuclear distances to target electronically-excited molecular states. The molecular intermediate can generally be of a different type, depending on the case, ranging from a strongly-bound molecule with a covalent bonding to a molecule that is a weakly-bound or an unbound van-der-Waals complex. Subsequently, in the second part, the generated intermediate undergoes further photo-control, leading to its dissociation into the intended products.

The specific excitation scenario of the ultrafast molecule making is set by the involved molecular states and the transitions among them that are photo-induced by the laser pulse. Since different intensity regimes are best suited for coherently controlling different scenarios, in order to handle diverse excitation situations, feasibility with both weak and strong fields is essential. So far, following many years without any experimental realization of coherent control of ultrafast molecule making (CC-UMM) despite its importance, CC-UMM was successfully demonstrated experimentally only in the strong-field regime [1,2,3]. Strong shaped femtosecond pulses controlled there the making of Mg_2 molecules from thermally-hot pairs of colliding Mg atoms via a non-resonant two-photon transition followed by multiple Raman transitions.

Here, we experimentally demonstrate for the first time coherent control of ultrafast molecule making in the weak-field regime [4]. It is achieved even under thermally hot conditions typical of chemical reactions, which are extremely challenging due to the initial incoherent population of a vast number of scattering eigenstates. The weak-field regime corresponds to a photo-excitation that is fully described within the corresponding lowest-order time-dependent perturbation theory. For a two-photon excitation, it is the second-order one. We coherently control by weak linearly-chirped femtosecond pulses the making of KAr complexes from thermally-hot pairs of colliding K and Ar atoms via a resonance-mediated two-photon transition. Our ab initio studies are in excellent agreement with the experiments and explain them. The control mechanism is identified to combine Franck-Condon filtering and phase-dependent shaped excitation of the selected excitation channels. The former purifies the huge thermal ensemble of excitation channels and selects a sub-ensemble of channels that is susceptible for coherent control, while the latter realizes their control by manipulating intra-channel interferences. Our experiments are also the first to achieve weak-field femtosecond coherent control of any initially-unbound system. The demonstrated control of the KAr system serves as a basic model for controlling triatomic systems, with an atom and a diatomic molecule as the reactants, that are non-reactive in their ground electronic state and all their excited electronic states are weakly-bound or unbound.

With the weak-field feasibility, the toolbox for coherent control of ultrafast molecule making can now handle many new excitation scenarios that their control is superior or only possible with weak fields. This opens up new feasible routes for the coherent control of binary chemical photoreactions.

References:

1. L. Levin, W. Skomorowski, L. Rybak, R. Kosloff, C. P. Koch, and Z. Amitay, Physical Review Letters 114, 233003 (2015).
2. L. Levin, W. Skomorowski, R. Kosloff, C. P. Koch, and Z. Amitay, Journal of Physics B: Atomic, Molecular and Optical Physics 48, 184004 (2015).
3. L. Levin, D. M. Reich, M. Geva, R. Kosloff, C. P. Koch, and Z. Amitay, Journal of Physics B: Atomic, Molecular and Optical Physics 54, 144007 (2021).
4. M. Geva, Y. Langbeheim, A. Landau and Z. Amitay, arXiv:2301.05951.

Poster no. P_PC-23

Proton transport from the membrane interface and the bulk solution to the Gramicidin channel

Zohar Klein and Nadav Amdursky

[a] *Chemistry Department, Technion, Shulich Faculty, floor 2, room 203*

E-mail: Zohar.klein@campus.technion.ac.il

Abstract

Gramicidin is a peptide secreted by the soil bacterium *Bacillus brevis.* Gramicidin dimer creates an ion channel in the lipid bilayer, selective to protons and other monovalent cations. In this research, we want to investigate whether protons reach Gramicidin through the bulk or the membrane's surface. To answer that question, we use the photoacid 8-hydroxy-1,3,6-pyrenetrisulfonate (HPTS), which can be dissolved in the bulk solution or tethered to the membrane (C_{12}HPTS). The photoacid releases its proton in its excited state, and that proton can reach the Gramicidin channel. By time-resolved fluorescence and electrical measurements, we can follow the kinetics of the proton pass through the Gramicidin.

References

1. Debra L. Wyatt, D. L., de Godoy, C. M. G., Cukierman, S., Enhancement of Proton Transfer in Ion Channels by Membrane Phosphate Headgroups. J. Phys. Chem. B 113, 6725–6731 (2009)
2. Cukierman, S., The Transfer of Protons in Water Wires Inside Proteins. Frontiers in Bioscience 8, s1118-1139, (2003)

Soft Matter and Biophysics

Poster no. P_SB_01

Solid-state Molecular Protonics Devices of Solid-Supported Biological Membranes Reveal the Mechanism of Long-Range Lateral Proton Transport

Ambili Ramanthrikkovil Variyam,[a] Mikhail Stolov,[b] Jiajun Feng,[a] and Nadav Amdursky[a],*

[a]*Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 3200003, Israel.*

[b]*Wolfson Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa 3200003, Israel.*

E-mail: amdursky@technion.ac.il

Lateral proton transport (PT) on the surface of biological membranes is a fundamental biochemical process in the bioenergetics of living cells, but a lack of available experimental techniques has resulted in a limited understanding of its mechanism. Here, we present a molecular protonics experimental approach to investigate lateral PT across membranes by measuring long-range (70 μm) lateral proton conduction via a few layers of lipid bilayers in a solid-state-like environment, i.e., without having bulk water surrounding the membrane. This configuration enables focusing on lateral proton conduction across the surface of the membrane while decoupling it from bulk water. Hence, by controlling the relative humidity of the environment, we can directly explore the role of water in the lateral PT process. We show that proton conduction is dependent on the number of water molecules and their structure and on membrane composition, where we explore the role of the head group, the tail saturation, the membrane phase, and membrane fluidity. The measured PT as a function of temperature shows an inverse temperature dependency, which we explain by the desorption/adsorption of water molecules into the solid membrane platform. We explain our findings by discussing the role of percolating hydrogen bonding within the membrane structure in a Grotthuss-like mechanism.

References:

1. Teissie, J.; Prats, M.; Soucaille, P.; Tocanne, J. F., Evidence for conduction of protons along the interface between water and a polar lipid monolayer. Proc. Natl. Acad. Sci. U.S.A. 1985, 82 (10), 3217-3221.

2. Alexiev, U.; Mollaaghababa, R.; Scherrer, P.; Khorana, H. G.; Heyn, M. P., Rapid long-range proton diffusion along the surface of the purple membrane and delayed proton transfer into the bulk. Proc. Natl. Acad. Sci. U.S.A. 1995, 92 (2), 372-376.

Poster no. P_SB_02

The role of hydroxyproline in proton transport across collagen structures

Anna Orieshyna1[a], Jennifer L Puetzer[b], and Nadav Amdursky*[a]

[a] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 3200003, Israel*

[b] *Department of Biomedical Engineering, Virginia Commonwealth University, Richmond, VA 23220, USA*

E-mail: amdursky@technion.ac.il

Collagen is one of the most studied proteins due to its fundamental role in creating fibrillar structures and supporting tissues in our bodies. Accordingly, collagen is also one of the most used proteins for making tissue-engineered scaffolds for various types of tissues. One of the unique hallmarks of collagen is the presence of the hydroxyproline (Hyp) amino acid residue, which is being formed enzymatically following collagen translation. To date, the role of Hyp within collagen was solely ascribed to the structure of the final fibril. Here, considering the high abundance of Hyp within collagen and its ability to participate in hydrogen bonding, we hypothesize a new role for the presence of Hyp in collagen, which is to support proton transport (PT) across the collagen fibrillar structure. To explore the possibility of collagen to mediate protons, we use here both the natural fibril configuration of collagen as well as two different scaffold configurations, one is based on the self-coupling between collagen fibrils and the other using an external cross-linker. For this purpose, we explore three different collagen-based hydrogels: the first is based on the self-assembly of natural collagen fibrils, the second and third are based on covalently linking between collagen fibrils, one via a self-coupling method, and the other with an additional crosslinker (glutaraldehyde). Following the formation and the structural and morphological characterization of the hydrogel, we introduce here a 2-step reaction that target the Hyp residue for our investigation of its role in PT across the collagen structure. Such chemical reaction is involving 1) attaching methanesulfonyl to the -OH of Hyp, followed by 2) removing the oxidized methanesulfonyl, thus, in the end, we are reverting Hyp to Pro. We explore the PT efficiency at each step of the reaction using electrical measurements and show that adding the methanesulfonyl group vastly enhances PT, while reverting Hyp to Pro significantly reduces PT efficiency (compared to the initial point) with different efficiencies for the various collagen-based hydrogels. Our findings here are the first to open the discussion about the physiological role of PT across collagen within the ECM, for example in signal transduction. The ability of collagen to support PT can assist in our understanding of the physiological roles of collagen. From a practical perspective, we show here the ability to tune the electronic (protonic) properties of collagen-based scaffolds that were prepared in different methodologies while still having only collagen in the scaffold, i.e., without the integration of foreign electronic mediators, which can be important to any use of collagen in tissue engineering applications.

Poster no. P_SB_03

Thiolate-Stabilized Peptide Hydrogel Shells on Noble Metal Nanoparticles

Arghyadeep Basu, [a] and Lev Chuntonov*[a]

[a] *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel.*

E-mail: arghadeep@campus.technion.ac.il and chunt@technion.ac.il

Peptide-functionalized nanoparticles are considered important biocompatible nanomaterials with a wide range of applications. The development of biocompatible nanocoating, as well as a thorough understanding of their intricate structures is pivotal for their effective usage. We have functionalized colloidal metal nanoparticles with M(I)-GSH hydrogel shells (where M is a coinage metal, namely, Cu, Ag, or Au, and glutathione or GSH is a short tripeptide).[1,2,3] These hydrogel shells on the nanoparticle surface present a combination of two distinctive properties: a few nanometer-thick hydrogel shells on the nanoparticle surface offer possibilities to use their soft framework for loading and scaffolding, and the nanoparticle core displays localized plasmon resonance. We have analyzed the shell's molecular structure on the nanoparticle surface and in the bulk, by theoretical and experimental methods such as density functional theory, isotope labeling, and two-dimensional infrared spectroscopy (2DIR). 2DIR study shows that hydrogel shells have pronounced spectroscopic signatures of the parallel beta-sheet-like conformation whereas density functional computational modeling of the M(I)-GSH aggregate, suggests that aggregation of glutathione peptides occurs in parallel strand configuration via kinetic pathways. Other analytical techniques such as dynamic light scattering spectroscopy (DLS), localized plasmon resonance spectroscopy (LSPR), X-ray photoelectron spectroscopy (XPS), and thiol-sensitive absorption spectroscopy further suggest that the thickness of the shell on metal nanoparticle surface is ~ 5-7 nm and the hydrogel is composed of stacked patches of parallel beta-sheets involving ca. 8-9 GSH strands. Interestingly molecular structure of the M(I)-GSH aggregate on the nanoparticle surface and in the bulk hydrogel are identical. We have reported the optimal condition where a few nanometer-thick peptide shells could be grown on a metal nanoparticle surface while avoiding the formation of a bulk hydrogel. Nanoparticles with hydrogel shells have the potential to be a valuable advancement in the field of biocompatible nanomaterials.

Acknowledgements: This research was supported by the Israel Science Foundation (grant 293/20 to L.C.).

References:

1. Ghosh, A.; Prasad, AK.; Chuntonov, L. Two-Dimensional Infrared Spectroscopy Reveals Molecular Self-Assembly on the Surface of Silver Nanoparticles. *J Phys Chem Lett*. 2019, *10*(*10)*, 2481-2486.

2. Basu, A.; Vaskevich, A.; Chuntonov, L. Glutathione Self-Assembles into a Shell of Hydrogen-Bonded Intermolecular Aggregates on "Naked" Silver Nanoparticles. *J Phys Chem B*. 2021,*125*(*3)*, 895-906.

3. Basu, A.; Tolbatov, I.; Marrone, A.; Vaskevich, A.; Chuntonov, L. Noble Metal Nanoparticles with Nanogel Coatings: Coinage Metal Thiolate-Stabilized Glutathione Hydrogel Shells. *Manuscript just accepted*. 2024.

Poster no. P_SB_04

Percolation in Networks of Liquid Diodes

Camilla Sammartino[a], Yair Shokef[a], Bat-El Pinchasik[a]

[a] *School of Mechanical Engineering, Faculty of Engineering, Tel Aviv University*

E-mail: pinchasik@tauex.tau.ac.il

Liquid diodes are surface structures that facilitate the spontaneous flow of liquids in a specific direction. In nature, they are used to increase water collection and uptake, reproduction, and feeding. However, pump-free large networks with directional properties are exceptional and are typically limited up to a few centimeters. Here, we simulate, design, and 3D print networks consisting of hundreds of liquid diode (**Figure 1**). We provide structural and wettability guidelines for directional transport of liquids through these networks and introduce percolation theory in order to identify the threshold between a connected network, which allows fluid to reach specific points, and a disconnected network. By constructing well-defined networks with uni- and bidirectional pathways, we experimentally demonstrate the applicability of models describing isotropically directed percolation. We accurately predict the network permeability and the liquid final state. These guidelines are highly promising for the development of structures for spontaneous, yet predictable, directional liquid transport. In addition, they comprise an initial realization of complex liquid circuits, analogoues to electric circuits.

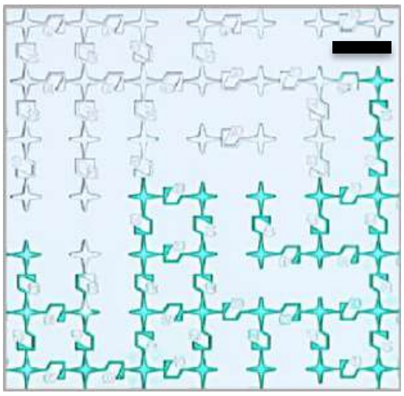


Figure 1: Liquid spreading through a network of 3D printed liquid diodes (top view). Scale bar corresponds to 1 cm.

Acknowledgements: This research was supported by the Israel Science Foundation (grant No. 1323/19).

References:

(1) Sammartino, C.; Rennick, M.; Kusumaatmaja, H.; Pinchasik, B.-E. Three-Dimensional Printed Liquid Diodes with Tunable Velocity: Design Guidelines and Applications for Liquid Collection and Transport. *Phys. Fluids* **2022**, *34* (11), 112113.

(2) Sammartino, C.; Shokef, Y.; Pinchasik, B.-E. Percolation in Networks of Liquid Diodes. *J. Phys. Chem. Lett.* **2023**, *14* (34), 7697–7702.

(3) Li, J.; Song, Y.; Zheng, H.; Feng, S.; Xu, W.; Wang, Z. Designing Biomimetic Liquid Diodes. *Soft Matter* **2019**, *15* (9), 1902–1915.

Poster no. P_SB_05

Universal Relation between Entropy and Kinetics

Benjamin Sorkin,[a] Haim Diamant,*[a] and Gil Ariel†[b]

[a] *School of Chemistry and Center for Physics and Chemistry of Living Systems, Tel Aviv University, 69978 Tel Aviv, Israel.*
[b] *Department of Mathematics, Bar-Ilan University, 52000 Ramat Gan, Israel.*

E-mail: *hdiamant@tau.ac.il, †arielg@math.biu.ac.il

The theory of equilibrium thermodynamics is well established and key to the characterization of material properties. Out of equilibrium, for example in the presence of driving or activity, materials are routinely characterized by kinetic properties such as conductivities and diffusion coefficients, while thermodynamic quantities may be ill-defined or difficult to estimate. Relating thermodynamic quantities to kinetic ones is therefore a conceptual challenge with many practical benefits.

Based on first principles, we prove a rigorous inequality relating the entropy and the information content of the dynamic propagator of particle configurations. We do so by comparing two equivalent pictures – distinguishable particles undergoing diffusion, and indistinguishable particles that mix and approach steady state faster. The relation is universal and applicable to steady states arbitrarily far from thermal equilibrium. Applying the general relation to diffusive dynamics yields a relation between the entropy and the (normal or anomalous) diffusion coefficient. It can be used to obtain practical bounds for the late-time diffusion coefficient from the calculated thermodynamic entropy or, conversely, to estimate the entropy based on measured diffusion coefficients.

We demonstrate the validity and usefulness of the relation through several examples and discuss its broad range of applications for systems far from equilibrium, ranging from motile particles within swarms to diffusing proteins in the crowded environment of the cytoplasm.

A joint work with Haim Diamant (Tel Aviv University) and Gil Ariel (Bar-Ilan University).

Acknowledgements: We thank David Dean, Ofek Lauber Bonomo, Oren Raz, Shlomi Reuveni, and Tom Witten for illuminating discussions. The research has been supported by the Israel Science Foundation (Grant No. 986/18).

References:

B. Sorkin, H. Diamant, and G. Ariel, Universal relation between entropy and kinetics, *Phys. Rev. Lett.* **131**, 147101 (2023).

Poster no. P_SB_06

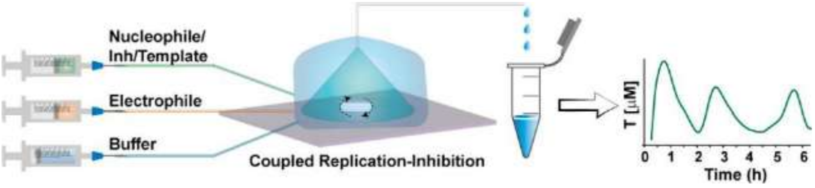
Oscillation of a Peptide in a Flow System

Bhawna Sharma,[a] Shovan Kumar Sen [a] and Gonen Ashkenasy*[a]

[a] *Department of Chemistry, Ben-Gurion University of the Negev, 84105 Beer Sheva, Israel*

E-mail: gonenash@bgu.ac.il

Living organisms are replete with rhythmic and oscillatory behavior at all levels, to the extent that oscillations have been designated as a defining attribute of life. To mimic such functions, synthetic oscillators were recently studied, presenting decayed cycles in batch, or sustained oscillatory kinetics under flow conditions. Considering the peptides functionality in early chemical evolution, and their central role in current bio-nanotechnology, we now disclose a peptide-based oscillator. The oscillatory behavior was achieved by coupling coiled-coil-based replication processes as positive feedback to controlled initiation and inhibition in a continuously stirred tank reactor (CSTR). Our results highlight that assembly into the supramolecular structure and specific interactions with the replication substrates are crucial for oscillations. The replication-inhibition processes were first studied in batch, yielding a single oscillatory cycle. Experimental and theoretical characterization of the oscillatory process under variable flow and environmental (pH, redox) conditions allowed us to devise reasonably sustained oscillations (Scheme 1). We propose that studies in this direction might open the way to design extremely robust oscillation networks that mimic the autonomous behavior of proteins in cells (e.g., in the cyanobacteria circadian clock), and hence hint to viable pathways that accelerated the transition from functional peptides to existing enzymes.



Scheme 1: Oscillation of a peptide in a flow reactor (CSTR)

References:

1. Dev, D.; Wagner, N.; Pramanik, B.; Sharma, B.; Maity, I.; Cohen-Luria, R.; Peacock-Lopez, E.; Ashkenasy, G. A Peptide-based oscillator. *J. Am. Chem. Soc.* **2023**, *145*, 26279–26286.

Poster no. P_SB_07

Rheological Behavior of Branched Supramolecular Polymers

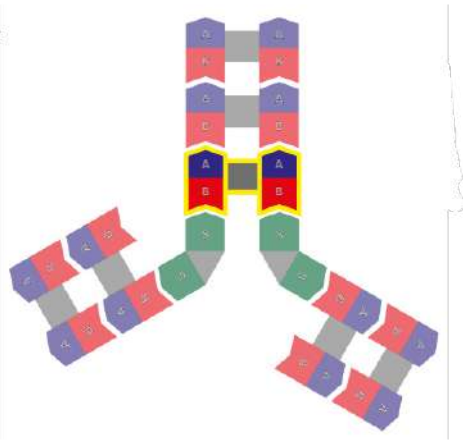
Carmel Cohen,[a] Ishay Columbus,[a] Nawal Fahoum,[a] Maya Davidovich-Pinhas*[b] and Roy Shenhar*[a]

[a] Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel. [b] Faculty of Biotechnology & Food Engineering, Russell Berrie Nanotechnology Institute, Technion, Israel Institute of Technology, Haifa, 3200003, Israel.

E-mail: carmel.cohen@mail.huji.ac.il, roy.shenhar@mail.huji.ac.il

Supramolecular polymers represent a unique family of polymers, in which the repeat units are connected by non-covalent interactions such as hydrogen bonds. This virtue makes them specifically intriguing, because under certain conditions they could disassemble into individual molecules and give rise to low viscosity solutions, whereas under different conditions they behave like conventional polymeric chains that tend to entangle, resulting in elastic materials. Environmentally responsiveness and self-healing are thus part of their identity.

We recently introduced branching – a fundamental aspect in polymer science – into supramolecular polymers, and showed its dramatic influence on the solution viscosity.[1] In this work, we studied the rheological behavior of branched supramolecular polymers and compared it to the known behavior of linear supramolecular polymers.[2] Interestingly, we found that branching leads to an unusual frequency-dependent response of the storage and loss moduli, which raises the possibility for a complex relaxation mechanism that is unique to branched supramolecular systems.



References:

1. [1] Columbus, I.; Eren, N.; Elitsur, R.; Davidovich-Pinhas, M.; Shenhar, R. Branched supramolecular copolymers: inducing branching in bisurea-based monomers using multi-sulfonate molecules. Macromolecules 2022, 55, 472-87.

2. Vereroudakis, E. Vlassopoulos, D. Tunable dynamic properties of hydrogen-bonded supramolecular assemblies in solution. Prog. Polym. Sci. 2021, 112, 101321.

Poster no. P_SB_08

Design principles of transcription factor recognition specificity to DNA in embryonic stem cells

David Lukatsky
Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, Israel

Abstract

Molecular understanding of how transcription factors (TFs) recognize genomic DNA in living cells still remains incomplete. I will present our most recent results on such TF-DNA molecular recognition mechanisms in embryonic stem cells (ESCs). In particular, using statistical mechanics modeling of TF-DNA binding for a number of human TFs, we show that TF-DNA binding specificity is distributed between three major modes of recognition. The first contribution stems from the local genomic GC content, the second one is determined by non-consensus repetitive DNA sequence elements termed short tandem repeats (STRs), and the final contribution stems from specific *k*-mer features. Surprisingly, we identify that the local genomic GC content represents a major contribution for a number of key TFs responsible for the ESCs development.

Poster no. P_SB_09

DNA Information-editing Tools for ReconfigurableNanoparticle Architectures

*Elad Arad[a] and Oleg Gang[a,b,c]

.[a]*Department of Chemical Engineering, Columbia University in the City of New York, NY, USA*

.[b] *Department of Applied Physics and Mathematics, Columbia University in the City of New York, NY, USA*

.[c] *Brookhaven National Laboratory, Upton, NY, USA*

E-mail: eladarad.ea@gmail.com

Biological organisms have developed comprehensive machinery for organizing matter into structures with specific functions and for reconfiguring their states in response to external signals. Unlike biology, most nanomaterials remain static, unable to adapt, change or reconfigure in response to stimulation. Transforming materials into molecular machines requires a dynamic nature with precise activation mechanisms and behavior. DNA nanotechnology methods offer a powerful means of controlling matter at the nanoscale, especially when combined with other types of nanoparticles. However, there are no methods of orchestrating reconfiguration of these complex nanostructures. Herein we aim to unravel the principles for transforming static DNA-origami into dynamic material using CRISPR-Cas technology. Controlling and editing the DNA backbone using CRISPR-Cas sequence-editing, reconfiguration of the DNA scaffold will exert control over its covalent bonds, conformation, and states. As a proof of concept, we aim to create a DNA/nanoparticle lattice with reconfigurable d-spacings.Using Cas editing we aim to achieve supramolecular asymmetry in the DNA-crystal. This goal converges biological methods and nanotechnology, achieving precise and dynamic structures while applying (specific-editing tools to manipulate biopolymer system (the DNA origami

Poster no. P_SB_10

Staphylococcus aureus functional amyloids catalyze degradation of β-lactam antibiotics

Elad Arad [a,b], Kasper Busk Pedersen [c], Orit Malka [b], Sisira Mambram Kunnath [b], Nimrod Golan [d], Polina Aibinder [e], Birgit Schiøtt [c,f], Hanna Rapaport [a,e], Meytal Landau [d,g] and Raz Jelinek [a,b]*

[a]Ilse Katz Institute (IKI) for Nanoscale Science and Technology, Ben Gurion University of the Negev, Beer Sheva 8410501, Israel. [b]Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 8410501, Israel. [c]Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark. [d]Department of Biology, Technion-Israel Institute of Technology, Haifa 3200003, Israel. [e]Avram and Stella Goldstein-Goren Department of Biotechnology Engineering, Ben Gurion University of the Negev,Beer Sheva 8410501, Israel. [f]Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark. [g]Centre for Structural Systems Biology (CSSB), and European Molecular Biology Laboratory (EMBL), Hamburg 22607, Germany.

E-mail: E.A eladarad.ea@gmail.com; R.J razj@bgu.ac.il

Antibiotic resistance of bacteria is considered one of the most alarming developments in modern medicine. While varied pathways for bacteria acquiring antibiotic resistance have been identified, there still are open questions concerning the mechanisms underlying resistance. Here, we show that alpha phenol-soluble modulins (PSMαs), functional bacterial amyloids secreted by *Staphylococcus aureus*, catalyze hydrolysis of β-lactams, a prominent class of antibiotic compounds. Specifically, we show that PSMα2 and, particularly, PSMα3 catalyze hydrolysis of the amide-like bond of the four membered β-lactam ring of nitrocefin, a prominent β-lactam surrogate. Microscopic and spectroscopic examination of several PSMα3 variants and analysis of the correlation with catalytic activities allowed mapping of the catalytic sites on the amyloid fibrils' surface, specifically underscoring the key roles of the cross-α fibril organization, and the combined electrostatic and nucleophilic functions of lysine array. This study unveils a previously unknown activity of functional amyloids as catalytic agents affecting antibiotic compound degradation, underlying possible antibiotic resistance mechanisms associated with bacterial biofilms

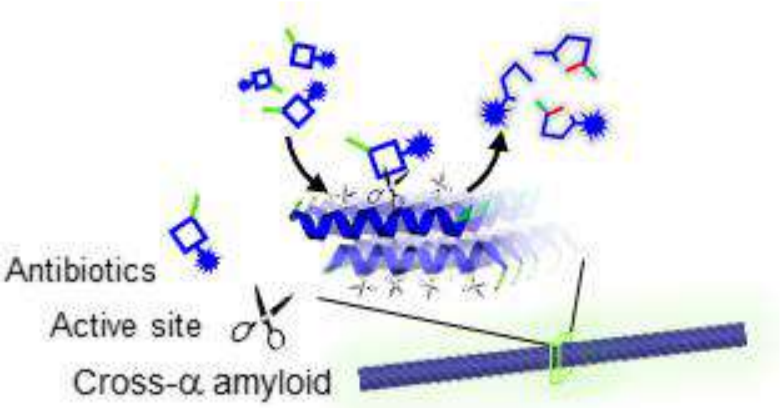


Figure 1: Catalytic β-lactam degradation using bacterial cross-α amyloids

References:

(1) Arad, E.; B. Pedersen, K.; Malka, O.; Mambram Kunnath, S.; Golan, N.; Aibinder, P.; Schiøtt, B.; Rapaport, H.; Landau, M.; Jelinek, R. Staphylococcus Aureus Functional Amyloids Catalyze Degradation of β-Lactam Antibiotics. *Nat. Commun.* **2023**. https://doi.org/https://doi.org/10.1038/s41467-023-43624-1.

(2) Arad, E.; Jelinek, R. Catalytic Amyloids. *Trends Chem.* **2022**. https://doi.org/10.1016/j.trechm.2022.07.001.

Poster no. P_SB_11

Distributed Specificity of TF-DNA Recognition in Embryonic Stem Cells

Mikhail Povolotskii[a] and David Lukatsky[a]

[a] *Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, Israel.*

E-mail: mikhailp@post.bgu.ac.il, lukatsky@bgu.ac.il

Transcription factors (TFs) bind genomic DNA regulating gene expression and developmental programs in embryonic stem cells (ESCs). Even though comprehensive genome-wide molecular maps for TF-DNA binding are experimentally available for key pluripotency-associated TFs, the understanding of molecular design principles responsible for TF-DNA recognition remains incomplete. Using statistical mechanics modeling and numerical analysis of the available experimental data, we show that the sequence-dependent TF-DNA binding specificity is distributed between three major contributions. Surprisingly, the first contribution, the local GC content, represents a dominant molecular factor for some proteins such as cMyc. The second contribution, specifically recognized short sequences of nucleobases called k-mers, turns out to be dominant for some other proteins, such as Pou5f1 (Oct4). The third contribution, non-consensus short tandem repeats (STRs), is also highly predictive for a significant fraction of TFs. Interestingly, we find that the local GC content contributes more to the TF-DNA recognition in those genome regions where it is higher, while the k-mer based specificity is more significant in genomic locations with lower GC content. Depending on the stage of cell development, some TFs such as Otx2 demonstrate the ability of binding to the DNA regions with both high and low GC content, and they exploit different types of specificity in these two cases, either GC content or k-mers, respectively.

Poster no. P_SB_12

Macrocyclic Diacetylene based multifunctional soft nanostructures

Nila Nandha Kadamannil,[a] Jung-Moo Heo,[b] Daewoong Jang,[b] Haksu Lee,[b] Ran Zalk,[c] Gabriel A Frank,[c][d][e] Jong-Man Kim*[b] and Raz Jelinek*[a,c]

[a] Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 8410501, Israel. [b] Department of Chemical Engineering, Hanyang University, Seoul 04763, Korea. [c] Ilse Katz Institute for Nanoscale Science & Technology, Ben Gurion University of the Negev, Beer Sheva 8410501, Israel. [d] The National Institute for Biotechnology in the Negev, Ben-Gurion University of the Negev, Beer Sheva 8410501, Israel. [e] Department of Life Sciences, Ben-Gurion University of the Negev, Beer Sheva 8410501, Israel]

E-mail: jmk@hanyang.ac.kr, razj@bgu.ac.il

Functional supramolecular materials exhibit essential features, including structural versatility and tunable applications. Macrocyclic Diacetylene (MCDA) are diacetylene containing cyclic amphiphilic compounds that self-assemble by non-covalent interactions into nanotubular arrays in water. We constructed nanotubes, nano-toroids and microporous films utilizing the self/co-assembly of various MCDA molecules with small molecules, other linear diacetylene molecules or nanoparticles and later subjecting them to UV-induced topochemical polymerization.

We applied single particle cryo-electron microscopy (cryo-EM), a method traditionally used for structure determination of biological macromolecules, to obtain high-resolution structures of synthetic non-biological filaments formed by photopolymerization of MCDA amphiphilic monomers. Tomographic analysis showed that the MCDA monomers self-assemble into hollow nanotubes upon dispersion in water. Single particle analysis revealed tubes consist of six pairs of covalently bonded filaments held together by hydrophobic interactions. Each filament comprises macrocyclic rings stacked in parallel "chair" conformations. The hollow MCDA nanotube structures we found may account for the efficient scavenging of amphiphilic pollutants in water and the subsequent photodegradation of the guest species.

In addition, we constructed hierarchically self-assembled fluorescent and photocatalytic “nano-bagels” comprising MCDA and 8-Anilino-2-naphthalene sulphonate (ANS), a negatively charged aromatic fluorescent dye. The nano-toroid assemblies consist of intertwined nanofibers and aligned macrocyclic diacetylene monomers. Mechanistic analysis reveals the critical role of ANS in shaping the toroidal organization of the MDA nanofibers. Notably, the display of amine moieties on the nano-bagel surface was employed to form a metallic gold coating, either as Au nanoparticles (“poppyseed nano-bagel”) or as extended Au sheets. The Au-coated nano-toroid assemblies constitute effective platforms for photocatalysis and SERS-based analyte enhancement.

Facile synthesis of ultrathin ‘beehive-like’ soft microporous films by light induced co-assembly and topochemical polymerization of two diacetylene derivatives, MCDA-EDEA, bis-ADA along with carbon-dot (C-dot) nanoparticles was achieved. Non-covalent interactions of C-dots to both MCDA-EDEA and bis-ADA attributes to the uniform pore size and long-range ordering in film. In addition, conjugated polydiacetylene rigid networks also provides stability and definition to the microporous distribution. The high surface and hydrophobic pockets of MCDA-EDEA/bis-ADA/C-dot microporous films were utilized for efficient adsorption and photocatalytic degradation of water pollutant dyes like rhodamine 6g. The porous nature of film along with electron rich polydiacetylene networks and anthraquinone cores make them ideal candidates as electrode materials for supercapacitors as well.

References:

1. Kadamannil, N. N. *et al.* High-Resolution Cryo-Electron Microscopy Reveals the Unique Striated Hollow Structure of Photocatalytic Macrocyclic Polydiacetylene Nanotubes. *J. Am. Chem. Soc.* **144**, 17889–17896 (2022).

2. Kadamannil, N. N., Jang, D., Lee, H., Kim, J.-M. & Jelinek, R. Macrocyclic Diacetylene / Sulfonate Fluorophore Hierarchical Multifunctional Nanotoroids. *Small Methods*, 2301286 (2024).

.

Poster no. P_SB_13

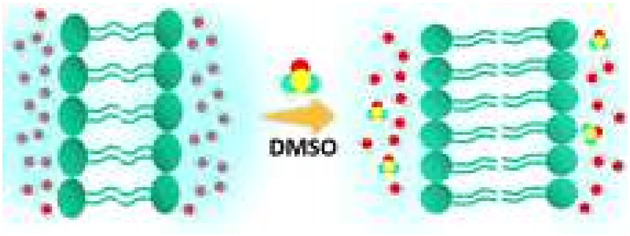
The Effect of Phospholipids Dehydration on Lubrication

Yihui Dong[1], Nir Kampf[1*], Yaelle Schilt[2], Wei Ca[3], Uri Raviv[2] and Jacob Klein[1]

Weizmann Institute of Science[1], Institute of Chemistry, The Hebrew University of Jerusalem, Israel[2], Department of Physical Chemistry, School of Chemistry, Tel Aviv University, Israel[3]

E-mail: nir.kampf@weizmann.ac.il

In our previous studies (i.e. 1-2), we demonstrate the efficiency of PC lipids in reducing surface friction, with the understanding that highly hydrated PC head-groups participating in the hydration lubrication mechanism. In the biophysical context, the robustness of phosphatidylcholine (PC) lipids at biological surfaces is very much effecting its functional properties such as pressure resistance and friction, in particular, at articular cartilage surfaces where low friction is crucial for joint wellbeing. The puzzling question is: how the removal of water from the lipids layer will affect the lubrication? We used DMSO as the dehydrating material, as well as several experimental approaches, including atomic force microscopy, small- and wide-angle X-ray scattering and all-atom molecular dynamics simulations to elucidate this. Our results show that DMSO clearly removes hydration water from the lipid head-groups, this is offset by both higher areal head-group density and by rigidity-enhancement of the lipid bilayers. Remarkably, and unexpectedly, nanotribological measurements, made by surface force balance technique, show (3) that the dehydration has little effect on the friction. This sheds strong light on the robustness of lipid-based hydration lubrication in biological systems, despite the ubiquitous presence of bio-osmolytes which compete for hydration water.



References:

1. Sorkin R., Kampf N., Zhu L, Klein J. (2016) Soft Matter. 12, 10, p. 2773-2784.
2. Angayarkanni S. A., Kampf N, Klein J. (2019) Langmuir. 35, 48, p. 15469-15480.
3. Dong Y., Kampf N., Schilt Y., Cao W., Raviv U., Klein J. (2022) Nanoscale. 14, 48, p. 18241-18252.

Poster no. P_SB_14

Structural colors produced from organic liquid crystals yield highly efficient photonic systems

Tali Lemcoff [a], Lotem Alus [b], Johannes S. Haataja [c], Avital Wagner [a], Dan Oron [b], Keshet Shavit [a], Lahav Heitner [a], Lukas Schertel [d], Benjamin A. Palmer [a]*

[a] Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel. [b] Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot, Israel. [c] Department of Applied Physics, Aalto University School of Science, Espoo, Finland. [d] Department of Physics, University of Fribourg, Fribourg, Switzerland

E-mail: lemcofft@post.bgu.ac.il

Millions of years before we began to manipulate light using synthetic structures, biological systems were optimizing nanometer-scale architectures to produce striking optical effects based on reflectance, refraction, or scattering of light. Among the biological materials used to create photonic structures, organic crystals stand out due to their extremely high refractive indices, which make them some of nature's most efficient photonic materials. Thus far it was thought that the crystalline nature of these materials was fundamental to generating high refractive indices. However, we show two examples where structural colors are produced from liquid crystalline nanospheres. In cleaner shrimp[1], one of the most efficient white colors in nature is produced by nanospheres in a liquid crystalline phase of isoxanthopterin (Fig. 1a-c). In damselflies, blue to green colors are produced from similar nanospheres by combining structural and pigmentary colors[2](Fig. 1d-f). The brilliant white structural color in cleaner shrimp is produced by multiple scattering from dense arrays of liquid crystalline nanospheres packed in chromatophores. The high refractive index ($n \approx 2.0$) and extreme birefringence (~30%) of the nanospheres derive from the radial alignment of stacked, liquid crystalline isoxanthopterin assemblies. This arrangement results in the same molecular orientation as in biogenic crystalline isoxanthopterin[3], with the alignment of the highly polarizable plane of isoxanthopterin tangential to the particle surface. These results show that the optical properties of biological reflective systems are due to the alignment of the highly polarizable molecules rather than on their crystallinity *per se*. Most strikingly, the thickness of the white layer in cleaner shrimp is extremely thin (<10 μm) compared to synthetic state of the art highly reflective white coatings (150-600 μm). Numerical simulations reveal that birefringence, originating from the molecular arrangement of isoxanthopterin molecules, diminishes the unfavorable effects of optical crowding and enables broadband scattering almost up to the maximal packing for spheres (Fig. 1g). Birefringence thus enables increased scattering and is crucial in reducing the thickness of material required to produce high scattering. These results could contribute to the design of biologically inspired replacements for harmful artificial scatterers like TiO_2.

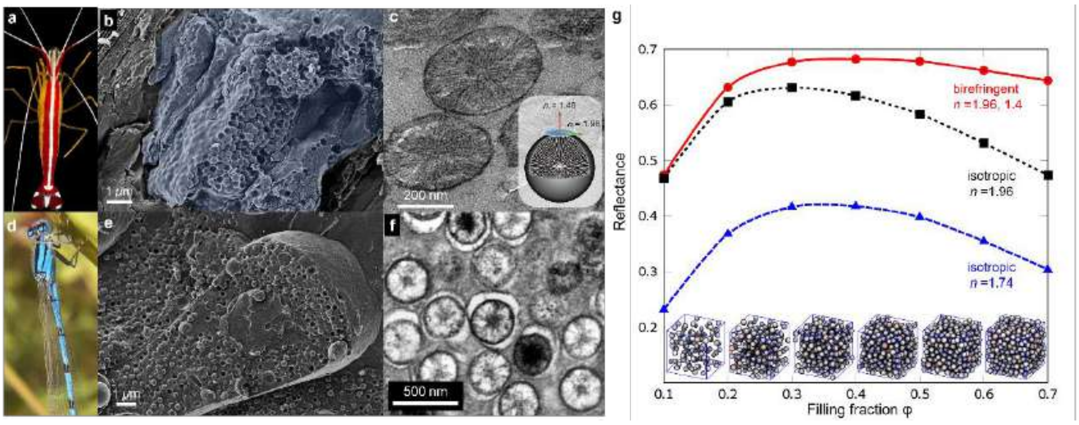


Figure 1. a) The Pacific cleaner shrimp (*L. amboinensis*). **b)** cryo-SEM image of nanospheres densely packed in a white chromatophore cell. **c)** Thin-tissue TEM image of the nanospheres showing the spoke-like, spherulitic structure. **d)** Blue-tailed damselfly (*I. elegans*). **e)** cryo-SEM image of nanospheres packed in a chromatophore cell in the damselfly eye. **f)** thin tissue TEM image of the nanospheres (reproduced from ref. 2). **g)** MD and FDTD simulations of 5 × 5 × 5-μm³ photonic glass slabs comprising nanospheres with varying refractive index. Total reflectance values for 305-nm isotropic (blue and black traces) and birefringent (red trace) particles as a function of filling fraction. Unlike in the isotropic cases, the birefringent particles show high reflectance even up to 70% filling fractions.

References:

1) Lemcoff, T. *et al.*, *Nat. Photonics* (2023)
2) Prum, R. O., Cole, J. A. & Torres, R. H., *J. Exp. Biol.* 207, 3999–4009 (2004)
3) Palmer, B. A. *et al.*, *Nat. Nanotechnol.* 15, 138–144 (2020).

Poster no. P_SB_15

4D-printed pH sensitive hydrogels

Timna Korem[1], Salome Azoulay-Ginsburg[2], Roey J. Amir[2]

1. Alpha program, Tel Aviv Youth University, Tel Aviv University, Tel Aviv 6997801, Israel
2. Department of Organic Chemistry, School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 6997801, Israel

E-mail: Timna.korem@gmail.com, salome@tauex.tau.ac.il, amirroey@tauex.tau.ac.il.

Hydrogels are 3D structures assembled from either covalently crosslinked or physically held networks of polymer chains, capable of holding a large amount of water. Smart 3D-printed hydrogels can react to environmental stimuli by changing their structure/shape and are referred to as 4D printed materials. In response to stimuli, the polymer chains can get further away one from the other, causing the swelling of the hydrogel. The swelling of the hydrogel, can on one hand, lead the hydrogel to absorb more water from the surrounding, and on the other hand, allow substances to be released from the hydrogel to the surrounding by diffusion. This research focused on pH sensitive hydrogels as potential drug delivery systems.

One of our goals was to better understand the swelling and release mechanisms of 3D printed pH sensitive hydrogels. To achieve this, we used acrylic acid (AA) as a monomer to 3D print polyacrylic acid (PAA), which when reacting with a base becomes negatively charged. The repulsion between these negative charges causes the PAA chains to move away from each other, resulting in observed swelling of the hydrogel. In addition, hydrogels printed from solutions containing only responsive monomers swelled significantly more than hydrogels, which contained a mixture of responsive and non-responsive monomers. When placed in acidic solutions the hydrogels shrunk due to protonation of the carboxylate side-groups, decreasing both the repulsion between the chains and their hydrophilicity.

We next used 4-nitrophenol as a model for drug encapsulation and release. Surprisingly, our findings contradicted our initial expectation that loaded substance would diffuse out faster upon swelling. The hydrogels which were placed in acidic solution released approximately double the amount of the loaded substance compared to those in basic solution. Therefore, we hypothesize that during the shrinkage, the hydrogels forced out the loaded cargo molecules.

The final goal of this research was to print hydrogels containing layers from two different solutions; one contains responsive monomers and the second non-responsive monomers, and to study the effect of pH changes on these hydrogels. As the DLP printer isn't designed for printing from more than one solution, we developed a new method of printing and tested different options for replacing the resin in the printer's vat. We found that the order in which the solutions are applied had great significance. Specifically, only when the non-responsive monomer solution was used first was the printing successful, resulting in fully printed models. When placed in a basic solution, the bilayer hydrogels folded due to the different degree of swelling between the responsive PAA based layer and the non-responsive layer.

Overall, this project improved our understanding of the properties of pH responsive hydrogels and the parameters that can be tuned to control their response. The obtained results and knowledge will help to design responsive hydrogels for specific applications such as sustained drug delivery system.

Poster no. P_SB_16

Glycoproteins as a Platform for Making Proton-Conductive FreeStanding Biopolymers

Ziyu Yang, Amit Kumar Sarkar, and Nadav Amdursky*

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 3200003, Israel

E-mail: amdursky@technion.ac.il

Biopolymers are an attractive environmentally friendly alternative to common synthetic polymers, whereas primarily proteins and polysaccharides are the biomacromolecules that are used for making the biopolymer. Due to the breadth of side chains of such biomacromolecules capable of participating in hydrogen bonding, proteins and polysaccharide biopolymers were also used for the making of proton-conductive biopolymers. Here, we introduce a new platform for combining the merits of both proteins and polysaccharides while using a glycosylated protein for making the biopolymer. We use mucin as our starting point, whereas being a waste of the food industry, it is a highly available and low-cost glycoprotein. We show how we can use different chemical strategies to target either the glycan part or specific amino acids for both crosslinking between the different glycoproteins, thus making a freestanding biopolymer, as well as for introducing superior proton conductivity properties to the formed biopolymer. The resultant proton-conductive soft biopolymer is an appealing candidate for any soft bioelectronic application.

Poster no. P_SB_17

Controlling Macroscale Morphology in DNA-based Assembly Using Acoustic Energy

Z.A. Arnon, S. Piperno, D.C. Redeker, E. Randall, A. Tkachenko, H. Shpaisman and O. Gang

One of the main challenges of developing bottom-up designed materials is the issue of scaling their formation and shaping them into a desired morphology. A high degree of nanoscale control hinders the ability to form nanomaterials with predefined macroscale morphology. DNA nanotechnology allows accurate spatial control at the nanoscale which enables fabrication of intricate organizations; yet, structural arrangement at the macroscale remains a challenge. We developed an assembly approach driven by acoustic waves in order to control the morphology of DNA-assembled materials at the scales from tens of microns to millimeters, thus complementing a nanoscale assembly regime offered by DNA-guided methods. Specifically, we explored the use of standing surface acoustic waves (SSAW) to direct assembly and control morphology of DNA origami based crystal lattices. By controlling both acoustic forces and temperature, we investigated the assembly process at different scales by a combination of optical microscopy, small-angle x-ray scattering and electron microscopy techniques. We further studied the nucleation, crystal fusion and growth under different acoustic conditions. The developed approach allows to form macroscale nanomaterials with prescribed morphology, as defined by the acoustic field, while their nanoscale organization is programmed by DNA. Our experimental observations are supported by a model that incorporates nucleation dynamics, diffusion-limited growth, and the effects of acoustic driving. The model provided valuable insights into the impact of acoustic waves on suppressed nucleation and crystal growth. Overall, our study demonstrates the potential of acoustic waves as a complementary method for controlling the morphology of DNA-assembled nanomaterials at the macroscale. This approach expands the scope of DNA nanotechnology and paves the way for the fabrication of nanomaterials with tailored properties and functionalities for a wide range of applications.

Theoretical Chemistry

Poster no. P_TC_01

Frac%onal spin in atomic systems using density functional theory

Alon Hayman, Dr. Tamar Stein and Dr. Eli Kraisler
Fritz Haber Research Centre for Molecular Dynamics and Institute of Chemistry, The Hebrew University of Jerusalem, Israel
Alon.hayman@mail.huji.ac.il, Tamar.stein@mail.huji.ac.il, Eli.kraisler@mail.huji.ac.il

Density-functional theory (DFT) is a popular approach for solving the many-electron problem, and it is based on mapping the real, interacting electron system into a non-interacting one. While DFT is theoretically exact, a part of it - the exchange-correlation (xc) functional cannot be calculated directly and should always be approximated.

One approach of developing accurate and predictive exchange-correlation approximations is by means of satisfying exact properties of many-electron systems. Here we focus on the behaviour of the energy, as we vary the spin of the system.

We used three different exchange-correlation functionals, namely, the LSDA, PBE and exact exchange to investigate how presence of a fractional spin affects the behaviour of atomic systems, and then analyse said behaviour.

We find that varying the system's spin does in fact change the energy of the system, contrary to expectation from the flat-plane condition by Yang et al.

Under and overestimation of the energy (convexity and concavity of the E(S) curve) is observed and depends on the system and on the spin value. However, all three approximations examined, including exact exchange deviate in the same manner.

Dependence of the frontier energy levels on the spin shows at times a very peculiar behaviour, which depends on the nature of the orbitals.

For exact exchange, a derivative discontinuity accompanied by a plateau in the potential is observed.

Poster no. P_TC_02

Effects of Water Molecules on Hydrogen Cyanide Clusters

Tamar Stein, Amit Daniely[a] and Ariella Juni

a Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem

E-mail: ariellahjuni@gmail.com

This study investigates the formation of organic molecules in space. We investigated the impact of water molecules (H_2O) on the isomerization of Hydrogen Cyanide (HCN). These two compounds are common in the interstellar medium, and researching the environment in which these molecules exist can inform us about chemical evolution in space. With the use of computer calculations based on the DFT theory, we discovered different clusters of water and hydrogen cyanide with varied ratios. With each cluster, we ionized the system, and examined the change that occurred. We noticed many proton transitions from the water molecule to the other molecules in various clusters. Also, we discovered HCN isomerization in small clusters, but not in larger clusters because the water interferes with the HCN's ability to isomerize. Additionally, a chemical reaction occurred in one cluster consisting of two water molecules and one HCN molecule, resulting in the formation of an OHCHNH (**Figure 1**). We can conclude that water disrupts the isomerization of the HCN, and hydrogens tend to migrate from water to HCN. These findings contribute to the understanding of complex chemistry in space, and we can continue to look for life in space once we understand the behavior of organic molecules in space.

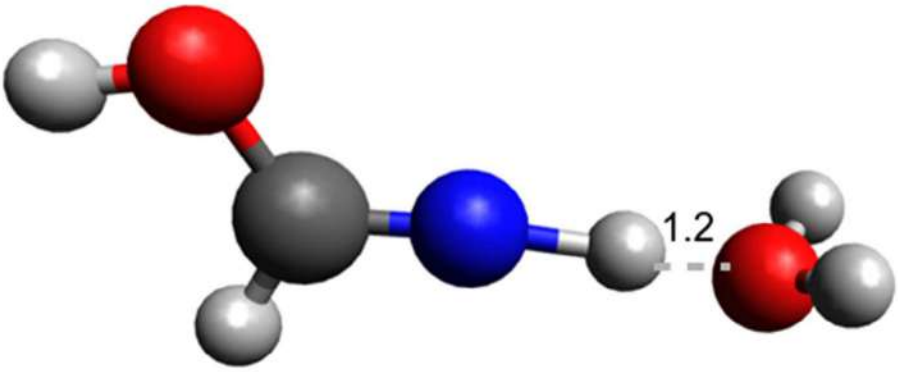


Figure 1: *The OHCHNH molecule found. With white representing hydrogen, red representing oxygen, black representing carbon and blue representing nitrogen.*

Acknowledgements: We want to thank the Alpha program who enabled this study to happen, and to the Fritz Haber Research Center for Molecular Dynamics in which the study took place.

References:

1. Sandford, S. A., Nuevo, M., Bera, P. P., & Lee, T. J. (2020). Prebiotic astrochemistry and the formation of molecules of astrobiological interest in interstellar clouds and Protostellar disks. Chemical reviews, 120(11), 4616-4659.
2. Zamir, A., & Stein, T. (2022). Isomerization of hydrogen cyanide and hydrogen isocyanide in a cluster environment: quantum chemical study. The Journal of Chemical Physics, 156(5), 054307

Poster no. P_TC_03

The COMPAS Project: A Computational Database of Polycyclic Aromatic Systems. Phase 2: cata-condensed Hetero-Polycyclic Aromatic Systems

Eduardo Mayo Yanes[a] , Sabyasachi Chakraborty[a] and Renana Gershoni-Poranne*[a]

[a] *Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel*

E-mail: rporanne@technion.ac.il

Polycyclic aromatic systems are highly important to numerous applications, especially to organic electronics and optoelectronics. High-throughput screening and generative models can help to identify new molecules that can advance these technologies but require large amounts of high-quality data, which is expensive to generate. We present the largest freely available data set of geometries and properties of cata-condensed poly(hetero)cyclic aromatic molecules calculated to date. Our data set contains ~500k molecules comprising 11 types of aromatic and antiaromatic building blocks calculated at the GFN1-xTB level and is representative of a highly diverse chemical space. The methodologies used to enumerate and compute the various structures and their electronic properties (including HOMO-LUMO gap, vertical and adiabatic ionization potential, and electron affinity) are detailed. Additionally, we benchmark the values against a ~50k data set calculated at the CAM-B3LYP-D3BJ/def2-SVP level and develop a fitting scheme to correct the xTB values to higher accuracy. These new data sets represent the second installment in the COMputational database of Polycyclic Aromatic Systems (COMPAS) Project.

Acknowledgements: We thank the Technion – Institute of Technology, the Branco Weiss Fellowship (awarded to R.G.P) and Prof. Peter Chen (ETH Zurich).

Poster no. P_TC_04

Accurate electronic structure calculations based on a non-empirical, localization based optimal tuning of a screened range-separated hybrid functional

Guy Ohad,*[a] Stephen E. Gant,[b,c] Dahvyd Wing,[a] Michal Hartstein,[a] Jonah B. Haber,[b,c] María Camarasa-Gómez,[a] Ayala V. Cohen,[a] Francisca Sagredo,[b,c] Marina R. Filip,[d] Tim Gould,[e] Jeffery B. Neaton,[b,c,f] and Leeor Kronik.[a]

[a] Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovoth, Israel.

[b] Department of Physics, University of California, Berkeley, CA, United States.

[c] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

[d] Department of Physics, University of Oxford, Oxford, United Kingdom.

[e] Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, QLD 4111, Australia.

[f] Kavli Energy NanoSciences Institute at Berkeley, University of California, Berkeley, CA, United States.

E-mail: guy.ohad@weizmann.ac.il

Accurate prediction of the electronic structure of molecules and solids, entirely within density functional theory, has been a long-standing challenge. Optimal tuning of range-separated hybrid functionals has emerged as a highly accurate method for predicting fundamental gaps of molecules based on enforcing the ionization potential (IP) theorem. Recently, we developed a simple and inexpensive method for solid-state band gap predictions based on an ansatz that generalizes the IP theorem to the removal of charge from a localized Wannier function. Here we present applications of the method to three-dimensional solids, notably simple semiconductors and insultaors, halide perovskites, and metal oxides, demonstrating quantitative accuracy in band gaps and optical absorption spectra with respect to experiment and a comparable level of accuracy to many-body perturbation theory calculations. We further demonstrate the merit of using the optimally tuned eigensystem as a starting point in combined *GW* plus Bethe-Salpeter calculations. Additionally, we demonstrate the usefulness of the approach for nano-sized systems by studying one-dimensional molecular chains of increasing size, from the monomer limit to the infinite polymer limit. By comparing our results with other localization-based methods and where available with experiment, we show that Wannier-localization-based optimal tuning is highly accurate in predicting ionization potentials throughout the evolution of the chain length.

Acknowledgements: This work was supported via U.S.-Israel NSF–Binational Science Foundation Grant No. DMR-2015991 and by the Israel Science Foundation. This work used the Stampede2 supercomputer at the Texas Advanced Computing Center (TACC) at the University of Texas at Austin through allocation DMR190070 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services and Support (ACCESS) program, which is supported by National Science Foundation grants 2138259, 2138286, 2138307, 2137603, and 2138296. The authors also acknowledge TACC for providing high performance computing (Frontera) resources that have contributed to the research results reported within this paper. M.C.-G. was additionally supported by the Azrieli Foundation through the award of an Azrieli International Postdoctoral Fellowship. M.R.F acknowledges support from the UK Engineering and Physical Sciences Research Council (EPSRC), Grant EP/V010840/1. T.G. and L.K. were supported by an Australian Research Council (ARC) Discovery Project (DP200100033). T.G. was supported by an ARC Future Fellowship (FT210100663). L.K. was additionally supported by the Aryeh and Mintzi Katzman Professorial Chair and the Helen and Martin Kimmel Award for Innovative Investigation.

Poster no. P_TC_05

Coherent Spatial Control of Wave Packet Dynamics on Quantum Lattices

[a] *Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA*
[b] *Department of Chemistry and Biochemistry, University of Nevada, 4505 S Maryland Pkwy, Las Vegas, Nevada 89154, USA*

* e-mail: iliat@mit.edu

Quantum lattices are pivotal in the burgeoning fields of quantum materials and information science. Novel experimental techniques allow the preparation and monitoring of wave packet dynamics on quantum lattices with high spatiotemporal resolution. We present an analytical study of wave packet diffusivity and diffusion length on tight-binding quantum lattices subject to stochastic noise. Our analysis reveals the crucial role of spatial coherence and predicts a set of novel phenomena: (1) noise can enhance the transient diffusivity and diffusion length of spatially extended initial states; (2) standing or traveling initial states, with large momentum, spread faster than a localized initial state and exhibit a noise-induced peak in the transient diffusivity; (3) the differences in the diffusivity or diffusion length of extended and localized initial states have a universal dependence on initial width. These predictions suggest the possibility of controlling the wave packet dynamics by spatial manipulations, which will have implications for materials science and quantum technologies. Time permitting, our presentation will also delve into the diffusivity in systems with static energy disorder. Preliminary analysis indicates that static energy disorder can increase the rate of transient wave packet expansion in sufficiently spatially extended initial states (when the initial width exceeds the lattice constant). Interestingly, this enhancement effect is qualitatively similar to the noise-induced effects and suggest a potential interplay between noise and disorder in real systems.

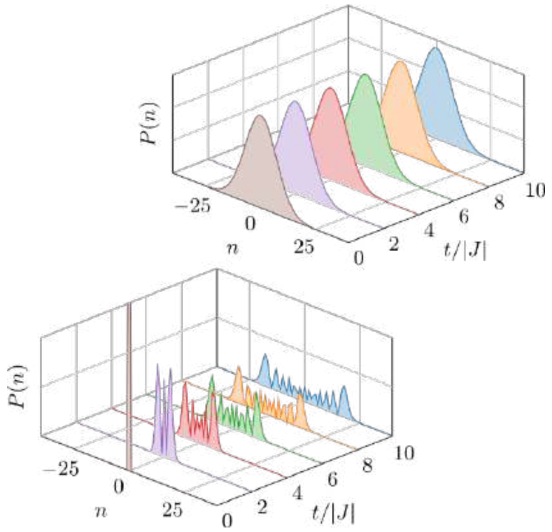


Figure 1: Spreading of spatially localized vs extended initial states on a tight binding quantum lattice.

Acknowledgments: The work is supported by the NSF (Grants No. CHE1800301 and No. CHE2324300), and the MIT Sloan fund.

References:

1. I. Tutunnikov, C. Chuang, J. Cao, “Coherent Spatial Control of Wave Packet Dynamics on Quantum Lattices”, J. Phys. Chem. Lett. 2023, 14, 51, 11632–11639

Poster no. P_TC_06

The chemistry of dark matter

Roy E. Hoffman

The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.

E-mail: royh63@gmail.com

Tachyons are proposed as a candidate for dark matter. Extended special relativity theory shows that faster-than-light particles (tachyons) can exist but cannot interconvert with regular matter (bradyons). Tachyons are expected to have properties and interaction with each other like bradyons but only interact with bradyons via gravitational attraction.

The chemistry of tachyonic dark matter is expected to be like regular matter. Since there is no gravitational evidence of large tachyonic objects, its chemistry is likely to be like that of the early universe that consisted of mostly hydrogen and helium. Any tachyonic-matter asymmetry is likely to be minor and manifested in the concentration of trace elements such a beryllium. The symbol ˆ is proposed to indicate tachyonic matter and ˇ to indicate tachyonic antimatter.

References:

1. R. E. Hoffman, *A tachyon interaction model that explains many of the mysteries in physics*, J. Phys. Astron. **2**, 120-123 (2013).
2. R. E. Hoffman, A tachyonic model of dark matter, submitted to **Phys. Lett. B.**

Poster no. P_TC_07

Identifying Structure-Property Relationships in peri-Condensed Polybenzenoid Hydrocarbons using Interpretable Deep-Learning

S. Erez[a] and R. Gershoni-Poranne[a]

[a]*Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel*

E-mail: erezshany@campus.technion.ac.il, rporanne@technion.ac.il

Peri-condensed polybenzenoid hydrocarbons (PBHs) are an important class of compounds that feature in many different functions. They serve as model systems for graphene nanoflakes and allow characterization of various molecular properties, including conductivity and magnetism. In this work, we established the first computationally-generated database of peri-condensed PBH, COMPAS-3, and have begun to investigate the effects of peri-condensation on two molecular properties: relative energy and HOMO-LUMO gap. The data generated and structural features identified will later serve to train deep-learning models for inverse design of novel functional PBHs.

References:

(1) Wahab, A. Exploring the Uncharted Chemical Space of Polybenzenoid Hydrocarbons. Diss. ETH Zurich, **2023**

(2) Weiss, T., Wahab, A., Bronstein, A., and Gershoni-Poranne, R. J. Org. Chem **2023**, 88, 14, 9645–9656

(3) Wahab, A., Pfuderer, L., Paenurk, E. and Gershoni-Poranne, R. *J. Chem. Inf. Model*. **2022**, *62*, 3704