



Metal-Directed Assembly and Metal-Organic Frameworks

ICS Symposium Honoring Wolf Prize Laureates Makoto Fujita and Omar M. Yaghi

Book of Abstracts















Coordination Self-Assembly: From the Origins to the Latest Advances

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Molecular self-assembly based on coordination chemistry has made an explosive development in recent years. Over the last >25 years, we have been showing that the simple combination of transition metals with bridging organic ligands gives rise to the quantitative self-assembly of nanosized, discrete and infinite frameworks. Representative examples include square molecules (1990),[1] square grid sheets (1994),[2] linked-ring molecules (1994),[3] cages (1995),[4] capsules (1999),[5] swellable networks (2002),[6] and tubes (2004)[7] that are self-assembled from simple and small components. Originated from these earlier works, current interests in our group focus on i) molecular confinement effects in coordination cages, ii) solution chemistry in crystalline porous complexes (as applied to "crystalline sponge method"; 2013),[6] and iii) and giant self-assemblies (Figure 1; 2016).[7]



Figure 1. X-ray structure of M₄₈L₉₆ complex

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Covalent Chemistry Beyond Molecules

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Linking molecular building units by strong bonds to make crystalline extended structures (Reticular Chemistry) has given rise to metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), thus bringing the precision and versatility of covalent chemistry beyond the atoms and molecules. [1-4] The key advance in this regard has been the development of strategies to overcome the "crystallization problem", and the use of metal-oxide clusters as secondary building units to impart unprecedented structural robustness, high surface area, and permanent porosity. [5] To date, thousands of MOFs and COFs are made as crystalline materials. The molecular units thus reticulated become part of a new environment where they have (a) lower degrees of freedom because they are fixed into position within the framework; (b) well-defined spatial arrangements where their properties are influenced by the intricacies of the pores; and (c) ordered patterns onto which functional groups can be covalently attached to produce chemical complexity. The notion of covalent chemistry beyond molecules is further strengthened by the fact that covalent reactions can be carried out on such frameworks, with full retention of their crystallinity and porosity. MOFs are exemplars of how this chemistry has led to porosity with designed metrics and functionality, chemically-rich sequences of information within their frameworks, and well-defined mesoscopic constructs in which nanoMOFs enclose inorganic nanocrystals and give them new levels of spatial definition, stability, and functionality. The advent of COFs extends the field of organic chemistry beyond discrete molecules (0D) and polymers (1D) into "infinite" two and three dimensions. Molecular weaving, the mutual interlacing of long threads at the molecular level, was first accomplished in COF to make the true woven material. [6] This discovery combines the porosity and robustness of frameworks with mechanically deformable and stretchable capability.



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Materials Beyond Cyclodextrins Emergence Opens Up a Whole New World of Wonders

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During the past decade members of my research group have made two momentous discoveries in the area of carbohydrate materials, each having the potential to become a 'disruptive technology' for environmentally friendly products and sustainable processes. The two materials, both of which incorporate cyclic sugars known as cyclodextrins (CDs), are readily available from starch and are inexpensive and environmentally benign. Promising as these materials are for technologies ranging from food processing to gold mining, they also constitute exquisite examples of molecular self-assembly processes, aided and abetted by molecular recognition where: (i) the four-fold γ -CD molecular symmetry with eight glucose units orchestrates the spontaneous formation of the first edible metal-organic frameworks (MOFs) containing alkali metal (M⁺) cations, and (ii) the selective second-sphere coordination of potassium tetrabromoaurate (KAuBr₄) by α -CD, with its six glucose units, leads to the selective bulk separation of the gold salt by precipitation, even in the presence of other precious metals. The secret behind the CD-MOF formation is the simultaneous coordination of M^+ ions to both primary and secondary γ -CD toroidal faces, promoting the assembly of $(\gamma$ -CD)₆ cubes linked in an infinite 3D network. Crystallization under mild conditions vields CD-MOF cubes having dimensions of up to 5 mm, where the extended molecular structures are retained even upon evacuation to yield a highly porous material capable of accommodating small molecules in its pores. In the case of CO₂, highly selective uptake is shown to involve reversible formation of carbonic acid under Le Chatelier-like control at 25 °C. The same CD-MOFs also serve as chiral stationary phases for the chromatographic separation of flavors and fragrances, as well as separating aromatic compounds such as xylene isomeric mixtures. Initially following the discovery of CD-MOFs, we assumed that the nature of the anion accompanying the M⁺ cations was of little or no significance. Not so! We discovered that when the anion is AuBr₄⁻, a 3D channel-like superstructure results, wherein the gold-containing anions are interspersed along the CD units. The key enabling discovery came when we observed that, when dilute aqueous solutions of KAuBr₄⁻ and α -CD are mixed under ambient conditions, an off-white precipitate forms in near-quantitative yield. X-Ray diffraction characterization of the resulting complex, { $[K(OH_2)_6][AuBr_4]/(\alpha-CD)_2$ }, revealed a superstructure embodying a perfect lock-and-key component match that drives the precipitation of the gold-bearing adduct. Transmission electron microscopy showed that the precipitate is composed of high-aspect ratio nanowires having lengths in the tens of micrometers range. This discovery heralds a potential game-changer for recovering elemental gold from ores to electronic waste. The gold isolation process is simple, selective, scalable, and cost-efficient. The only requirement prior to the addition of α -CD is that the goldbearing materials be dissolved in aqueous KBr and Br₂ solutions, which are relatively safe to handle, unlike the current cyanide-based leaching process used in 83% of the world's gold production.

Nanostructured materials by covalent self-assembly

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One of the most exciting developments in chemistry during the last two decades is construction of nanostructured objects or materials from small building blocks by self-assembly. However, most of these studies utilize weak noncovalent interactions between building blocks, which allow a reversible process ultimately leading to the formation of thermodynamically most stable species. Some years ago, we reported the direct synthesis of nanometer–sized polymer hollow spheres without needs for any pre-organized structures or templates, and core-removal. In this work, flat and rigid–core tectons with multiple functional groups isotropically predisposed in all directions were cross–linked with linear linkers through irreversible covalent bond formation. These polymer capsules are useful in many applications including targeted drug delivery, photodynamic therapy, catalysis, and imaging. Extending this work, we also demonstrated the synthesis and isolation of micrometer–scale 2D polymer sheets of single–molecular thickness, which may find interesting applications including separation, optoelectronics and sensor. This strategy has also been extended to synthesize other nanostructured materials including hollow nanotubular toroidal polymer microrings. These are rare examples of covalent self-assembly under kinetic control [1], and some of recent progress will be presented.

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Understanding Electrofreezing at the Molecular Level with Pyroelectric Crystals

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with D. Ehre, S. Curland, E. Meirzadeh, I. Lubomirsky, Weizmann Institute of Science Ch. Allolio, D.Harris, Hebrew University of Jerusalem

Pyroelectric crystals are useful systems for the elucidation of structures and functions of materials.[1] I shall illustrate in this lecture their use for the determination of the mechanism of electrofreezing on the molecular level. Electrofreezing of super-cooled water, discovered at the 19th century is of topical importance in the pure and applied sciences. Yet, the mechanism of this process at the molecular level remains unsettled. In early studies we reported that polar pyroelectric crystals induce ice nucleation at temperatures higher by 3-5°C in comparison to icing induced by analogous non-polar materials.[2]

More recently, by the application of polar crystals, we discovered that the temperature of super cooled water is augmented on positively charged surfaces, whereas reduced on negatively charged.[3] Consequently we observed the occurrence of pyroelectric currents, which flow on hydrophilic faces residing parallel to the polar axes of the amino acids L-cysteine, DL-alanine, Laspartic acid, D-4-hydroxyphenylglycine and LiTaO₃.[4,5] This pyroelectric current can be cancelled when linking the hemihedral faces of those crystals with a metallic conductive paint. However, no such currents are observed on analogous hydrophobic surfaces. Consequently, by comparing the icing temperatures, measured exactly on the same surface, in the presence and the absence of the electric current, the effect of the pyroelectric charges on the icing temperature could be isolated from other factors. These studies suggested that the charges responsible for ice nucleation are OH⁻ ions, which migrate towards and consequently incorporate within the agueous Debye layers residing near the positive charged surfaces. Subsequently, proton ordered ice-like nuclei of the required size, as needed for triggering the icing, are created. These results were supported by molecular dynamics simulations, which suggest that electrofreezing is a chemical process affected by OH⁻ ions.[5] Moreover, in recent studies we demonstrated that the pyroelectric effect operates also in the icing on Agl, used for the glaciation of warm clouds.[6]



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Designing, Describing and Disseminating New Materials using the Network Topology Approach

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This talk will describe how network topology analysis is applied to different fields of solid-state chemistry, especially Metal-Organic Frameworks (MOFs), but also group 14 allotropes and related compounds, ice polymorphs, zeolites, supramolecular (organic) solid-state chemistry, Zintl phases, and cathode materials for Li-ion batteries.[1] Recent IUPAC recommendations and ongoing work on the terminology and nomenclature of MOFs will also be discussed.[2] Finally I will mention how metal–organic frameworks challenge our perceptions about the properties of crystalline materials.[3]



Image: A complicated silver(I) compound with thousands of atoms in the unit cell reduced to one single geometrical object, the **srs**-net, improving understanding and communication of the structure. Instead of describing the structure by 96 individual coordination entities comprising Ag(I) ions, large organic ligands and nitrate counter ions, we can use twelve interpenetrating **srs**-nets.[4]

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Computational Design of Functionalized Metal–Organic Framework Nodes for Catalysis

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Metal-organic frameworks (MOFs) are attracting the attention of many scientists because of their high selectivity in gas separations, catalytic activity, and magnetic properties. We have combined theory and experiment to understand the activity of metal catalysts supported on Zr_6 nodes in metal–organic frameworks (MOFs) for reactions related to natural gas conversion, like catalytic oligomerization of abundant C1, C2, and C3 hydrocarbons to longer congeners or selective oxidation to alcohols or other fuel molecules, while avoiding overoxidation to water and carbon dioxide. For Ni and Co,[1,2] computational studies provide important insights with respect to the catalytic mechanism(s) for observed ethylene dimerization after metal-decoration of the MOF NU-1000. Rh complexes have been installed on the Zr_6 nodes of not only NU-1000, but also the related metal–organic framework UiO-67, and the zeolite DAY; influences of the supports on ethylene hydrogenation and dimerization have been assessed.[3] A library of transition metals (TMs), ranging from first row TMs to noble metals, is now being screened computationally to search for optimal catalysts, and structure-function relationships are beginning to emerge from this theory-driven approach.[4]



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Diffusion NMR in Supramolecular Systems and Beyond

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Diffusion NMR and diffusion ordered spectroscopy (DOSY) have developed into an important analytical tool which can assist in the characterization of supramolecular systems in solution.[1] In the lecture, after a brief introduction of the technique, we will present the contribution of diffusion NMR to the field of molecular cages and capsules concentrating more on hydrogen bond-based molecular capsules. The use of diffusion NMR in studying self-assembled polymers will be mentioned briefly. We will demonstrate the effect that exchange may have on the diffusion NMR results when diffusion is measured using the longitudinal eddy current delay (LED)-based sequences generally used in DOSY. Finally, we will introduce the angular double pulsed-field gradient (d-PFG) NMR sequence[2] and we will demonstrate how this sequence provides a mean to obtain microstructural information in dense micro-emulsions, plants and neuronal tissues.

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Lanthanide Organic Polyhedra

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Coordination cage compounds have received growing attentions in the last several decades because of their potential applications in molecular sensing, biomimetic catalysis, stabilization of fleeting species, drug-delivery et al. By employing the metal-driven assembly strategy, numerous of metallocages build with transition metals have been reported. However, coordination selfassembly with lanthanide ions has seldom been reported due to their unpredictable and labile coordination numbers/geometries. Nevertheless, lanthanide ions have a lot of optical, electromagnetic and catalytic properties to offer to the aesthetically appealing 3D supramolecular assemblies. We are interested in the rare earth supramolecular chemistry, in particular the designed self-assembly and fine-tuned photophysical properties of multinuclear lanthanide-organic polyhedral (LOPs) complexes. Precise synthesis of a variety of LOPs with different molecular composition and geometrical configuration has been accomplished in our group recently.[1-2] Photophysical including chiroptical properties of the LOPs have been demonstrated, with proof-ofconcept applications such as high selective and efficient sensing toward biological relevant molecules/ions,[3-4] ion seperation,[5] single-molecular radiometric luminescent thermometers,[6] photosensitizers et al. We envisage these LOPs will find wide applications in the biomedical and material fields.



Figure 1. Lanthanide supramolecular chemistry: Structure and function.

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Concerted folding-and-assembly of short peptides via coordination

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Folding and assembly are respectively intra- and inter-molecular processes for spontaneously generating well-defined protein structures in natural systems. However, in synthetic fields, such processes have been utilized independently for constructions of well-defined nanostructures to date. Recently, our research group have developed the *folding-and-assembly* strategy, in which short peptide fragments can self-assemble into a well-defined nanostructure through concerted processes of folding and assembly triggered by metal coordination. We propose this new synthetic strategy is especially useful for creating unique nanostructures with multiple peptide entanglements. In this presentation, a variety of unique nanostructures such as porous coordination networks composed of polyproline II helices,[1,2] interlocking molecules based on Ω -shaped loops,[3,4] and others,[5] will be reported.



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Made in Israel: Metallo-Organic Materials and Devices

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Electrochromic coatings change color as a function of an applied potential. This interesting property is useful for various applications, including smart windows, color displays, and sensors. Fabricating low-cost electrochromic coatings that have appealing colors, and large optical contrasts, as well as long-term stability, remains an engineering challenge. Organic polymers, metal oxides, and liquid crystals have been promising candidates. Our molecular materials are based on structurally well-defined metal complexes that can be deposited from solution, offer a wide range of colors, and have metal-centered stable and reversible redox chemistry.[1-3] In this talk, the latest developments will be discussed.



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Molecular Face-Rotating Polyhedra

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In nature, protein subunits on the capsids of many icosahedral viruses form rotational patterns, and mathematicians also incorporate asymmetric patterns into faces of polyhedra. Here we use prochiral truxene or tetraphenylethylene (Figure A, B) derivatives as building blocks to construct a series of molecular polyhedra with rotational patterns on faces, which we term as Face-Rotating Polyhedra (FRP). The relative stability of these polyhedra enables separation by chiral HPLC and full characterization. We investigate the assembly process and the kinetics of interconversion of the polyhedra by a combination of chiral HPLC, CD, MS and NMR. These FRP represent a special form of molecular chirality.



Figure 1. Face-Rotating Polyhedra

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Smart Soft Materials Fabricated under Nonequilibrated Conditions

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Machine technology frequently puts magnetic or electrostatic repulsive forces to practical use, as in maglev trains, vehicle suspensions or non-contact bearings. In contrast, materials design overwhelmingly focuses on attractive interactions, such as in the many advanced polymer-based composites, where inorganic fillers interact



with a polymer matrix to improve mechanical properties. However, articular cartilage strikingly illustrates how electrostatic repulsion can be harnessed to achieve unparalleled functional efficiency: it permits virtually frictionless mechanical motion within joints, even under high compression. Here we describe a composite hydrogel with anisotropic mechanical properties dominated by electrostatic repulsion between negatively charged unilamellar titanate nanosheets embedded within it. Crucial to the behaviour of this hydrogel is the serendipitous discovery of cofacial nanosheet alignment in aqueous colloidal dispersions subjected to a strong magnetic field, which maximizes electrostatic repulsion6 and thereby induces a quasi-crystalline structural

ordering over macroscopic length scales and with uniformly large face-to-face nanosheet separation. We fix this transiently induced structural order by transforming the dispersion into a hydrogel using light-triggered in situ vinyl polymerization. The resultant hvdroael. containing charged inorganic structures that align cofacially in a magnetic flux, deforms easily under shear forces applied parallel to the embedded nanosheets vet resists compressive forces applied orthogonally. We anticipate that the concept of embedding anisotropic repulsive electrostatics within a

composite material, inspired by articular cartilage, will open up new possibilities for developing soft materials with unusual functions. More recently, we reported a highly oriented thin film of a carbon nitride polymer, which shows anomalous mechanical responses to minute fluctuations in the ambient humidity. The lecture may also highlight selfhealable polymer glass recently published.

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Website: globalscience.berkeley.edu

The ability to perform science and innovation is distributed unequally; only scientists from few countries have the means to address problems affecting the world (science exclusivity). Developing countries lack the reliability of a rigorous scientific culture. This is often perpetuated by the absence of strong scientific leadership and sustainable mentoring traditions, corruption and unethical scientific practices, lack of an idea generation system, or underdeveloped institutional foundations.

The Berkeley Global Science Institute (BGSI) was established to address the 'science exclusivity' problem and to promote an even distribution of research capacity throughout the world. BGSI's mission is to partner with institutions of learning abroad to establish freestanding centers of global science, in which emerging scholars can plug into impactful research that focuses on solving local problems before they become global. Each center of global science is founded upon a partnership with both a higher education institution and their respective local and national governments. Our activities at the local level involve: (i) establishing state-of-the-art research infrastructure; (ii) recruiting local, regional, and international research talent; (iii) preparing funding from local and national governments; (iv) establishing industrial collaborations; (v) producing high impact publications in prestigious journals and magazines; (vi) connecting local emerging scholars to the global science community; (vii) providing new opportunities for emerging scholars through mentorship; and (viii) using science as a language and tool for peace and prosperity. The research that is identified and developed is based on the host country's societal priorities, but in all centers, research programs have focused on at least one of the following sectors: agriculture, education, environment, energy, or water. Through BGSI's work, research programs have been initiated in various forms and to various extents in Vietnam, Indonesia, Malaysia, Argentina, Jordan, Saudi Arabia, Mexico, South Korea, China, Kuwait, United Arab Emirates, and Japan. In these places, >1000 international emerging scholars (students and early career researchers) have benefited from our partnership with >200 international emerging scholars benefiting from direct mentorship. As a result, >85 high impact research articles, many of which are in the most prestigious journals ever achieved by these countries, and patents have been jointly published in the last 5 years.





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