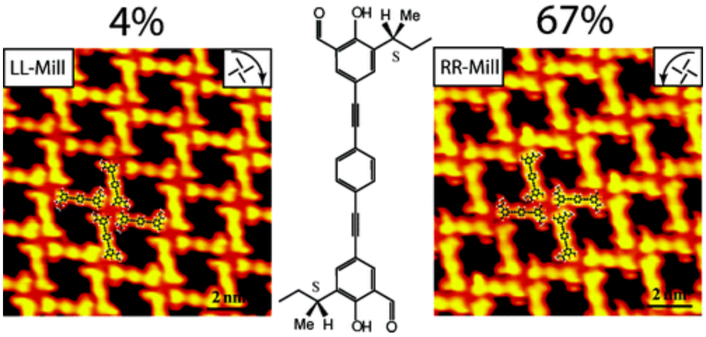
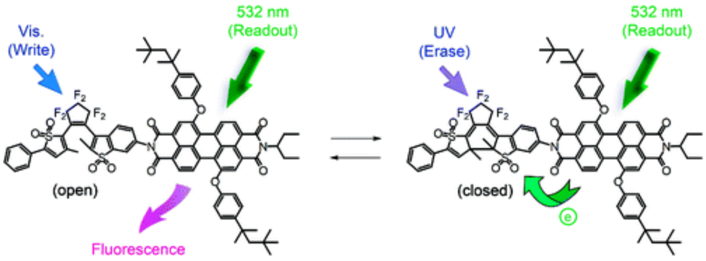
- Controlling Chiral Organization of Molecular Rods on Au(111) by Molecular Design
  Knudsen, M. M.; Kalashnyk, N.; Masini, F.; Cramer, J. R.; Lægsgaard, E.; Besenbacher, F.; Linderoth, T. R.; Gothelf, K. V. *J. Am. Chem. Soc.* **2011**, *133*, 4896-4905.
  Abstract:



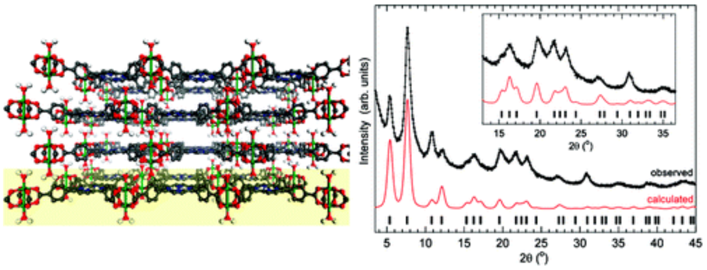
Chiral self-assembled structures formed from organic molecules adsorbed on surfaces have been the subject of intense investigation in the recent decade, owing both to relevance in applications such as enantiospecific heterogeneous catalysis or chiral separation as well as to fundamental interest, for example, in relation to the origin of biomolecular homochirality. A central target is rational design of molecular building blocks allowing transfer of chirality from the molecular to the supramolecular level. We previously studied the surface self-assembly of a class of linear compounds based on an oligo(phenylene ethynylene) backbone, which were shown to form a characteristic windmill adsorption pattern on the Au(111) surface. However, since these prochiral compounds were intrinsically achiral, domains with oppositely oriented windmill motifs and related conformational surface enantiomers were always realized in equal proportion. Here we report on the enantioselective, high yield chemical synthesis of a structurally related but intrinsically chiral compound in which two peripheral tert-butyl substituents are replaced by sec-butyl groups, each containing an (S) chiral center. Using scanning tunneling microscopy under ultrahigh vacuum conditions, we characterize the adsorption structures formed from this compound on the Au(111) surface. The perturbation introduced by the modified molecular design is found to be sufficiently small so structures form that are closely analogous to those observed for the original tert-butyl substituted compound. However, as demonstrated from careful statistical analysis of high-resolution STM images, the introduction of the two chiral (S)-sec-butyl substituents leads to a strong preference for windmill motifs with one orientation, demonstrating control of the chiral organization of the molecular backbones through rational molecular design.

- Single-Molecule Fluorescence Photoswitching of a Diarylethene−Perylenebisimide Dyad: Non-destructive Fluorescence Readout
  Fukaminato, T.; Doi, T.; Tamaoki, N.; Okuno, K.; Ishibashi, Y.; Miyasaka, H.; Irie, M. *J. Am. Chem. Soc.* **2011**, *133*, 4984-4990.
  Abstract:



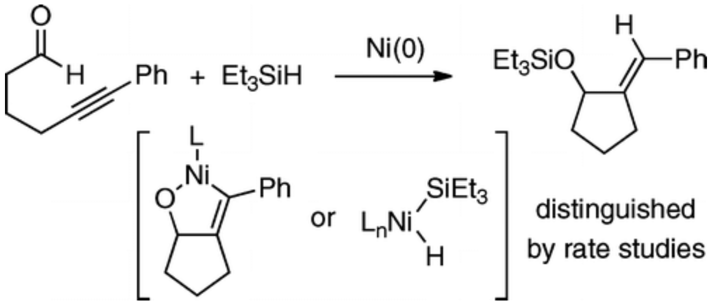
Single-molecule fluorescence photoswitching plays an essential role in ultrahigh-density (Tbits/inch^2) optical memories and super-high-resolution fluorescence imaging. Although several fluorescent photochromic molecules and fluorescent proteins have been applied, so far, to optical memories and super-high-resolution imaging, their performance is unsatisfactory because of the absence of “non-destructive fluorescence readout capability”. Here we report on a new molecular design principle of a molecule having non-destructive readout capability. The molecule is composed of acceptor photochromic diarylethene and donor fluorescent perylenebisimide units. The fluorescence is reversibly quenched when the diarylethene unit converts between the open- and the closed-ring isomers upon irradiation with visible and UV light. The fluorescence quenching is based on an electron transfer from the donor to the acceptor units. The fluorescence photoswitching and non-destructive readout capability were demonstrated in solution (an ensemble state) and at the single-molecule level. Femtosecond time-resolved transient and fluorescent lifetime measurements confirmed that the fluorescence quenching is attributed to the intramolecular electron transfer.

- Highly Crystalline Nanofilm by Layering of Porphyrin Metal–Organic Framework Sheets
  Motoyama, S.; Makiura, R.; Sakata, O.; Kitagawa, H. *J. Am. Chem. Soc.* **2011**, *133*, 5640–5643.
  Abstract:



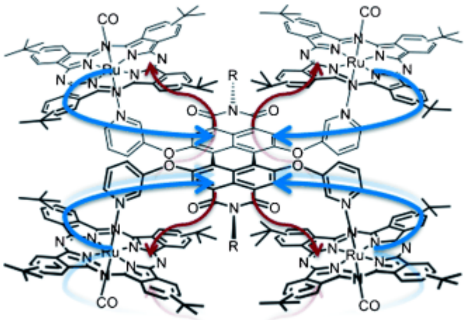
Layer-structured metal–organic framework (MOF) nanofilms (NAFS-2) consisting of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP) molecules and copper ion metal linkers were assembled on a gold or a silicon surface by applying a solution-based layer-by-layer growth technique coupled with the Langmuir–Blodgett method. Synchrotron X-ray diffraction measurements showed that NAFS-2 exhibits highly crystalline order in both the in-plane and out-of-plane orientations. Each MOF sheet (monolayer) adheres without pillaring units, and the nanofilm maintains its highly crystalline order above 200 °C. The results provide an excellent demonstration of how to exercise in a facile way fine control of the assembly of molecule-based hybrid objects and their thermal stability, which is a key issue for the future use of MOFs in potential applications in nanodevices.

- Mechanistic Study of Nickel-Catalyzed Ynal Reductive Cyclizations through Kinetic Analysis
  Baxter, R. D.; Montgomery, J. *J. Am. Chem. Soc.* **2011**, *133*, 5728–5731.
  Abstract:



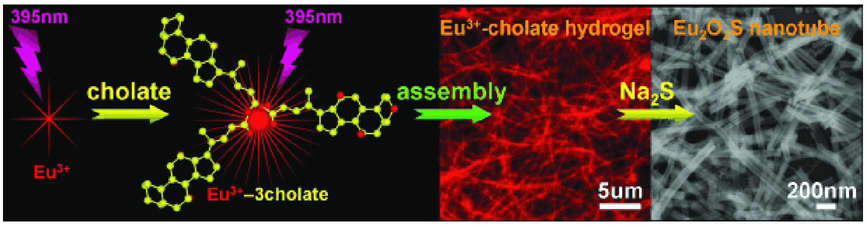
The mechanism of nickel-catalyzed, silane-mediated reductive cyclization of ynals has been evaluated. The cyclizations are first-order in [Ni] and [ynal] and zeroth-order in [silane]. These results, in combination with the lack of rapid silane consumption upon reaction initiation, are inconsistent with mechanisms involving reaction initiation by oxidative addition of Ni(0) to the silane. Silane consumption occurs only when both the alkyne and aldehyde are present. Mechanisms involving rate-determining oxidative cyclization to a metallacycle followed by rapid reaction with the silane are consistent with the data obtained.

- Synthesis, Characterization, and Photoinduced Energy and Electron Transfer in a Supramolecular Tetrakis (Ruthenium(II) Phthalocyanine) Perylenediimide Pentad
  Jiménez, A. J.; Grimm, B.; Gunderson, V. C.; Vagnini, M. T.; Calderon, S. K.; Morgade, S. R.; Wasielewski, M. R.; Guldi, D. M.; Torres, T. *Chem. Eur. J.* **2011**, *17*, 5024–5032.
  Abstract:



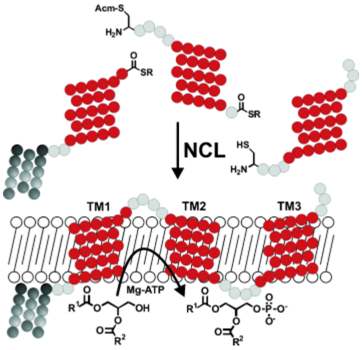
Metal coordination was probed as a versatile approach for designing a novel electron donor/acceptor hybrid [PDIpy$_4${Ru(CO)Pc}$_4$] (1), in which four pyridines placed at the bay region of a perylenediimides (PDIpy$_4$) coordinate with four ruthenium phthalocyanine units [Ru(CO)Pc]. This structural motif was expected to promote strong electronic coupling between the electron donors and the electron acceptor, a hypothesis that was confirmed in a full-fledged physicochemical investigation focusing on the ground and excited state reactivities. As far as the ground state is concerned, absorption and electrochemical assays indeed reveal a notable redistribution of electron density, that is, from the electron-donating [Ru(CO)Pc] to the electron-accepting PDIpy$_4$. The most important thing to note in this context is that both the [Ru(CO)Pc] oxidation and the PDIpy4 reduction are rendered more difficult in 1 than in the individual building blocks. Likewise, in the excited state, strong electronic communication is the inception for a rapid charge-transfer process in photoexcited 1. Regardless of exciting [Ru(CO)Pc] or PDIpy4, spectral characteristics of the [RuPc] radical cation (broad absorptive features from 425 to 600 nm with a maximum at 575 nm, as well as a band centered at 725 nm) and of the PDI radical anion (780 nm maximum) emerge. The correspondingly formed radical ion pair state lasts for up to several hundred picoseconds in toluene, for example. On the other hand, employing more polar solvents, such as dichloromethane, destabilizes the radical ion pair state

- Lanthanide-Containing Photoluminescent Materials: From Hybrid Hydrogel to Inorganic Nanotubes
  Qiao, Y.; Lin, Y.; Zhang, S.; Huang, J. *Chem. Eur. J.* **2011**, *17*, 5180–5187.
  Abstract:



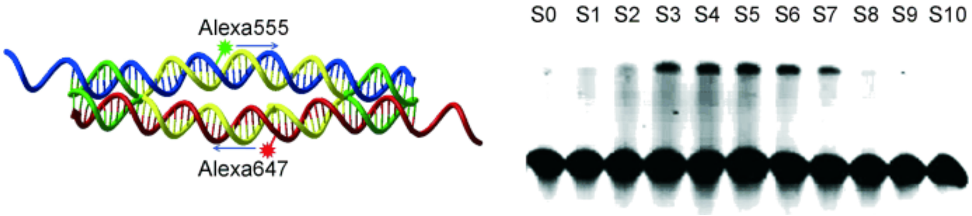
Functional photoluminescent materials are emerging as a fascinating subject with versatile applicability. In this work, luminescent organic–inorganic hybrid hydrogels are facilely designed through supramolecular self-assembly of sodium cholate, and lanthanide ions such as Eu3+, Tb3+, and Eu3+/Tb3+. Fluorescence microscopy and TEM visualization demonstrates the existence of spontaneously self-assembled nanofibers and 3D networks in hybrid hydrogel. Photoluminescence enhancement of lanthanide ions is realized through coordination with cholate and co-assembly into 1D nanofibers, which can successfully shield the Eu3+ from being quenched by water. The photoluminescence emission intensity of a hybrid hydrogel exhibits strong dependence on europium/cholate molar ratio, with maximum emission appearing at a stoichiometry of 1:3. Furthermore, the emission color of a lanthanide–cholate hydrogel can be tuned by utilizing different lanthanide ions or co-doping ions. Moreover, photoluminescent lanthanide oxysulfide inorganic nanotubes are synthesized by means of a self-templating approach based on lanthanide–cholate supramolecular hydrogels. To the best of our knowledge, this is the first time that the lanthanide oxysulfide inorganic nanotubes are prepared in solution under mild conditions.

- Total Chemical Synthesis of an Integral Membrane Enzyme: Diacylglycerol Kinase from *Escherichia coli*.
  Lahiri, S.; Brehs, M.; Olschewski, D.; Becker, C. F. W. *Angew. Chem. Int. Ed.* **2011**, *50*, 3988–3992.
  <u>Abstract:</u>



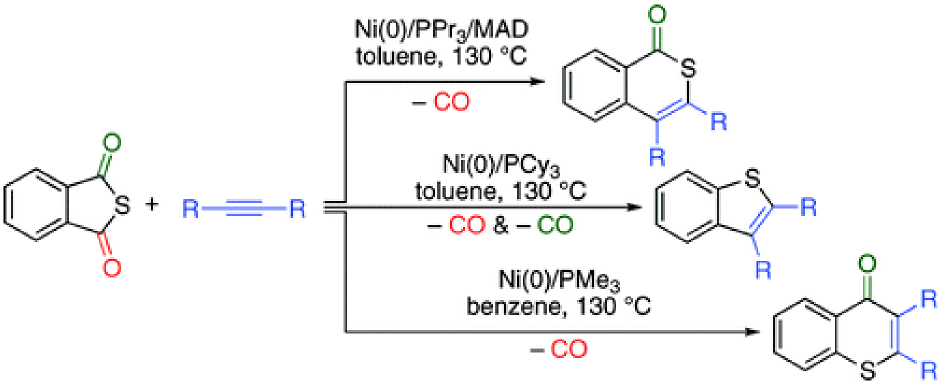
From the ground up: Chemical synthesis provided direct access to a catalytically active membrane-embedded kinase with three transmembrane domains (TMs). Three key segments formed from the individual amino acids (represented by red and gray balls) by solid-phase peptide synthesis were connected by native chemical ligation (NCL; see picture); the synthetic protein underwent spontaneous folding in detergent micelles. ATP=adenosine 5′-triphosphate.

- A DNA Tile Actuator with Eleven Discrete States
  Zhang, Z.; Olsen, E. M.; Kryger, M.; Voigt, N. V.; Tørring, T.; Gültekin, E.; Nielsen, M.; Mohammad Zadegan, R.; Andersen, E. S.; Nielsen, M. M.; Kjems, J.; Birkedal, V.; Gothelf, K. V. *Angew. Chem. Int. Ed.* **2011**, *50*, 3983–3987.
  <u>Abstract:</u>



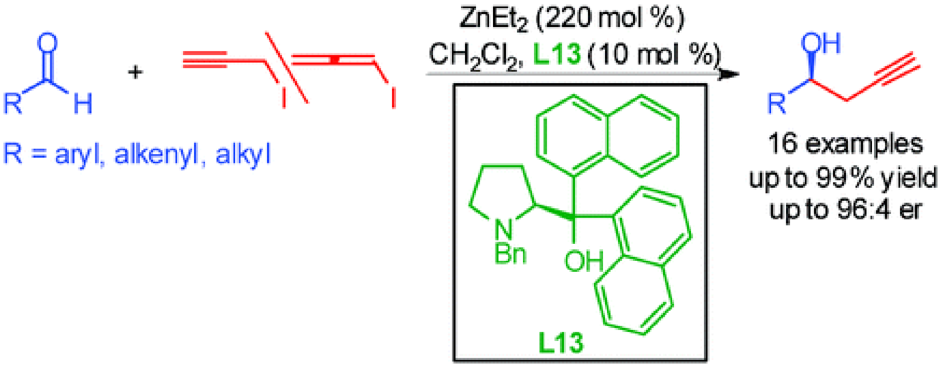
Elegant control: A DNA actuator based on the most fundamental motif in DNA nanotechnology, the double crossover tile, has a linear sliding-gauge type of motion among eleven different states (see picture). The actuator has the ability to fine-tune the distances between attached components (resolution of less than 1 nm) for both physical studies and chemical control.

- Nickel-Catalyzed Cycloadditions of Thiophthalic Anhydrides with Alkynes
  Inami, T.; Baba, Y.; Kurahashi, T.; Matsubara, S. *Org. Lett.* **2011**, *13*, 1912-1915.
  Abstract:



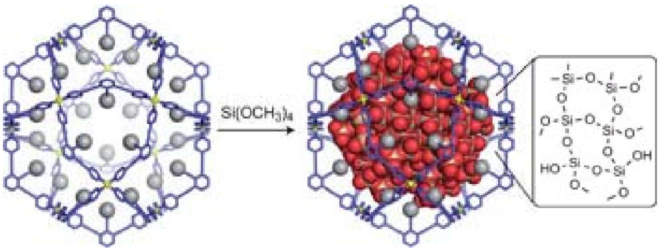
Nickel-catalyzed cycloadditions have been developed where thiophthalic anhydrides react with alkynes to afford substituted sulfur-containing heterocyclic compounds. Selective formations of thioisocoumarins, benzothiophenes, and thiochromones were accomplished with three different reaction conditions.

- Ligand-accelerated Enantioselective Propargylation of Aldehydes via Allenylzinc Reagents
  Trost, B. M.; Ngai, M.-Y.; Dong, G. *Org. Lett.* **2011**, *13*, 1900–1903.
  Abstract:



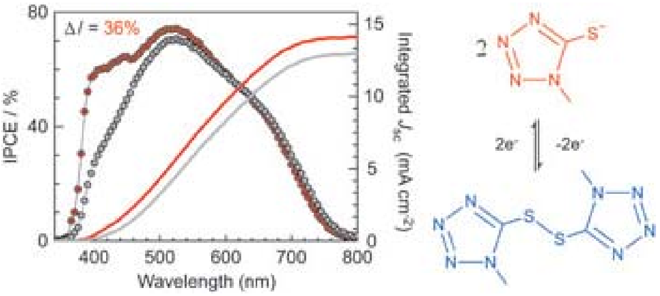
An enantioselective propargylation of aldehydes using an allenylzinc reagent generated in situ via a zinc–iodine exchange reaction is described. The enantioselectivity is controlled by addition of a catalytic amount of readily accessible and highly tunable amino alcohol ligand L13. A wide range of aldehydes can be propargylated to afford valuable and versatile homopropargyl alcohols in good to excellent yields with high levels of enantiopurity.

- Template synthesis of precisely monodisperse silica nanoparticles within self-assembled organometallic spheres
  Suzuki, K.; Sato, S.; Fujita, M. *Nature Chem.* **2010**, *2*, 25-29.
  Abstract:



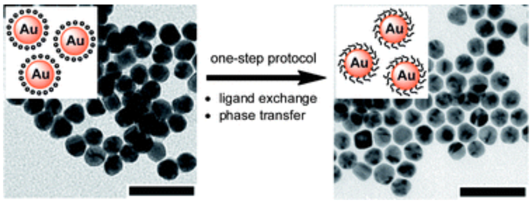
One of the key challenges in materials science is to control the size and shape of inorganic nanoparticles with a high degree of precision, as these parameters have a significant influence on the nanoparticles' properties and potential applications. Here, we describe the preparation of highly monodisperse silica nanoparticles smaller than 5 nm in diameter by using self-assembled, hollow, spherical compounds as ‘endo-templates’. These coordination complexes with pendant sugar groups lining their interiors—assembled from 12 metal ions and 24 bis-pyridyl ligands containing glucose substituents—acted as structurally well-defined templates for the sol–gel condensation of alkoxysilanes. The polydispersities of the silica nanoparticles made with this method approached unity, with $M_w/M_n < 1.01$. The component ligands are modified easily, which enables an accurate expansion of the coordination complex and the subsequent control of the monodisperse silica nanoparticles that span molecular weights of 5,000 to 31,000 Da (corresponding to 2–4 nm in diameter). This method could be applicable to the preparation of other inorganic nanoparticles.

- An organic redox electrolyte to rival triiodide/iodide in dye-sensitized solar cells
  Wang, M.; Chamberland, N.; Breau, L.; Moser, J.-E.; Humphry-Baker, R.; Marsan, B.; Zakeeruddin, S. M.; Grätzel, M. *Nature Chem.*, **2010**, *2*, 385-389.
  Abstract:



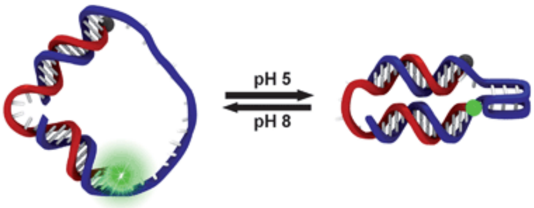
Dye-sensitized solar cells (DSCs) have achieved impressive conversion efficiencies for solar energy of over 11% with an electrolyte that contains triiodide/iodide as a redox couple. Although triiodide/iodide redox couples work efficiently in DSCs, they suffer from two major disadvantages: electrolytes that contain triiodide/iodide corrode electrical contacts made of silver (which reduces the options for the scale up of DSCs to module size) and triiodide partially absorbs visible light. Here, we present a new disulfide/thiolate redox couple that has negligible absorption in the visible spectral range, a very attractive feature for flexible DSCs that use transparent conductors as current collectors. Using this novel, iodide-free redox electrolyte in conjunction with a sensitized heterojunction, we achieved an unprecedented efficiency of 6.4% under standard illumination test conditions. This novel redox couple offers a viable pathway to develop efficient DSCs with attractive properties for scale up and practical applications.

- Synthesis and characterization of azidoalkyl-functionalized gold nanoparticles as scaffolds for “click”-chemistry derivatization
  Baranov, D.; Kadnikova, E. N. *J. Mater. Chem.* **2011**, *21*, 6152-6157.
  Abstract:



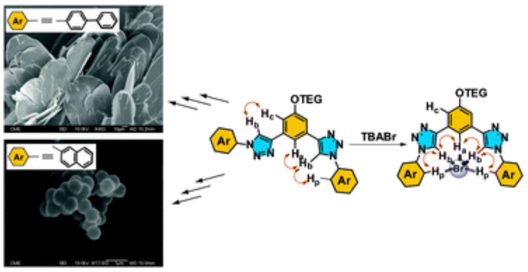
We demonstrate how water-soluble gold nanoparticles prepared by the citrate reduction method can be functionalized with 11-azidoundecane-1-thiol in a single-step procedure, which combines phase transfer and ligand exchange. The advantages of our method include high reproducibility, low cost of gold nanoparticle production, and rapid and clean ligand exchange, with minimal intermediate steps and none of the laborious efforts. The resulting azido-functionalized nanoparticles were characterized by ^{1}H NMR and UV-visible spectroscopy, and visualized by transmission electron microscopy (TEM).

- Adaptive DNA-based materials for switching, sensing, and logic devices
  Campolongo, M. J.; Kahn, J. S.; Cheng, W.; Yang, D.; Gupton-Campolongo, T.; Luo, D. *J. Mater. Chem.* **2011**, *21*, 6113-6121.
  Abstract:



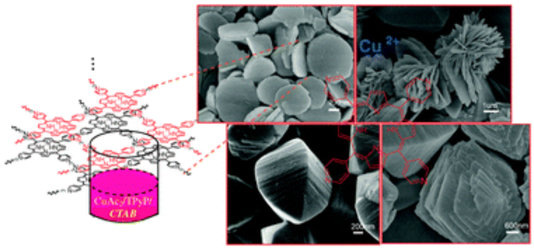
DNA-based materials that can adapt to their surroundings are of great interest for the development of next-generation switching, sensing, and logic devices. Through elaborate sequence design and chemical functionalization, numerous adaptive DNA-based materials have been developed that can reversibly switch conformations, act as dynamic sensors, perform logic operations, and even trigger macroscopic phase responses.

- Open aryl triazole receptors: planar sheets, spheres and anion binding
  García, F.; Torres, M. R.; Matesanz, E.; Sánchez, L. *Chem. Commun.* **2011**, *47*, 5016-5018.
  Abstract:



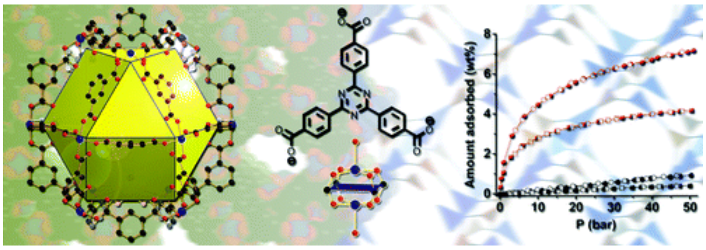
The morphology of the aggregates formed from the self-assembly of aryl triazole amphiphiles is disrupted upon the binding of a bromide anion due to the conformational changes experienced by these receptors.

- Facile synthesis of shape and size tunable porphyrinoid coordination polymers: from copper porphyrin nanoplates to microspindles
  Shi, N.; Xie, L.; Sun, H.; Duan, J.; Yin, G.; Xu, Z.; Huang, W. *Chem. Commun.* **2011**, *47*, 5055-5057.
  Abstract:



In this communication, size tunable copper porphyrin dispersed nanoplates, assembled nanoplates, and microspindles have been controllably fabricated *via* a simple surfactant-assisted solution route.

- Tuning the Topology and Functionality of Metal−Organic Frameworks by Ligand Design
  Zhao, D.; Timmons, D. J.; Yuan, D.; Zhou, H.-C. *Acc. Chem. Res.* **2011**, *44*, 123–133.
  Abstract:



Metal−organic frameworks (MOFs)—highly crystalline hybrid materials that combine metal ions with rigid organic ligands—have emerged as an important class of porous materials. The organic ligands add flexibility and diversity to the chemical structures and functions of these materials. In this Account, we summarize our laboratory's experience in tuning the topology and functionality of MOFs by ligand design.

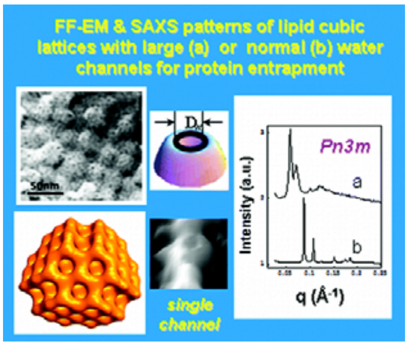
These investigations have led to new materials with interesting properties. By using a ligand that can adopt different symmetry conformations through free internal bond rotation, we have obtained two MOFs that are supramolecular stereoisomers of each other at different reaction temperatures. In another case, where the dimerized ligands function as a D_3-Piedfort unit spacer, we achieve chiral (10,3)-a networks.

In the design of MOF-based materials for hydrogen and methane storage, we focused on increasing the gas affinity of frameworks by using ligands with different geometries to control the pore size and effectively introduce unsaturated metal centers (UMCs) into the framework. Framework interpenetration in PCN-6 (PCN stands for porous coordination network) can lead to higher hydrogen uptake. Because of the proper alignment of the UMCs, PCN-12 holds the record for uptake of hydrogen at 77 K/760 Torr. In the case of methane storage, PCN-14 with anthracene-derived ligand achieves breakthrough storage capacity, at a level 28% higher than the U.S. Department of Energy target.

Selective gas adsorption requires a pore size comparable to that of the target gas molecules; therefore, we use bulky ligands and network interpenetration to reduce the pore size. In addition, with the help of an amphiphilic ligand, we were able to use temperature to continuously change pore size in a 2D layer MOF. Adding charge to an organic ligand can also stabilize frameworks. By ionizing the amine group within mesoMOF-1, the resulting electronic repulsion keeps the network from collapsing, giving rise to the first case of mesoporous MOF that demonstrates the type IV isotherm. We use dendritic hexacarboxylate ligands to synthesize an isoreticular series of MOFs with (3,24)-connected network topology. The cuboctahedral cages serve as building blocks that narrow the opening of the mesocavities into microwindows and stabilize these MOFs. The resulting materials have exceptionally high surface areas and hydrogen uptake capacities.

Despite the many achievements in MOF development, there is still ample opportunity for further exploration. We will be continuing our efforts and look forward to contributing to this blossoming field in the next decade.

- Self-Assembled Multicompartment Liquid Crystalline Lipid Carriers for Protein, Peptide, and Nucleic Acid Drug Delivery
  Angelova, A.; Angelov, B.; Mutafchieva, R.; Lesieur, S.; Couvreur, P. *Acc. Chem. Res.* **2011**, *44*, 147–156.
  Abstract:

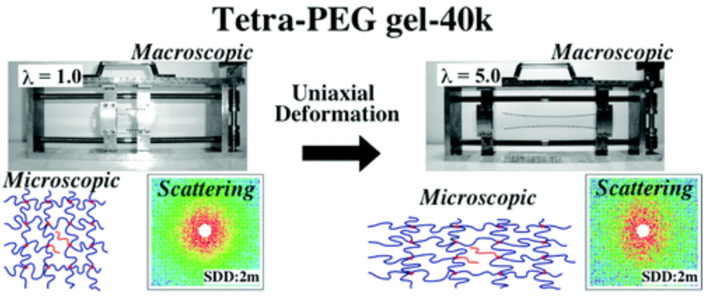


Lipids and lipopolymers self-assembled into biocompatible nano- and mesostructured functional materials offer many potential applications in medicine and diagnostics. In this Account, we demonstrate how high-resolution structural investigations of bicontinuous cubic templates made from lyotropic thermosensitive liquid-crystalline (LC) materials have initiated the development of innovative lipidopolymeric self-assembled nanocarriers. Such structures have tunable nanochannel sizes, morphologies, and hierarchical inner organizations and provide potential vehicles for the predictable loading and release of therapeutic proteins, peptides, or nucleic acids. This Account shows that structural studies of swelling of bicontinuous cubic lipid/water phases are essential for overcoming the nanoscale constraints for encapsulation of large therapeutic molecules in multicompartment lipid carriers.

For the systems described here, we have employed time-resolved small-angle X-ray scattering (SAXS) and high-resolution freeze-fracture electronic microscopy (FF-EM) to study the morphology and the dynamic topological transitions of these nanostructured multicomponent amphiphilic assemblies. Quasi-elastic light scattering and circular dichroism spectroscopy can provide additional information at the nanoscale about the behavior of lipid/protein self-assemblies under conditions that approximate physiological hydration.

We wanted to generalize these findings to control the stability and the hydration of the water nanochannels in liquid-crystalline lipid nanovehicles and confine therapeutic biomolecules within these structures. Therefore we analyzed the influence of amphiphilic and soluble additives (e.g. poly(ethylene glycol)monooleate (MO-PEG), octyl glucoside (OG), proteins) on the nanochannels' size in a diamond (D)-type bicontinuous cubic phase of the lipid glycerol monooleate (MO). At body temperature, we can stabilize long-living swollen states, corresponding to a diamond cubic phase with large water channels. Time-resolved X-ray diffraction (XRD) scans allowed us to detect metastable intermediate and coexisting structures and monitor the temperature-induced phase sequences of mixed systems containing glycerol monooleate, a soluble protein macromolecule, and an interfacial curvature modulating agent. These observed states correspond to the stages of the growth of the nanofluidic channel network.
With the application of a thermal stimulus, the system becomes progressively more ordered into a double-diamond cubic lattice formed by a bicontinuous lipid membrane. High-resolution freeze-fracture electronic microscopy indicates that nanodomains are induced by the inclusion of proteins into nanopockets of the supramolecular cubosomic assemblies. These results contribute to the understanding of the structure and dynamics of functionalized self-assembled lipid nanosystems during stimuli-triggered LC phase transformations.

- SANS Studies on Tetra-PEG Gel under Uniaxial Deformation
  Matsunaga, T.; Asai, H.; Akagi, Y.; Sakai, T.; Chung, U.; Shibayama, M. *Macromolecules* **2011**, *44*, 1203–1210.
  <u>Abstract:</u>



Studies on the deformation mechanism of polymer networks with small-angle neutron scattering (SANS) were carried out for Tetra-PEG gels, that is, poly(ethylene glycol) (PEG) networks prepared from tetra-functional A- and B-type macromers consisting of PEG by cross-end-coupling. Tetra-PEG gels are hydrogels with narrow-dispersed polymer chains. The molecular weights of the prepolymers were 20k and 40k. SANS measurements were conducted for uniaxially stretched Tetra-PEG gels. Although the SANS patterns for deformed Tetra-PEG gel-20k showed small anisotropy, that is, prolate and oblate patterns with respect to the stretching direction at low and high-q regions, respectively, Tetra-PEG gel-40k exhibited no anisotropy at all in the low-q region, even in a gel stretched by five times. This indicates that Tetra-PEG gel-40k is a homogeneous network free from inhomogeneities, such as dangling chains and entanglements and can be regarded as an "ideal" polymer network. The deformation mechanism of Tetra-PEG gels was discussed in comparison with those for phantom Gaussian chain model and others, suggesting that the concentration fluctuations by thermal motions surpass the chain anisotropy introduced by deformation.