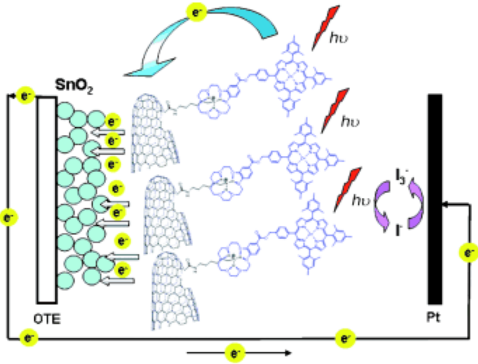
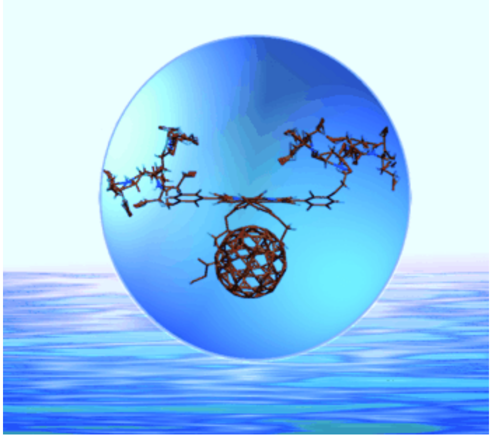
- A Carbon Nanohorn-Porphyrin Supramolecular Assembly for Photoinduced Electron-Transfer Processes
  Vizuete, M.; Gómez-Escalonilla, M. J.; Fierro, J. L. G.; Sandanayaka, A. S. D.; Hasobe, T.; Yudasaka, M.; Iijima, S.; Ito, O.; Langa, F. *Chem.-Eur. J.* **2010**, *16*, 10752-10763.
  Abstract:



OTE: Optically Transparent Electrode
OTE/SnO$_2$/CNH-sp-NH$_3^+$;Crown-ZnP

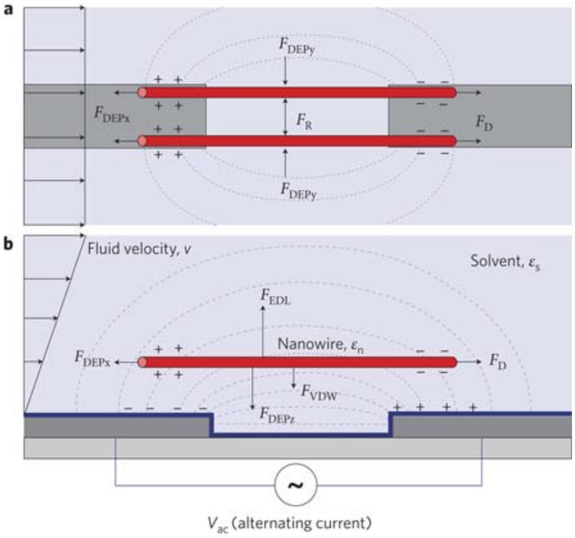
A supramolecular assembly of zinc porphyrin-carbon nanohorns (**CNH**s) was constructed in a polar solvent. An ammonium cation was covalently connected to the **CNH** through a spacer (sp) (**CNH**-sp-NH$_3^+$) and bound to a crown ether linked to a zinc porphyrin (Crown—ZnP). Nanohybrids **CNH**-sp-NH$_3^+$;Crown-ZnP and **CNH**-sp-NH$_3^+$ were characterized by several techniques, such as high-resolution transmission electron microscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy, and Raman spectroscopy. The photoinduced electron-transfer processes of the nanohybrids have been confirmed by using time-resolved absorption and fluorescence measurements by combining the steady-state spectral data. Fluorescence quenching of the ZnP unit by **CNH**-sp-NH$_3^+$ has been observed, therefore, photoinduced charge separation through the excited singlet state of the ZnP unit is suggested for the hybrid material, **CNH**-sp-NH$_3^+$;Crown-ZnP. As transient absorption spectral experiments reveal the formation of the radical cation of the ZnP unit, electron generation is suggested as a counterpart of the charge-separation on the **CNH**s; such an electron on the **CNH**s is further confirmed by migrating to the hexylviologen dication (HV^{2+}). Accumulation of the electron captured from HV$^{\cdot+}$ is observed as electron pooling in solution in the presence of a hole-shifting reagent. Photovoltaic performance with moderate efficiency is confirmed for **CNH**-sp-NH$_3^+$;Crown-ZnP deposited onto nanostructured SnO$_2$ films.

- Dendronizing and Metalating *trans*-2 C$_{60}$ Tetraaryl Porphyrins: A Versatile Approach Toward Water-Soluble Donor–Acceptor Conjugates
  Ruppert, M.; Spänig, F.; Wielopolski, M.; Jäger, C. M.; Bauer, W.; Clark, T.; Hirsch, A.; Guldi, D. M. *Chem.-Eur. J.* **2010**, *16*, 10797-10807.
  Abstract:



We have realized for the first time a series of truly water-soluble and tightly coupled porphyrin/C_{60} electron-donor–acceptor conjugates in which the charge separation and charge recombination dynamics are controlled by modifying the nature of the dendrimer and/or the choice of the central metal atom.

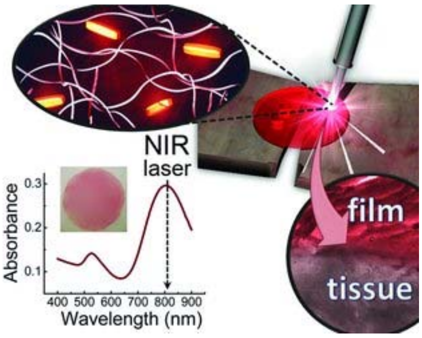
- High-yield self-limiting single-nanowire assembly with dielectrophoresis
  Freer, E. M.; Grachev, O.; Duan, X.; Martin, S.; Stumbo, D. P. *Nature Nanotechnology* **2010**, *5*, 525-530.
  Abstract:



Single-crystal nanowire transistors and other nanowire-based devices could have applications in large-area and flexible electronics if conventional top-down fabrication techniques can be integrated with high-precision bottom-up nanowire assembly. Here, we extend dielectrophoretic nanowire assembly to achieve a 98.5% yield of single nanowires assembled over 16,000 patterned electrode sites with submicrometre alignment precision. The balancing of surface, hydrodynamic and dielectrophoretic forces makes the self-assembly process controllable, and a hydrodynamic force component makes it self-limiting. Our approach represents a methodology to quantify nanowire assembly, and makes single nanowire assembly possible over an area limited only by the ability to reproduce process conditions uniformly.

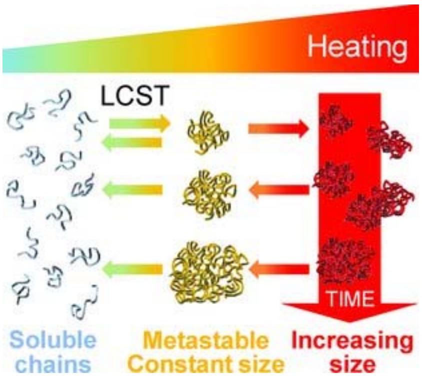
- Chitosan Films Doped with Gold Nanorods as Laser-Activatable Hybrid Bioadhesives
  Matteini, P.; Ratto, F.; Rossi, F.; Centi, S.; Dei, L.; Pini, R. *Adv. Mater.* **2010**, *22*, 4313–4316.

Abstract:



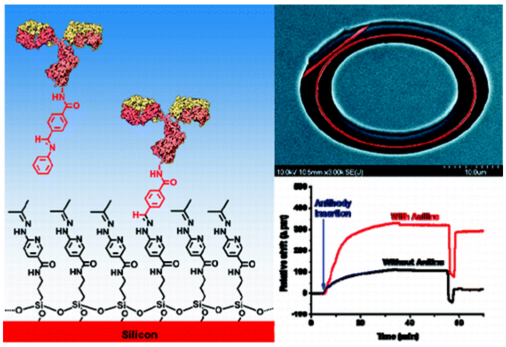
Biocompatible chitosan/gold nanorods films are fabricated and tested as laser-activatable adhesives. When exposed to near-infrared laser light the nanoparticles carry out efficient photothermal conversion, which activates the polar groups of chitosan strands and mediates functional adhesion with a biological tissue. This technology may enable a number of key applications in medicine including tissue repair, wound dressing and drug delivery.

- Encapsulation of Water-Insoluble Drugs in Polymer Capsules Prepared Using Mesoporous Silica Templates for Intracellular Drug Delivery
  Wang, Y.; Yan, Y.; Cui, J.; Hosta-Rigau, L.; Heath, J. K.; Nice, E. C.; Caruso, F. *Adv. Mater.* **2010**, *22*, 4293–4297.
  Abstract:



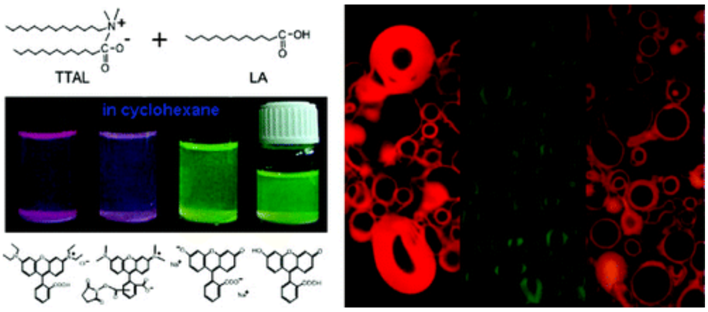
Water-insoluble compounds were encapsulated in polymer capsules through mesoporous silica nanoparticle-mediated layer-by-layer assembly. The drug-loaded capsules exhibit excellent colloidal stability and high potency to colorectal cancer cells *in vitro* with similar cytotoxicity to the free drug dissolved in organic solvent.

- Efficient Bioconjugation of Protein Capture Agents to Biosensor Surfaces Using Aniline-Catalyzed Hydrazone Ligation
  Byeon, J.-Y.; Limpoco, F. T.; Bailey, R. C. *Langmuir* **2010**, *26,* 15430–15435.
  Abstract:



Aniline-catalyzed hydrazone ligation between surface-immobilized hydrazines and aldehyde-modified antibodies is shown to be an efficient method for attaching protein capture agents to model oxide-coated biosensor substrates. Silicon photonic microring resonators are used to directly evaluate the efficiency of this surface bioconjugate reaction at various pHs and in the presence or absence of aniline as a nucleophilic catalyst. It is found that aniline significantly increases the net antibody loading for surfaces functionalized over a pH range from 4.5 to 7.4, allowing derivatization of substrates with reduced incubation time and sample consumption. This increase in antibody loading directly results in more sensitive antigen detection when functionalized microrings are employed in a label-free immunoassay. Furthermore, these experiments also reveal an interesting pH-dependent noncovalent binding trend that plays an important role in dictating the amount of antibody attached onto the substrate, highlighting the competing contributions of the bioconjugate reaction rate and the dynamic interactions that control opportunities for a solution-phase biomolecule to react with a substrate-bound reagent.

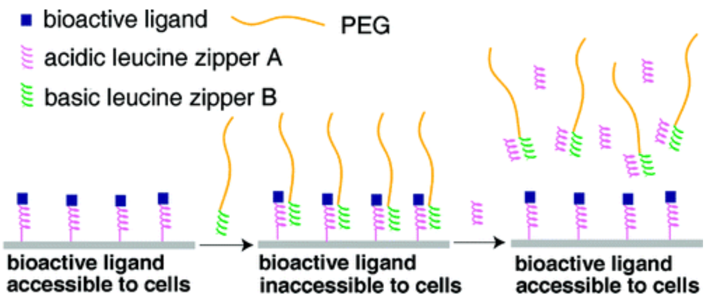
- Reverse Vesicles from a Salt-Free Catanionic Surfactant System: A Confocal Fluorescence Microscopy Study
  Li, H.; Xin, X.; Kalwarczyk, T.; Kalwarczyk, E.; Niton, P.; Hołyst, R.; Hao, J. *Langmuir* **2010**, *26*, 15210-15218.
  <u>Abstract:</u>



We give a detailed confocal fluorescence microscopy study on reverse vesicles from a salt-free catanionic surfactant system. When tetradecyltrimethylammonium laurate (TTAL) and lauric acid (LA) are mixed in cyclohexane at the presence of a small amount of water, stable reverse vesicular phases form spontaneously. The reverse vesicular phases can be easily labeled with dyes of varying molecular size and hydrophobicity while the dyes are nearly insoluble in cyclohexane without reverse vesicles. This indicates the reverse vesicular phases can be good candidates to host guest molecules. With the help of a fluorescence microscope combined a confocal method, the features of these interesting reverse supramolecular self-assemblies were revealed for the first time. Because of the absence of electrostatic repulsions and hydration forces between adjacent vesicles, the reverse vesicles have a strong propensity to aggregate with each other and form three-dimensional clusters.

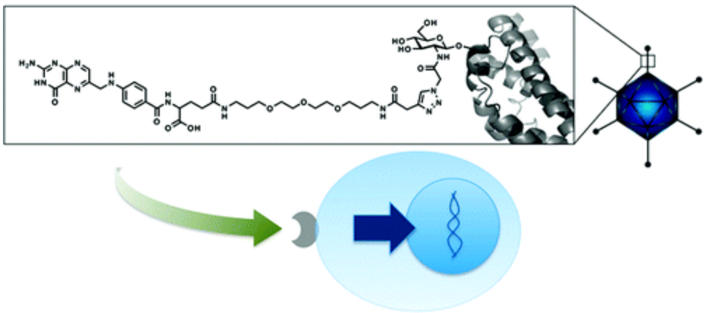
The size distributions of both individual reverse vesicles and clusters are polydisperse. Huge multilamellar reverse vesicles with closely stacked thick walls (giant reverse onions) were observed. Besides the spherical reverse vesicles and onions, other supramolecular structures such as tubes have also been detected and structural evolutions between different structures were noticed. These interesting supramolecular self-assemblies form in a nonpolar organic solvent may serve as ideal micro- or nanoreaction centers for biological reactions and synthesis of inorganic nanomaterials.

- Dynamic Presentation of Immobilized Ligands Regulated through Biomolecular Recognition
  Liu, B.; Liu, Y.; Riesberg, J. J.; Shen, W. *J. Am. Chem. Soc.* **2010**, *132*, 13630–13632.
  <u>Abstract:</u>



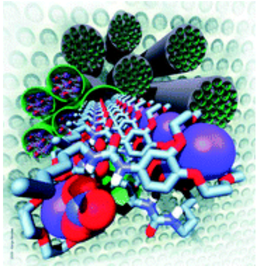
To mimic the dynamic regulation of signaling ligands immobilized on extracellular matrices or on the surfaces of neighboring cells for guidance of cell behavior and fate selection, we have harnessed biomolecular recognition in combination with polymer engineering to create dynamic surfaces on which the accessibility of immobilized ligands to cell surface receptors can be reversibly interconverted under physiological conditions. The cell-adhesive RGD peptide is chosen as a model ligand. RGD is fused to the C-terminus of a leucine zipper domain A, and this fusion polypeptide is immobilized on surfaces through a residue at the N-terminus. The immobilized RGD can be converted from a cell-accessible to a cell-inaccessible state by addition of a conjugate of poly(ethylene) glycol (PEG) and another leucine zipper domain B (B-PEG). Heterodimerization between A and B allows coimmobilization of the PEG, which shields RGD from access by cells. The shielded RGD can be converted back to a cell-accessible state by addition of nonimmobilized polypeptide A, which competes with the immobilized A for binding to B-PEG and removes B-PEG from the surface. This molecular design offers several advantages: the interconversion is reversible; the ligand remains immobilized during dynamic regulation so that cells are not exposed to the soluble form of the ligand that potentially has detrimental effects; the precision of the on/off states is assured by the molecular-level uniformity of the ligand and PEG coimmobilized through leucine zipper heterodimerization. The method can be readily adapted for dynamic regulation of other immobilized bioactive ligands of interest.

- Chemoselective Attachment of Small Molecule Effector Functionality to Human Adenoviruses Facilitates Gene Delivery to Cancer Cells
  Banerjee, P. S.; Ostapchuk, P.; Hearing, P.; Carrico, I. *J. Am. Chem. Soc.* **2010**, *132*, 13615–13617.
  <u>Abstract:</u>



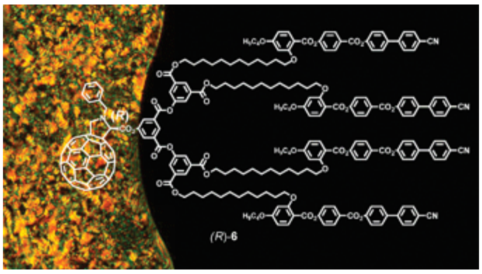
We demonstrate here a novel two-step “click” labeling process in which adenoviral particles are first metabolically labeled during production with unnatural azido sugars. Subsequent chemoselective modification allows access to viruses decorated with a broad array of effector functionality. Adenoviruses modified with folate, a known cancer-targeting motif, demonstrated a marked increase in gene delivery to a murine cancer cell line.

- Dynamic interactive systems: dynamic selection in hybrid organic–inorganic constitutional networks
  Barboiu, M. *Chem. Commun.* **2010**, *46*, 7466-7476.
  Abstract:



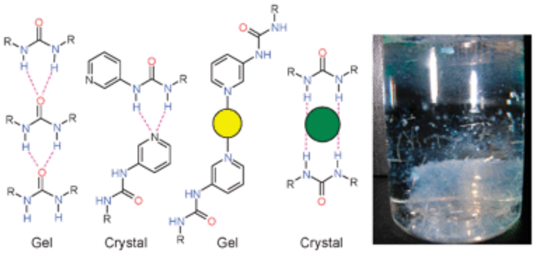
Dynamic interactive systems are defined by networks of exchanging and reversibly connected objects (supermolecules, polymers, biomolecules, biopolymers, pores, nanoplatforms, surfaces, liposomes, cells). They operate under natural selection to allow spatial/temporal and structural/functional adaptability in response to internal constitutional or to external stimulant factors. Herein we will discuss some selected examples of hybrid organic/inorganic *systems materials* (SYSMAT), covering (a) the sol–gel resolution of constitutional architectures from dynamic combinatorial libraries and (b) the generation of dynamic hybrid materials and *systems membranes* (SYSMEM) able to evolve inside pore functional architectures *via* ionic stimuli, so as to improve membrane transport functions.

- Optically active liquid-crystalline fullerodendrimers from enantiomerically pure fulleropyrrolidines
  Lincker, F.; Bourgun, P.; Stoeckli-Evans, H.; Saez, I. M.; Goodby, J. W.; Deschenaux, R. *Chem. Commun.* **2010**, *46*, 7522-7524.
  Abstract:



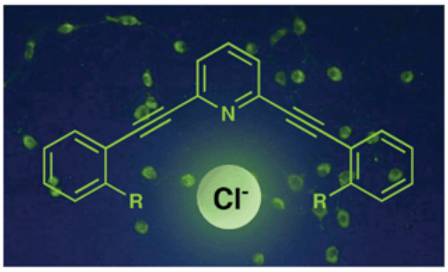
A synthetic methodology based on the 1,3-dipolar cycloaddition reaction was developed to design enantiomerically pure liquid-crystalline fullerodendrimers.

- Anion-tuned supramolecular gels: a natural evolution from urea supramolecular chemistry
  Steed, J. W. *Chem. Soc. Rev.* **2010**, *39*, 3686-3699.
  Abstract:



This *tutorial review* looks at the formation of low molecular weight gels from molecular principles using the well-explored supramolecular chemistry of ureas as an example. Synthesising lessons learned from classical urea inclusion chemistry, ureas in crystal engineering, ureas in self-assembly, urea functional groups in anion binding and sensing, and ureas as organocatalysts lead to the development and understanding of a new class of anion-tunable, urea-based soft materials. This review concludes with a look at emerging application areas for tunable gel-phase materials as controlled crystal growth media, both in templating metallic nanoparticles and in the growth and isolation of high quality crystals of molecular organic compounds, including polymorphic pharmaceuticals.

- Arylethynyl receptors for neutral molecules and anions: emerging applications in cellular imaging
  Carroll, C. N.; Naleway, J. J.; Haley, M. M.; Johnson, D. W. *Chem. Soc. Rev.* **2010**, *39*, 3875-3888.
  Abstract:

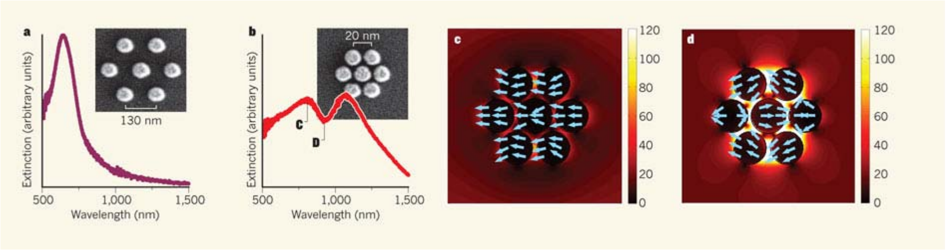


This *critical review* will focus on the application of shape-persistent receptors for anions that derive their rigidity and optoelectronic properties from the inclusion of arylethynyl linkages. It will highlight a few of the design strategies involved in engineering selective and sensitive fluorescent probes and how arylacetylenes can offer a design pathway to some of the more desirable properties of a selective sensor. Additionally, knowledge gained in the study of these receptors in organic media often leads to improved receptor design and the production of chromogenic and fluorogenic probes capable of detecting specific substrates among the multitude of ions present in biological systems. In this ocean of potential targets exists a large number of geometrically distinct anions, which present their own problems to the design of receptors with complementary binding for each preferred coordination geometry. Our interest in targeting charged substrates, specifically how previous work on receptors for cations or neutral guests can be adapted to anions, will be addressed. Additionally, we will focus on the design and development of supramolecular arylethynyl systems, their shape-persistence and fluorogenic or chromogenic optoelectronic responses to complexation. We will also examine briefly how the “chemistry in the cuvet” translates into biological media (125 references).

- 'Green' reversible addition-fragmentation chain-transfer (RAFT) polymerization
  Semsarilar, M.; Perrier, S. *Nature Chemistry* **2010**, *2*, 811–820.
  Abstract:

Reversible addition-fragmentation chain-transfer (RAFT) polymerization has revolutionized the field of polymer synthesis as a versatile tool for the production of complex polymeric architectures. As for all chemical processes, research and development in RAFT have to focus on the design and application of chemical products and processes that have a minimum environmental impact, and follow the principles of 'green' chemistry. In this Review, we summarize some of the green features of the RAFT process, and review the recent advances in the production of degradable polymers obtained from RAFT polymerization. Its use to modify biodegradable and renewable inorganic and organic materials to yield more functional products with enhanced applications is also covered. RAFT is a promising candidate for answering both the increasing need of modern society to employ highly functional polymeric materials and the global requirements for developing sustainable chemicals and processes.

- Nanoscience: Dark-hot resonances
  Stockman, M. I. *Nature* **2010**, *467*, 541-542.
  Abstract:

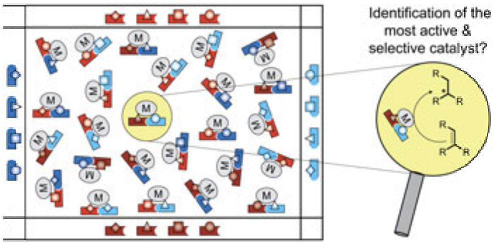


The resonant behaviour of clusters of gold nanoparticles has been tuned by gradually bringing the particles together. The approach could have many applications, including chemical and biological sensing.

Resonances are ubiquitous natural phenomena that occur on all spatial scales — from the largest distances in the Universe to the tiniest dimensions of elementary particles. They have great significance in both fundamental science and practical applications.

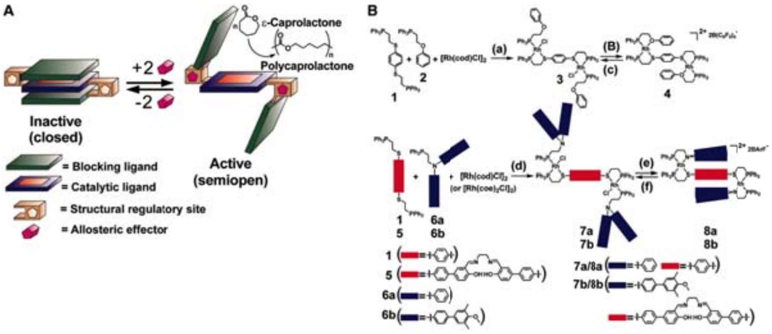
The authors studied the optical response of clusters comprising seven gold nanoparticles and found that, for interparticle separations of less than 60 nanometres, the pronounced spectral dip of a plasmonic Fano resonance emerges. **a**, **b**, Absorption spectra for interparticle separation of 130 nm (**a**) and 20 nm (**b**); insets display images of the clusters taken with a scanning electron microscope. The Fano dip is marked in **b** with a D. **c**, **d**, Simulated local optical fields and corresponding electrical currents (blue arrows) at the spectral wavelengths marked C and D in **b**. The vertical bars indicate the colour scale for the magnitude of the optical field (relative to the field to which the clusters are subjected). The optical field at the Fano dip's wavelength is characterized by bright 'hot spots' — compare **d** with **c**, in which such an effect is absent.

- A combinatorial approach to the identification of self-assembled ligands for rhodium-catalysed asymmetric hydrogenation
  Wieland, J.; Breit, B. *Nature Chemistry* **2010**, *2*, 832–837.
  Abstract:



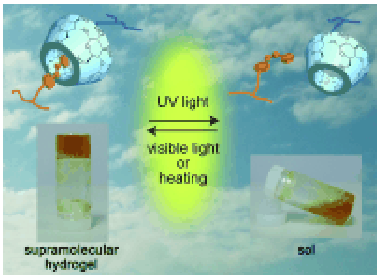
An effective and efficient means to catalyst discovery is the high-throughput screening of catalyst libraries. However, the current status of this approach suffers from a number of limitations, namely access to structurally diverse and meaningful ligand libraries and the enormous effort required for massive parallel screening of the resulting catalysts. We report an integrated solution to these drawbacks, which combines a diversity-oriented ligand synthesis, a catalyst-generation process driven by self-assembly and, finally, a combinatorial iterative library deconvolution strategy to identify the optimal catalyst. As a test case, rhodium-catalysed asymmetric hydrogenation was studied and, from a library of 120 self-assembling catalysts, highly enantioselective catalysts for the asymmetric hydrogenation of different olefinic substrates were identified within 17 experiments. Comparison of the results of the iterative library deconvolution strategy with those of the classic parallel-screening process confirmed the validity of this approach.

- Allosteric Supramolecular Triple-Layer Catalysts
  Yoon, H. J.; Kuwabara, J.; Kim, J.-H.; Mirkin, C. A. *Science* **2010**, *330*, 66 – 69.
  Abstract:



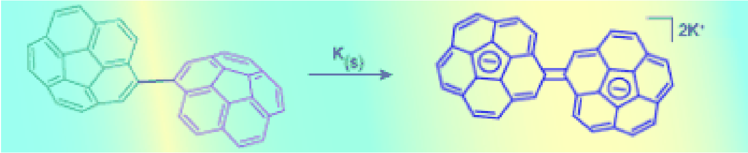
Allosteric regulation of organometallic catalysts could allow for greater control over reactions. We report an allosteric supramolecular structure in which a monometallic catalytic site has been buried in the middle layer of a triple-layer complex. Small molecules and elemental anions can open and close this complex and reversibly expose and conceal the catalytic center. The ring-opening polymerization of ε-caprolactone can be turned on by the in situ opening of the triple-layer complex and then completely turned off by reforming it through the abstraction of Cl^-, the allosteric effector agent, without appreciable loss of catalytic activity. This process can regulate the molecular weights of the resulting polymers.

- Photoswitchable Supramolecular Hydrogels Formed by Cyclodextrins and Azobenzene Polymers
  Tamesue, S.; Takashima, Y.; Yamaguchi, H.; Shinkai, S.; Harada, A. *Angew. Chem. Int. Ed.* **2010**, *49,* 7461–7464.
  Abstract:



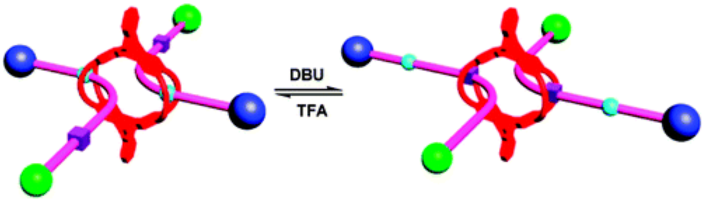
Shine a light: A supramolecular hydrogel is formed by the glucan curdlan equipped with α-cyclodextrins (CD-CUR) and azobenzene-modified poly(acrylic acid)(pAC12Azo). The sol–gel transition and the morphology of the supramolecular hydrogel can be switched by photoirradiation at the appropriate wavelength, which controls the formation of an inclusion complex between the α-cyclodextrins and the azobenzene moieties (see picture).

- The Bicorannulenyl Dianion: A Charged Overcrowded Ethylene
  Eisenberg, D.; Jackson, E. A.; Quimby, J. M.; Scott, L. T.; Shenhar, R. *Angew. Chem. Int. Ed.* **2010**, *49*, 7538–7542.
  Abstract:



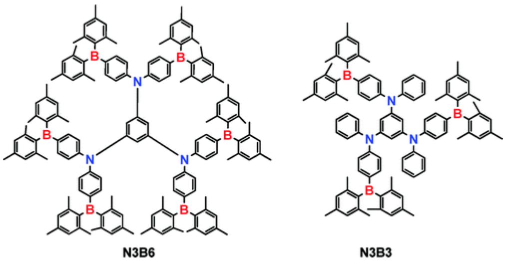
Super bowl: Bicorannulenyl, a large biaryl composed of two corannulene bowls, effectively becomes an overcrowded ethylene upon reduction to form a dianion (see picture). DFT calculations and NMR spectroscopic experiments reveal the double-bond character of the connection between the two bowls. Three stable diastereomers that interconvert through bowl inversions and central bond rotations were shown to exist.

- A New [3]Rotaxane Molecular Machine Based on a Dibenzylammonium Ion and a Triazolium Station
  Jiang, Y.; Guo, J.-B.; Chen, C.-F. *Org. Lett.* **2010**, *12*, 4248–4251.
  Abstract:



A novel two-station [3]rotaxane molecular machine based on triptycene-derived macrotricyclic host was conveniently synthesized by the click reaction and methylation of the subsequent 1,2,3-tiazole group. The shuttle process of the [3]rotaxane molecular machine can be reversibly achieved by acid−base control.

- Phenylene Bridged Boron−Nitrogen Containing
  Proń, A.; Baumgarten, M.; Müllen, K. *Org. Lett.* **2010**, *12*, 4236–4239.
  Abstract:



The synthesis and characterization of novel phenylene bridged boron−nitrogen containing π-conjugated dendrimers **N3B6** and **N3B3**, with peripheral boron atoms and 1,3,5-triaminobenzene moiety as a core, are presented. UV−vis absorption and emission measurements reveal that the optical properties of the resulting compounds can be controlled by changing the donor/acceptor ratio: a 1:1 ratio results in a more efficient charge transfer than the 1:2 ratio. This was proven by the red shift of the emission maxima and the stronger solvatochromic effect in **N3B3** compared to **N3B6**.