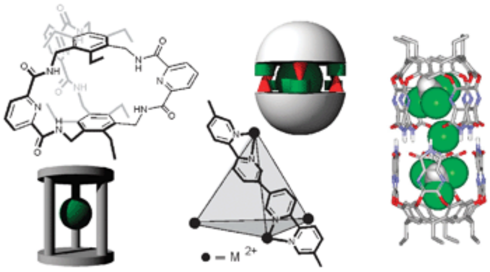
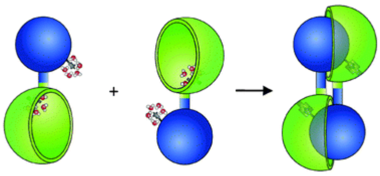
- Anion binding in covalent and self-assembled molecular capsules
  Ballester, P. *Chem. Soc. Rev.* **2010**, *39*, 3810-3830.
  Abstract:



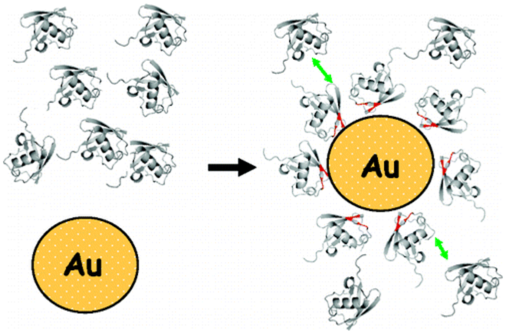
This *critical review* describes selected examples extracted from the extensive literature generated during the past 42 years on the topic of anion binding in molecular capsules. The goal of including anions in molecular capsules emerges from the idea of incorporating the traits exhibited by biological receptors into synthetic ones. At the outset of this research area the capsules were unimolecular. The scaffold of the receptor was designed to covalently link a series of functional groups that could converge into a cavity and to avoid its collapse. The initial examples involved the encapsulation of one monoatomic spherical anion. With time, the cavity size of the receptor was increased and encapsulation of polyatomic anions and co-encapsulation became a reality. Synthetic economy fueled the use of aggregates of self-complementary molecules rather than one large molecule as capsules. The main purpose of this review is to give a general overview of the topic which might be of interest to supramolecular or non supramolecular chemists alike (149 references).

- Ion-pair induced self-assembly in aqueous solvents
  Rehm, T. H.; Schmuck, C. *Chem. Soc. Rev.* **2010**, *39*, 3597-3611.
  Abstract:



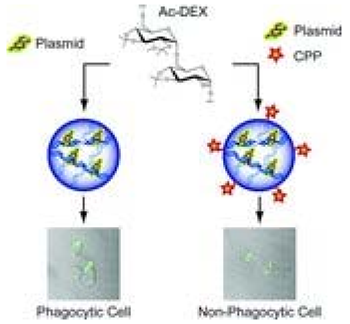
The intriguing advantages of supramolecular chemistry and particularly the application of self-assembly for the construction of defined nanostructures from small, preferably synthetically easily accessible molecules has become a promising area of modern chemistry in the last years. However, the main focus of early work was based on H-bond induced self-assembly which is limited to nonpolar organic solvents. In the past years the field started to shift more and more towards obtaining self-assembling architectures in polar solvents and even water. This *tutorial review* will discuss some representative examples for self-assembling systems in polar solvents in order to illustrate the different concepts and strategies that can be used. We will also briefly discuss the special properties of water as the ultimate protic solvent from the perspective of a supramolecular chemist to elucidate the challenges that this solvent still poses even today to obtain specific self-assembled nanostructures.

- Protein−Nanoparticle Interaction: Identification of the Ubiquitin−Gold Nanoparticle Interaction Site
  Calzolai, L.; Franchini, F.; Gilliland, D.; Rossi, F. *Nano Lett.* **2010**, *10*, 3101–3105.
  Abstract:



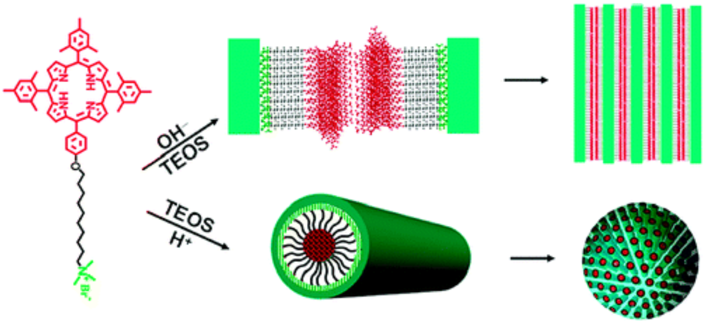
We demonstrate that it is possible to identify the protein−nanoparticle interaction site at amino acid scale in solution. Using NMR, chemical shift perturbation analysis, and dynamic light scattering we have identified a specific domain of human ubiquitin that interacts with gold nanoparticles. This method allows a detailed structural analysis of proteins absorbed onto surfaces of nanoparticles in physiological conditions and it will provide much needed experimental data for better modeling and prediction of protein−nanoparticle interactions.

- Acetal-Modified Dextran Microparticles with Controlled Degradation Kinetics and Surface Functionality for Gene Delivery in Phagocytic and Non-Phagocytic Cells
  Cohen, J. A.; Beaudette, T. T.; Cohen, J. L.; Broaders, K. E.; Bachelder, E. M.; Fréchet, J. M. J. *Adv. Mater.* **2010**, *22*, 3593-3597.
  Abstract:



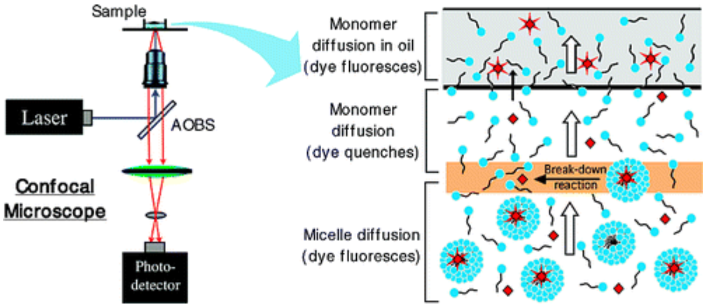
A microparticulate gene delivery system based on biodegradable and acid-sensitive acetal-modified dextran with unprecedented tunability of degradation rates and simplicity of surface functionalization is presented. When optimally formulated with small amounts of cationic polymers, these microparticles are capable of efficiently transfecting both phagocytic and non-phagocytic cells with minimal toxicity.

- Hierarchical Self-Assembly of Superlattice Hybrids Consisting of Periodic and Alternating Cores of Porphyrin Molecules Separated by Nanoscale Silica Walls
  Li, L.-L.; Fu, X.-F.; Ren, Z.; Zhao, Y.-G.; Feng, W.; Yan, C.-H. *Langmuir* **2010**, *26,* 15730–15733.
  Abstract:



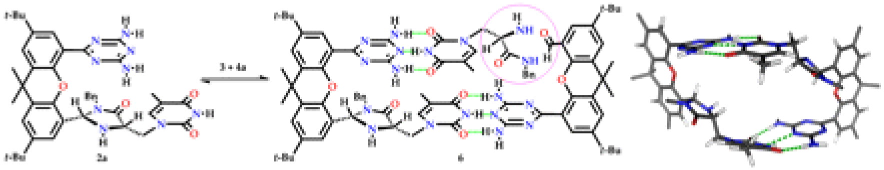
Molecularly engineered superlattice hybrids consisting of periodic and alternating cores of porphyrin molecules separated by nanoscale silica walls were synthesized through a one-step organic−inorganic hierarchical self-assembly approach. The self-assembly process not only could lock both porphyrin and inorganic building blocks into ordered 3D nanostructure but also could allow for the molecular-level controllable organization of porphyrin molecules in the central regions of the silica pore channels, which leads to the formation of porphyrin core−silica wall superlattice hybrids with molecular-scale and mesoscale ordering. It was demonstrated that both the mesostructure and morphology of the hybrids can be finely tailored by turning the cooperative self-assembly process. It is significant that the hybrids show self-assembled optical properties consistent with the orientational arrangement of the porphyrins within periodic nanoscale silica channels. The methodology introduced herein demonstrates high versatility with respect to the self-assembly of optical active macrocycles into highly ordered superlattice hybrid architectures.

- Fluorescence Visualization and Modeling of a Micelle-Free Zone Formed at the Interface between an Oil and an Aqueous Micellar Phase during Interfacial Surfactant Transport
  Bhole, N. S; Huang, F.; Maldarelli, C. *Langmuir* **2010**, *26*, 15761-15778.
  Abstract:



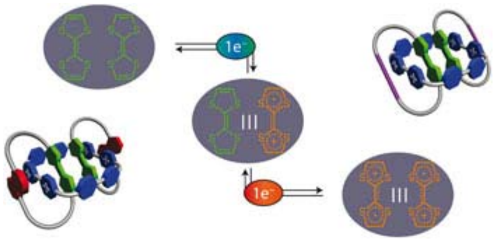
This study examines the transport of surfactant that occurs when an aqueous micellar phase is placed in contact with a clean oil phase in which the surfactant is soluble. Upon contact with oil, surfactant monomer on the aqueous side of the interface adsorbs onto the oil/water interface and subsequently desorbs into the oil and diffuses away from the surface. The depletion of aqueous monomer underneath the interface disturbs the monomer−micelle equilibrium, and aggregates break down to replenish the monomer concentration and accelerate the interfacial transport. The depletion of monomer and micelles drives the diffusive flux of these species toward the surface, and the combined effects of diffusion and aggregate kinetic disassembly, alongside kinetic adsorption and desorption at the interface and diffusion away from the interface into the oil, determine the interfacial transport rate. This interfacial transport is examined here in the quasi-static limit in which the diffusion of monomer and micelles in the aqueous phase is much slower than the time scale for micelle disassembly. In this limit, when the initial bulk concentration of micelles in the aqueous solution is small, the micelle diffusive flux to the surface cannot keep up with the micelle breakdown under the interface, and a micelle-free zone forms. This zone extends from the surface into the aqueous phase up to a boundary that demarcates the beginning of a zone, containing micelles, that extends further into the aqueous phase. Micelles diffuse from the micelle zone to the boundary, where they break down, causing the boundary to retreat. Released monomer diffuses through the micelle-free zone and partitions into the oil phase. The focus of this study is to verify this transport picture by visualizing the micelle-free zone and comparing the movement of the zone to predictions obtained from a transport model based on this two-zone picture. A small hydrophobic dye molecule (Nile red) is incorporated into the micelles; the dye fluoresces only in the hydrophobic environment of the micelles, providing visual contrast between the two zones. Through spatial mapping of the fluorescence using confocal microscopy, the movement of the micelle-free zone boundary can be measured and is shown to compare favorably with simulations of the transport model.

- Autocatalysis and organocatalysis with synthetic structures
  Kamioka, S.; Ajami, D.; Rebek, Jr, J. *Proc. Nat. Acad. Sci.* **2010**, *107*, 541-544.
  Abstract:



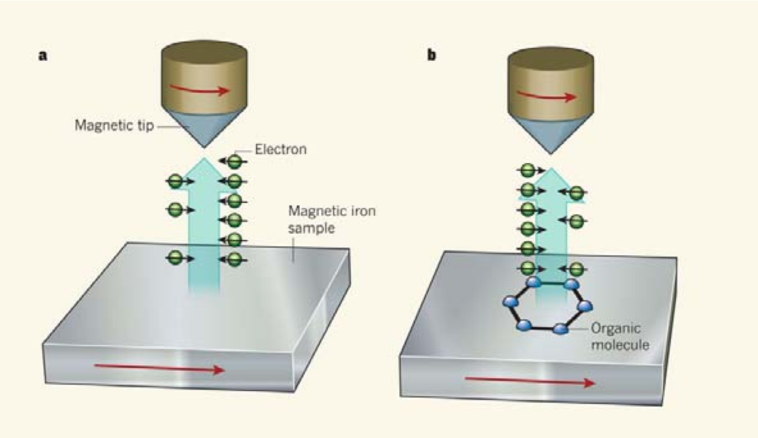
The discovery of ribozymes led to the proposal of an RNA world, where a single type of molecule was supposedly capable of self-replication and chemical catalysis. We show here that both autocatalysis and organocatalysis can be engineered into a synthetic structure. The compound is shown to selectively accelerate its own formation and catalyze either hydrogenation or nucleophilic addition to α,β-unsaturated aldehydes. The observed reactivity indicates that the components of a purported pre-RNA world conceivably include smaller organic molecules.

- Highly stable tetrathiafulvalene radical dimers in [3]catenanes
  Spruell, J. M.; Coskun, A.; Friedman, D. C.; Forgan, R. S.; Sarjeant, A. A.; Trabolsi, A.; Fahrenbach, A. C.; Barin, G.; Paxton, W. F.; Dey, S. K.; Olson, M. A.; Benítez, D.; Tkatchouk, E.; Colvin, M. T.; Carmielli, R.; Caldwell, S. T.; Rosair, G. M.; Hewage, S. G.; Duclairoir, F.; Seymour, J. L.; Slawin, A. M. Z.; Goddard III, W. A.; Wasielewski, M. R.; Cooke, G.; Stoddart, J. F. *Nature Chemistry* **2010**, *2*, 870–879.
  Abstract:



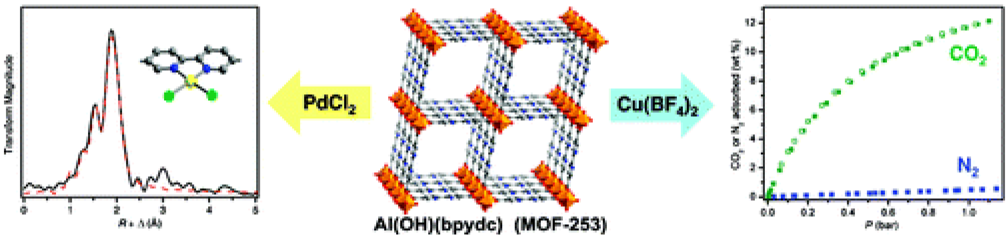
Two [3]catenane 'molecular flasks' have been designed to create stabilized, redox-controlled tetrathiafulvalene (TTF) dimers, enabling their spectrophotometric and structural properties to be probed in detail. The mechanically interlocked framework of the [3]catenanes creates the ideal arrangement and ultrahigh local concentration for the encircled TTF units to form stable dimers associated with their discrete oxidation states. These dimerization events represent an affinity *umpolung*, wherein the inversion in electronic affinity replaces the traditional TTF-bipyridinium interaction, which is over-ridden by stabilizing mixed-valence $(TTF)_2^{\bullet+}$ and radical-cation $(TTF^{\bullet+})_2$ states inside the 'molecular flasks.' The experimental data, collected in the solid state as well as in solution under ambient conditions, together with supporting quantum mechanical calculations, are consistent with the formation of stabilized paramagnetic mixed-valence dimers, and then diamagnetic radical-cation dimers following subsequent one-electron oxidations of the [3]catenanes.

- Surface science: Seeing the spin through
  Sanvito, S. *Nature* **2010**, *467*, 664-665.
  <u>Abstract:</u>



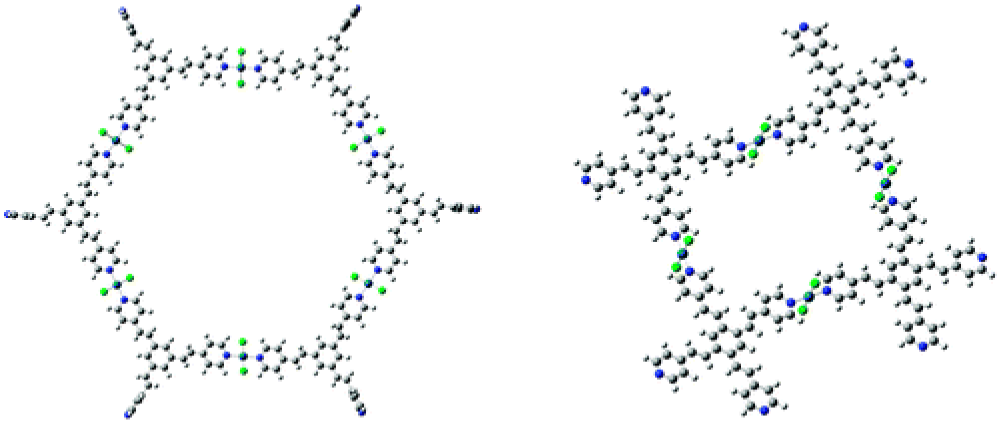
Interfaces can have quite different properties from those of their constituent materials. But it's surprising that the adsorption of a single organic molecule onto a magnetic surface can drastically modify that surface's magnetism.
Traditionally, magnetism and organic chemistry have not shared the same laboratory. In recent years, however, the two disciplines have become closer to each other as interest has blossomed in studying organic molecules as a transport medium for electronic spins.

- Metal Insertion in a Microporous Metal–Organic Framework Lined with 2,2′-Bipyridine
  Bloch, E. D.; Britt, D.; Lee, C.; Doonan, C. J.; Uribe-Romo, F. J.; Furukawa, H.; Long, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2010**, *132*, 14382–14384.
  <u>Abstract:</u>



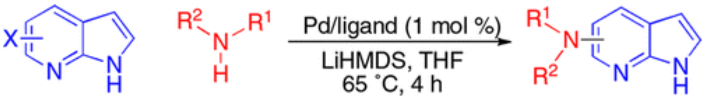
Reaction of AlCl3·6H2O with 2,2′-bipyridine-5,5′-dicarboxylic acid (H2bpydc) affords Al(OH)(bpydc) (1, MOF-253), the first metal–organic framework with open 2,2′-bipyridine (bpy) coordination sites. The material displays a BET surface area of 2160 m2/g and readily complexes metals to afford, for example, 1·xPdCl2 (x = 0.08, 0.83) and 1·0.97Cu(BF4)2. EXAFS spectroscopy performed on 1·0.83PdCl2 reveals the expected square planar coordination geometry, matching the structure of the model complex (bpy)PdCl2. Significantly, the selectivity factor for binding CO2 over N2 under typical flue gas conditions is observed to increase from 2.8 in 1 to 12 in 1·0.97Cu(BF4)2.

- Stepwise Assembly of Coordination-Based Metal–Organic Networks
  Kaminker, R.; Motiei, L.; Gulino, A.; Fragalà, I.; Shimon, L. J. W.; Evmenenko, G.; Dutta, P.; Iron, M. A.; van der Boom, M. E. *J. Am. Chem. Soc.* **2010**, *132*, 14554–14561.
  Abstract:



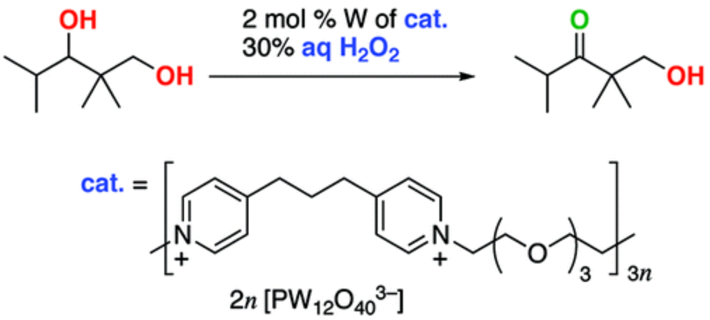
Metal–organic networks (MONs) were created by a stepwise solution deposition approach from vinylpyridine-based building blocks and PdCl2. The combined experimental and computational study demonstrates the formation of saturated, structurally organized systems on solid supports. The rigid nature and geometry of the components are well-suited to form honeycomb and parallelogram structures, as predicted by a computational study. Detailed structural information of the new MONs was obtained by optical (UV/vis) spectroscopy, ellipsometry, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and synchrotron X-ray reflectivity (XRR). Notably, the XPS elemental composition indicates the formation of a palladium coordination-based network.

- Palladium-Catalyzed Amination of Unprotected Halo-7-azaindoles
  Henderson, J. L.; McDermott, S. M.; Buchwald, S. L. *Org. Lett.* **2010**, *12*, 4438-4441.
  Abstract:



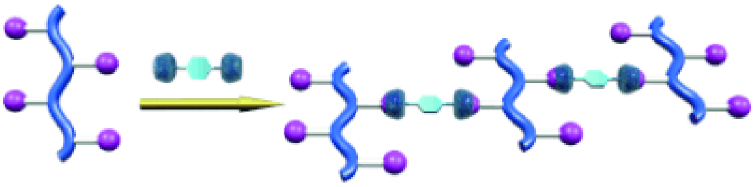
Simple and efficient procedures for the Pd-catalyzed cross-coupling of primary and secondary amines with halo-7-azaindoles(pyrrolo[2,3-*b*]pyridine) are presented. Previously, no general method was available to ensure the highly selective reaction of the heteroaryl halide in the presence of the unprotected azaindole *N*-H. Using palladium precatalysts recently reported by our group, such reactions are easily accomplished under mild conditions that can be applied to cross-coupling reactions with a wide array of aliphatic and aromatic amines.

- H_2O_2-Oxidation of Alcohols Promoted by Polymeric Phosphotungstate Catalysts
  Yamada, Y. M. A.; Keun Jin, C.; Uozumi, Y. *Org. Lett.* **2010**, *12*, 4540-4543.
  Abstract:



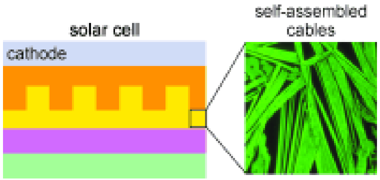
A novel polymeric phosphotungstate catalyst bearing a poly(ethylene oxide-pyridinium) matrix was developed that efficiently promoted oxidation of a variety of alcohols, including highly sterically demanding neopentyl alcohols, with hydrogen peroxide, to afford the corresponding carbonyl compounds in up to quantitative yield. The chemoselective oxidation of sterically hindered secondary alcohols in the presence of primary alcohols was achieved. The catalyst could be reused four times without any loss of catalytic activity.

- Supramolecular Cross-Linking of [60]Fullerene-Tagged Polyphenylacetylene by the Host–Guest Interaction of Calix[5]arene and [60]Fullerene
  Haino, T.; Hirai, E.; Fujiwara, Y.; Kashihara, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 7899–7903.
  <u>Abstract:</u>



Hand in hand: A polyphenylacetylene with C_{60} moieties can be cross-linked by a homoditopic tetrakiscalix[5]arene host by formation of a specific supramolecular complex (see picture). This noncovalent interaction leads to an increase of the molecular weight of the polymer and produces morphological changes upon addition of the host.

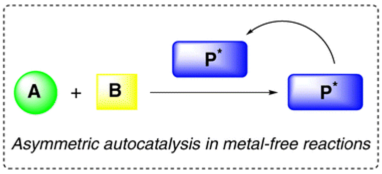
- Reticulated Heterojunctions for Photovoltaic Devices
  Gorodetsky, A. A.; Chiu, C. X.; Schiros, T.; Palma, M.; Cox, M.; Jia, Z.; Sattler, W.; Kymissis, I.; Steigerwald, M.; Nuckolls, C. *Angew. Chem. Int. Ed.* **2010**, *49*, 7909–7912.
  <u>Abstract:</u>



An organic semiconductor device is formed by the self-assembly on a transparent electrode surface. The donor (see picture; dibenzotetrathienocoronene, yellow layer) deposits as supramolecular cables, and the acceptor (C_{60}, orange) subsequently infiltrates this network. This network provides a donor–acceptor interface that is interwoven at the nanoscale. When incorporated into a solar cell, the active layer provides large increases in power conversion efficiencies.

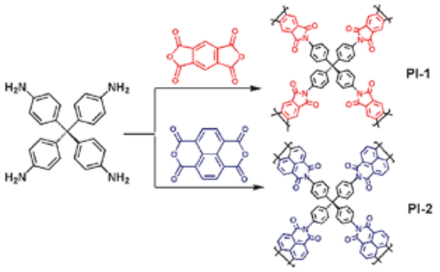
- When chiral product and catalyst are the same: discovery of asymmetric organoautocatalysis
  Tsogoeva, S. B. *Chem. Commun.* **2010**, *46*, 7662-7669.

Abstract:



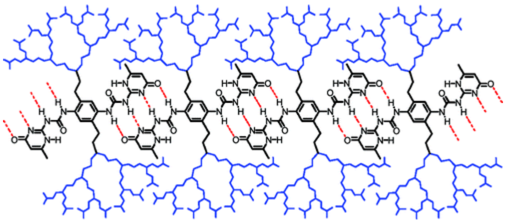
The process of asymmetric organoautocatalysis appears to be a natural extension to asymmetric organocatalysis, and holds implications for models on the origin of biological homochirality. The discovery of asymmetric organoautocatalysis (*i.e.* the process in which the chiral product of a purely organic reaction acts as an organocatalyst for its own formation under conservation of its absolute configuration) and more recent reports on related systems are discussed in this review.

- Microporous polyimide networks with large surface areas and their hydrogen storage properties
  Wang, Z.; Zhang, B.; Yu, H.; Sun, L.; Jiao, C.; Liu, W. *Chem. Commun.* **2010**, *46*, 7730-7732.
  Abstract:



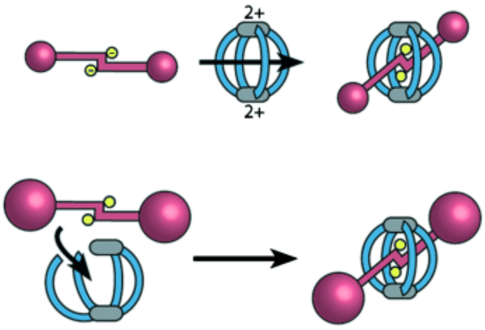
Microporous polyimide networks with BET surface areas up to 1407 m^2 g^{-1} and pore size distribution of 4–8 Å were synthesized. The respective effect of surface area and affinity between hydrogen molecule and polyimides on hydrogen storage properties were investigated.

- Synthesis and Self Assembling Properties of Rod-Like, 2-Ureido-4-pyrimidinone-Based Main Chain Supramolecular Dendronized Polymers
  Wong, C.-H.; Chan, W.-S.; Lo, C.-M.; Chow, H.-F.; Ngai, T.; Wong, K.-W. *Macromolecules* **2010**, *43*, 8389–8399.
  Abstract:



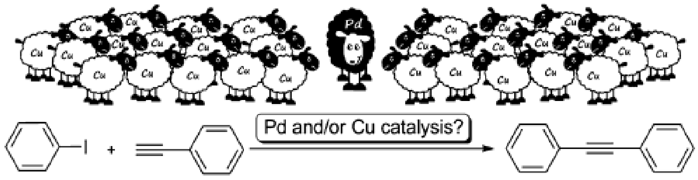
A series of G1−G3 supramolecular dendronized polymers **6** bearing dimeric 2-ureido-4-pyrimidinone (UPy) units on the main chain and aliphatic hydrocarbon dendrons as side chain appendages was prepared. Because of the high crystallinity and poor solubility of such rigid rod polymers, only the G3 dendron could confer the resulting polymer **6** (*n* = 3) with enough solubility to enable its characterization and property studies. It was found that the nature of the dendrons play an important role on the UPy binding strength, solubility and self-assembly properties. The reversible nature of the polymerization process was demonstrated in different solvent systems by viscosity studies. A double logarithmic plot of the specific viscosity against concentration revealed a deflection point at 26 mM in $CHCl_3$ at 26 and 40 °C. Below this critical concentration a straight line with a slope of 1.5 was obtained, while a slope of 4.0−4.2 was secured above this concentration. The data suggested that the associative interaction between the di-UPy monomer **5** (*n* = 3) increased nonlinearly with increasing monomer concentration. While the above investigations confirmed that these were main chain supramolecular dendronized polymers, UV−vis spectroscopic study revealed a large bathochromic shift (32 nm) with increasing polymer concentration in $CHCl_3$. This finding was consistent with the formation of J-type aggregates via stair-case stacking between interchain UPy rings. SEM morphological study also confirmed that the resulting polymers appeared as fibrous superbundles with a very high aspect ratio. A model was purposed to rationalize how such bundles could be assembled from the di-UPy dendritic macromonomer **5** via intrachain hydrogen bonding and interchain stacking interactions.

- A pH Switchable Pseudorotaxane Based on a Metal Cage and a Bis-anionic Thread
  Clever, G. H.; Shionoya, M. *Chem.-Eur. J.* **2010**, *16*, 11792-11796.
  Abstract:



Please let me in! A new kind of (pseudo)rotaxane is formed quantitatively when a bis-anionic thread is added to a molecular cage comprised of two positively charged metal complexes. The rotaxanation mechanism follows two alternative ways depending on the metal (Pd vs. Pt) and the stopper size of the guest (see figure).

- Dramatic Impact of ppb Levels of Palladium on the “Copper-Catalyzed” Sonogashira Coupling
  Gonda, Z.; Tolnai, G. L.; Novák, Z. *Chem.-Eur. J.* **2010**, *16*, 11822-11826.
  Abstract:



Palladacadabra! The effect of ppb levels of palladium on the “copper-catalyzed” Sonogashira coupling is reported. The observed high sensitivity to palladium impurities queries the existence of pure copper catalysis in the coupling of aryl iodides and terminal acetylenes (see figure).