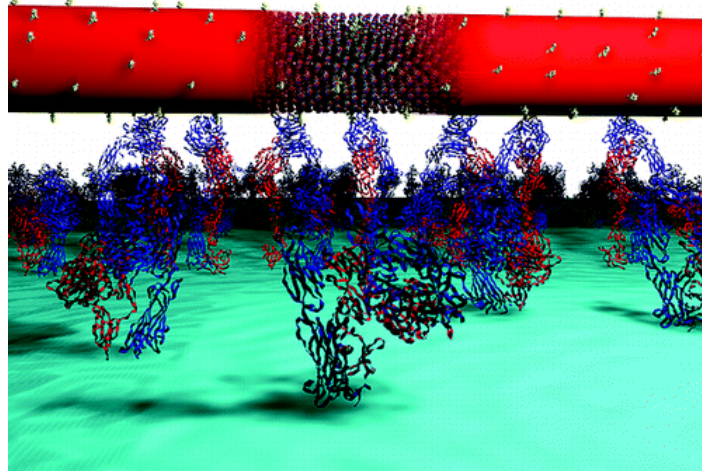
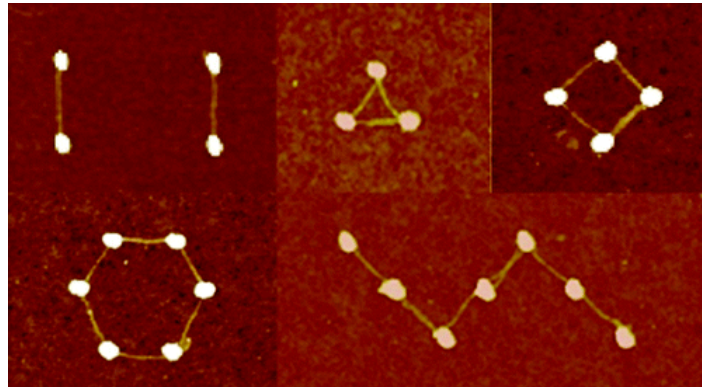


- Self-Assembly and Biomaterials  
Stupp, S. I. *Nano Lett.* **2010**, *10*, 4783–4786.  
Abstract:



An interesting field within the broad subject of biomaterials is the chemical and physical crafting of materials that can functionally substitute or help regenerate the organs and tissues of the human body. Regeneration is the new dimension of this field as opposed to the more established area of permanent implants and devices to substitute natural structures and functions. With the advent of nanoscience, the field is experiencing a renaissance by embracing the vision that artificial nanostructures of the self-assembling type could be designed for highly specific functions to promote regenerative processes.

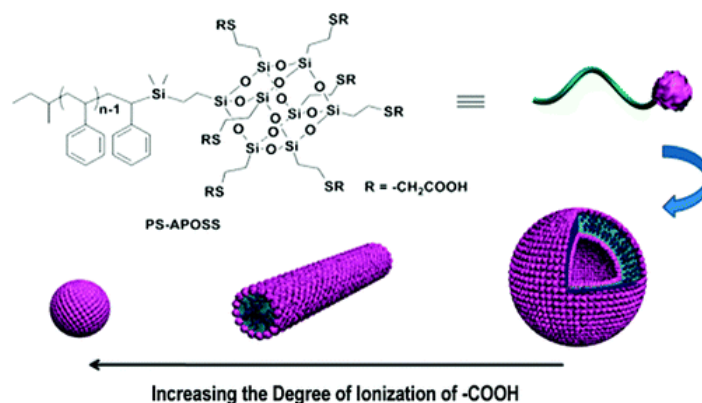
- Interconnecting Gold Islands with DNA Origami Nanotubes  
Ding, B.; Wu, H.; Xu, W.; Zhao, Z.; Liu, Y.; Yu, H.; Yan, H. *Nano Lett.* **2010**, *10*, 5065–5069.  
Abstract:



Scaffolded DNA origami has recently emerged as a versatile, programmable method to fold DNA into arbitrarily shaped nanostructures that are spatially addressable, with sub-10-nm resolution. Toward functional DNA nanotechnology, one of the key challenges is to integrate the bottom-up self-assembly of DNA origami with the top-down lithographic methods used to generate surface patterning. In this report we demonstrate that fixed length DNA origami nanotubes, modified with multiple thiol groups near both ends, can be used to connect surface patterned gold islands (tens of nanometers in diameter) fabricated by electron beam lithography (EBL). Atomic force microscopic imaging verified that the DNA origami nanotubes can be efficiently aligned between gold islands with various interisland distances and relative locations. This development represents progress toward the goal of bridging bottom-up and top-down assembly approaches.

- A Giant Surfactant of Polystyrene–(Carboxylic Acid-Functionalized Polyhedral Oligomeric Silsesquioxane) Amphiphile with Highly Stretched Polystyrene Tails in Micellar Assemblies  
Yu, X.; Zhong, S.; Li, X.; Tu, Y.; Yang, S.; Van Horn, R. M.; Ni, C.; Pochan, D. J.; Quirk, R. P.; Wesdemiotis, C.; Zhang, W. B.; Cheng, S. Z. D. *J. Am. Chem. Soc.* **2010**, *132*, 16741–16744.

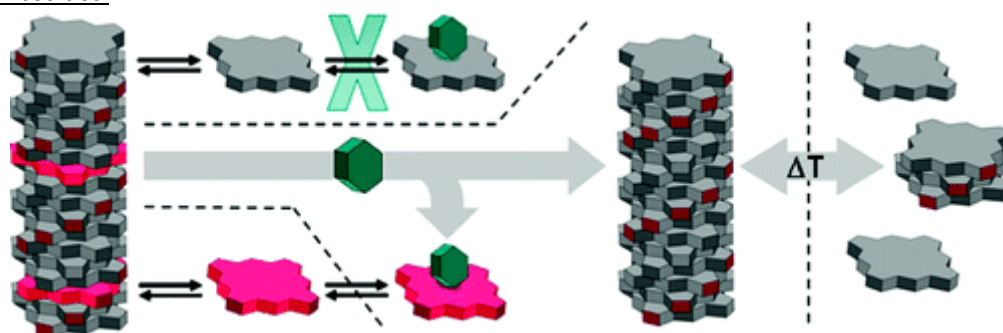
Abstract:



A novel giant surfactant possessing a well-defined hydrophilic head and a hydrophobic polymeric tail, polystyrene–(carboxylic acid-functionalized polyhedral oligomeric silsesquioxane) conjugate (PS–APOSS), has been designed and synthesized via living anionic polymerization, hydrosilylation, and thiol–ene “click” chemistry. PS–APOSS forms micelles in selective solvents, and the micellar morphology can be tuned from vesicles to wormlike cylinders and further to spheres by increasing the degree of ionization of the carboxylic acid. The effect of APOSS–APOSS interactions was proven to be essential in the morphological transformation of the micelles. The PS tails in these micellar cores were found to be highly stretched in comparison with those in traditional amphiphilic block copolymers, and this can be explained in terms of minimization of free energy. This novel class of giant surfactants expands the scope of macromolecular amphiphiles and provides a platform for the study of the basic physical principles of their self-assembly behavior.

- Chiral Memory via Chiral Amplification and Selective Depolymerization of Porphyrin Aggregates  
Helmich, F.; Lee, C. C.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2010**, *132*, 16753–16755.

Abstract:



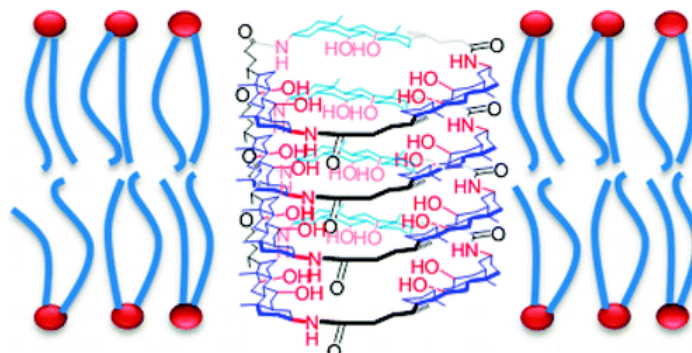
Chiral memory at the supramolecular level is obtained via a new approach using chiral Zn porphyrins and achiral Cu porphyrins. In a “sergeant-and-soldiers” experiment, the Zn “sergeant” transfers its own chirality to Cu “soldiers” and, after chiral amplification, the “sergeant” is removed from the coaggregates by axial ligation with a Lewis base. After this extraction, the preferred helicity observed

for the aggregates containing achiral Cu porphyrins reveals a chiral memory effect that is stable and can be erased and partially restored upon subsequent heating and cooling.

- Water-Templated Transmembrane Nanopores from Shape-Persistent Oligocholate Macrocycles

Cho, H.; Widanapathirana, H.; Zhao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 141–147.

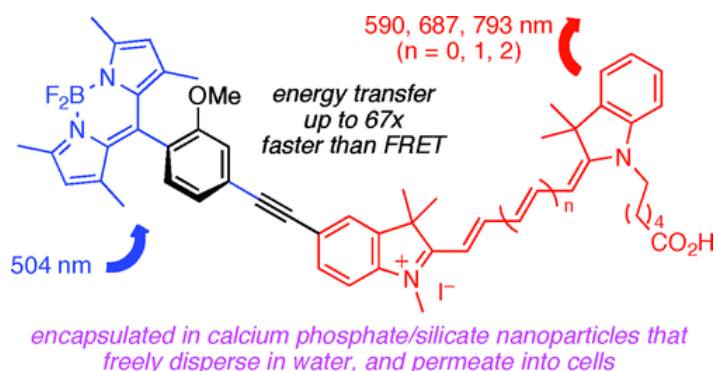
Abstract:



Hydrophobic interactions normally are not considered a major driving force for self-assembling in a hydrophobic environment. When macrocyclic oligocholates were placed within lipid membranes, however, the macrocycles pulled water molecules from the aqueous phase into their hydrophilic internal cavities. These water molecules had strong tendencies to aggregate in a hydrophobic environment and templated the macrocycles to self-assemble into transmembrane nanopores. This counterintuitive hydrophobic effect resulted in some highly unusual transport behavior. Cholesterol normally increases the hydrophobicity of lipid membranes and makes them less permeable to hydrophilic molecules. The permeability of glucose across the oligocholate-containing membranes, however, increased significantly upon the inclusion of cholesterol. Large hydrophilic molecules tend to have difficulty traversing a hydrophobic barrier. The cyclic cholate tetramer, however, was more effective at permeating maltotriose than glucose.

- Encapsulated Energy-Transfer Cassettes with Extremely Well Resolved Fluorescent Outputs
- Ueno, Y.; Jose, J.; Loudet, A.; Perez-Bolivar, C.; Anzenbacher Jr., P.; Burgess, K. *J. Am. Chem. Soc.* **2011**, *133*, 51–55.

Abstract:

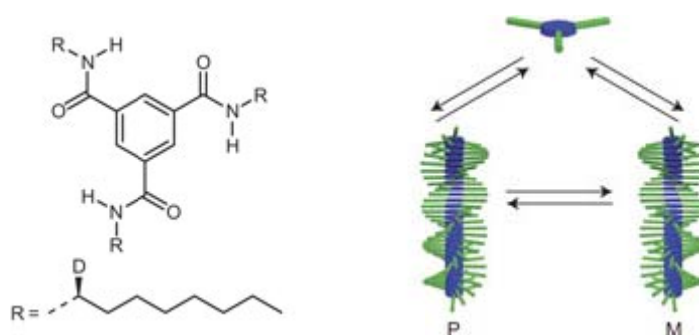


This paper concerns the development of water-compatible fluorescent imaging probes with tunable photonic properties that can be excited at a single wavelength. Bichromophoric cassettes 1a–1c consisting of a BODIPY donor and a cyanine acceptor were prepared using a simple synthetic route, and their photophysical properties were investigated. Upon excitation of the BODIPY moiety at 488

nm the excitation energy is transferred through an acetylene bridge to the cyanine dye acceptor, which emits light at approximately 600, 700, and 800 nm, i.e., with remarkable dispersions. This effect is facilitated by efficient energy transfer that gives a “quasi-Stokes” shift between 86 and 290 nm, opening a huge spectral window for imaging. The emissive properties of the cassettes depend on the energy-transfer (ET) mechanism: the faster the transfer, the more efficient it is. Measurements of rates of ET indicate that a through-bond ET takes place in the cassettes 1a and 1b that is 2 orders of magnitude faster than the classical through-space, Förster ET. In the case of cassette 1c, however, both mechanisms are possible, and the rate measurements do not allow us to discern between them. Thus, the cassettes 1a–1c are well suited for multiplexing experiments in biotechnological methods that involve a single laser excitation source. However, for widespread application of these probes, their solubility in aqueous media must be improved. Consequently, the probes were encapsulated in calcium phosphate/silicate nanoparticles (diameter ca. 22 nm) that are freely dispersible in water. This encapsulation process resulted in only minor changes in the photophysical properties of the cassettes. The system based on cassette 1a was chosen to probe how effectively these nanoparticles could be used to deliver the dyes into cells. Encapsulated cassette 1a permeated Clone 9 rat liver cells, where it localized in the mitochondria and fluoresced through the acceptor part, i.e., red. Overall, this paper reports readily accessible, cyanine-based through-bond ET cassettes that are lipophilic but can be encapsulated to form nanoparticles that disperse freely in water. These particles can be used to enter cells and to label organelles.

- The effect of isotopic substitution on the chirality of a self-assembled helix  
Cantekin, S.; Balkenende, D. W. R.; Smulders, M. M. J.; Palmans, A. R. A.; Meijer, E. W. *Nature Chem.* **2011**, *3*, 42–46.

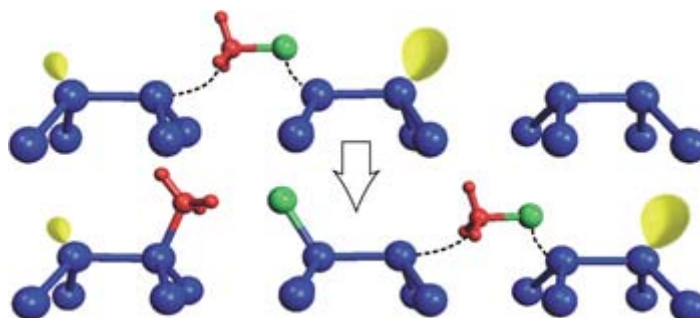
Abstract:



*N,N,N'*-trialkylbenzene-1,3,5-tricarboxamides (BTAs) self-assemble by means of strong, threefold  $\alpha$ -helix-type intermolecular hydrogen bonding into well-defined, helical, one-dimensional columnar aggregates. When a stereogenic centre is introduced into the alkyl side chains of these BTAs, strong Cotton effects are observed in dilute apolar solutions, indicating the preference for one helical conformation over the other. Here, we report the creation of a helical sense preference in self-assembled BTAs by introducing deuterium/hydrogen isotope chirality into the alkyl side chains. We determine the relative stabilities of the left- and right-handed helical conformations of these deuterated supramolecular polymers by performing a conformational analysis. Our findings show that the results of deuterium/hydrogen substitution in BTA-based supramolecular polymers and helical polyisocyanates are very similar, although the formation mechanisms differ. The selectively deuterated BTAs discussed here represent the first example of supramolecular chirality resulting from isotope substitution.

- Surface-mediated chain reaction through dissociative attachment  
Lim, T.; Polanyi, J. C.; Guo, H.; Ji, W. *Nature Chem.* **2011**, *3*, 85–89.

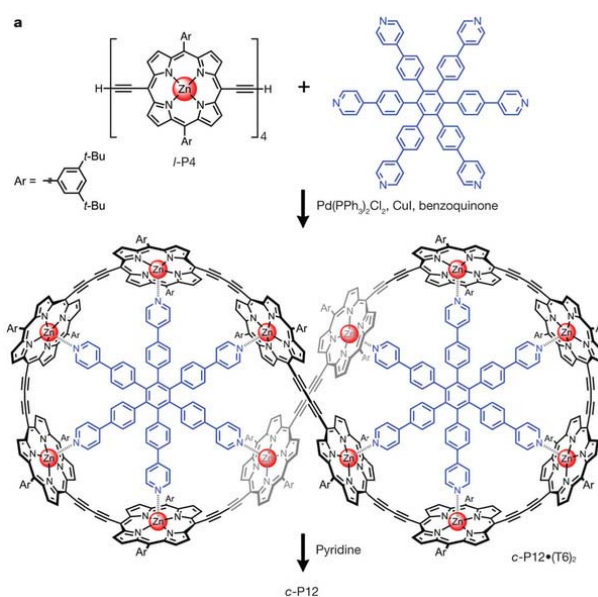
Abstract:



Chain reactions on a surface offer an important route to linear nanopatterning. We recently reported cooperative reactions on a silicon surface in which the reaction of one halogen atom with a silicon atom of a silicon dimer induced the halogenation of its neighbouring silicon atom through surface-mediated charge transfer. The reaction was unable to propagate further but here we describe how, by chemically bridging the gaps between the rows of these silicon dimers, this mechanism is able to form extended chains. The agents for chain growth are  $\text{CH}_3\text{Cl}$  molecules that dissociatively attach  $\text{CH}_3$  groups and chlorine atoms to silicon atoms from different dimers. By means of charge transfer through the surface, this gives rise to dangling bonds adjacent to the  $\text{CH}_3$  groups and chlorine atoms (in effect, 'free radicals') that dissociate further incoming  $\text{CH}_3\text{Cl}$  molecules, thereby providing the growing points for chains of indefinite length. This versatile mechanism of chain growth is examined in experiments and using *ab initio* theory.

- Vernier templating and synthesis of a 12-porphyrin nano-ring  
O'Sullivan, M. C.; Sprafke, J. K.; Kondratuk, D. V.; Rinfray, C.; Claridge, T. D. W.; Saywell, A.; Blunt, M. O.; O'Shea, J. N.; Beton, P. H.; Malfois, M.; Anderson, H. L. *Nature* **2011**, *469*, 72–75.

Abstract:



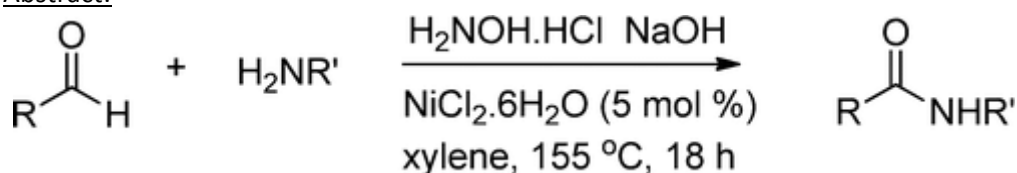
Templates are widely used to arrange molecular components so they can be covalently linked into complex molecules that are not readily accessible by classical synthetic. Nature uses sophisticated

templates such as the ribosome, whereas chemists use simple ions or small molecules. But as we tackle the synthesis of larger targets, we require larger templates—which themselves become synthetically challenging. Here we show that Vernier complexes can solve this problem: if the number of binding sites on the template,  $nT$ , is not a multiple of the number of binding sites on the molecular building blocks,  $nB$ , then small templates can direct the assembly of relatively large Vernier complexes where the number of binding sites in the product,  $nP$ , is the lowest common multiple of  $nB$  and  $nT$ . We illustrate the value of this concept for the covalent synthesis of challenging targets by using a simple six-site template to direct the synthesis of a 12-porphyrin nano-ring with a diameter of 4.7 nm, thus establishing Vernier templating as a powerful new strategy for the synthesis of large monodisperse macromolecules.

- Catalytic Acylation of Amines with Aldehydes or Aldoximes

Allen, C. L.; Davulcu, S.; Williams, J. M. J. *Org. Lett.* **2010**, *12*, 5096-5099.

Abstract:

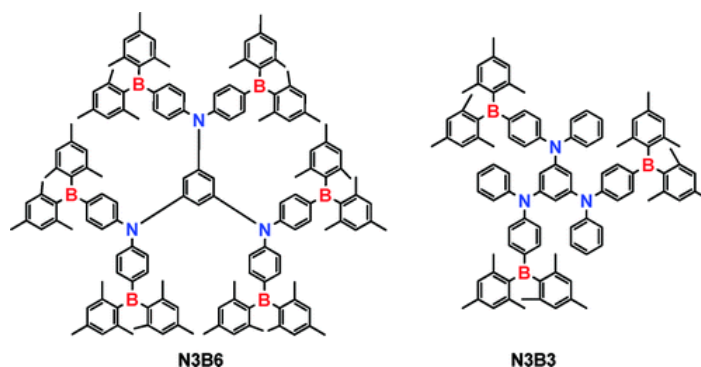


The simple nickel salt  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  catalyzes the coupling of aldoximes with amines to give secondary or tertiary amide products. The aldoxime can be prepared in situ from the corresponding aldehyde. The use of  $^{18}\text{O}$ -labeled oximes has allowed insight into the mechanism of this reaction.

- Phenylene Bridged Boron-Nitrogen Containing Dendrimers

Proń, A.; Baumgarten, M.; Müllen, K. *Org. Lett.* **2010**, *12*, 4236-4239.

Abstract:

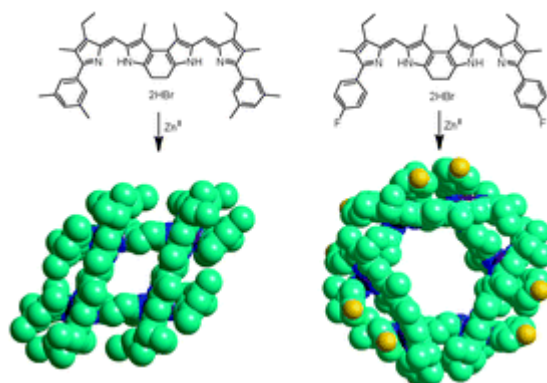


The synthesis and characterization of novel phenylene bridged boron-nitrogen containing  $\pi$ -conjugated dendrimers **N3B6** and **N3B3**, with peripheral boron atoms and 1,3,5-triaminobenzene moiety as a core, are presented. UV-vis absorption and emission measurements reveal that the optical properties 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**.

- Self-assembly of [2×2] grids and a hexagon using bis(dipyrrin)s

Ma, L.; Patrick, B. O.; Dolphin, D. *Chem. Commun.* **2011**, *47*, 704-706.

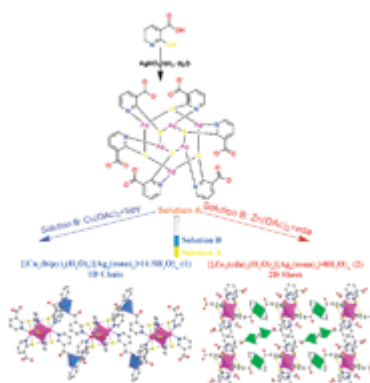
Abstract:



Neutral ZnII [2×2] grids (M4L4) and a hexagon structure (M6L6) were, for the first time, synthesized using bis(dipyrin)s and confirmed by X-ray diffraction analysis. The channel structures in the solid state result from several intermolecular noncovalent interactions.

- Stepwise assembly of two 3d–4d heterometallic coordination polymers based on a hexanuclear silver(I) metalloligand  
Sun, D.; Wang, D.-F.; Han, X.-G.; Zhang, N.; Huang, R.-B.; Zheng, L.-S. *Chem. Commun.* **2011**, 47, 746-748.

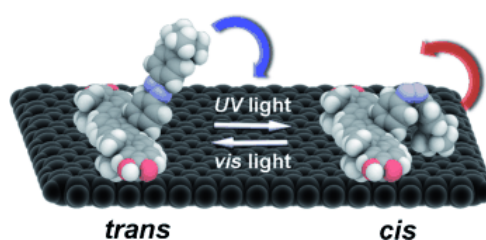
Abstract:



Two novel 3d–4d heterometallic coordination polymers  $\{[\text{Cu}_3(\text{bipy})_3(\text{H}_2\text{O})_5][\text{Ag}_6(\text{mna})_6] \cdot 11.5\text{H}_2\text{O}\}_n$  (1) and  $\{[\text{Zn}_3(\text{eda})_3(\text{H}_2\text{O})_4][\text{Ag}_6(\text{mna})_6] \cdot 8\text{H}_2\text{O}\}_n$  (2) were synthesized based on a hexanuclear silver(I) metalloligand by a three-step synthetic method (bipy = 2, 2'-bipyridine, eda = ethylenediamine and  $\text{H}_2\text{mna}$  = 2-mercaptonicotinic acid). The photoluminescence behaviors of 1 and 2 were also discussed.

- Photoswitching Vertically Oriented Azobenzene Self-Assembled Monolayers at the Solid–Liquid Interface  
Bléger, D.; Ciesielski, A.; Samorì, P., Hecht, S. *Chem.-Eur. J.* **2010**, 16, 14256-14260.

Abstract:



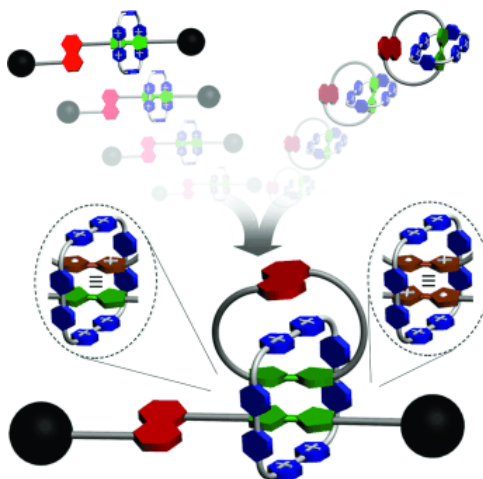
Up or down? Making use of self-assembly, the graphite surface is decorated with upright oriented photochromic units organized by a terfluorene platform. The azobenzenes within the monolayer

could be converted from the trans to the cis form leading to substantial and reversible structural reorganization, as revealed by scanning tunneling microscopy (STM) studies.

- A Multistate Switchable [3]Rotacatenane

Barin, G.; Coskun, A.; Friedman, D. C.; Olson, M. A.; Colvin, M. T.; Carmielli, R.; Dey, S. K.; Bozdemir, O. A.; Wasielewski, M. R.; Stoddart, J. F. *Chem.-Eur. J.* **2011**, *17*, 213-222.

Abstract:



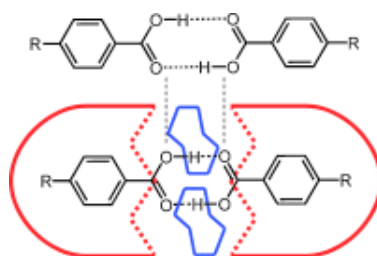
Rotacatenanes are exotic molecular compounds that can be visualized as a unique combination of a [2]catenane and a [2]rotaxane, thereby combining both the circumrotation of the ring component (rotary motion) and the shuttling of the dumbbell component (translational motion) in one structure. Herein, we describe a strategy for the synthesis of a new switchable [3]rotacatenane and the investigation of its switching properties, which rely on the formation of tetrathiafulvalene (TTF) radical  $\pi$ -dimer interactions—namely, the mixed-valence state  $(\text{TTF}_2)^+$  and the radical-cation dimer state  $(\text{TTF}^+)_2$ —under ambient conditions. A template-directed approach, based on donor–acceptor interactions, has been developed, resulting in an improved yield of the key precursor [2]catenane, prior to rotacatenation. The nature of the binding between the [2]catenane and selected  $\pi$ -electron-rich templates has been elucidated by using X-ray crystallography and UV/Vis spectroscopy as well as isothermal titration microcalorimetry. The multistate switching mechanism of the [3]rotacatenane has been demonstrated by cyclic voltammetry and EPR spectroscopy. Most notably, the radical-cation dimer state  $(\text{TTF}^+)_2$  has been shown to enter into an equilibrium by forming the co-conformation in which the two 1,5-dioxynaphthalene (DNP) units co-occupy the cavity of tetracationic cyclophane, thus enforcing the separation of TTF radical-cation dimer  $(\text{TTF}^+)_2$ . The population ratio of this equilibrium state was found to be 1:1. We believe that this research demonstrates the power of constructing complex molecular machines using template-directed protocols, enabling us to make the transition from simple molecular switches to their multistate variants for enhancing information storage in molecular electronic devices.

- Encapsulated Carboxylic Acid Dimers with Compressed Hydrogen Bonds

Ajami, D.; Tolstoy, P. M.; Dube, H.; Odermatt, S.; Koeppe, B.; Guo, J.; Limbach, H. H.; Rebek, J. Jr. *Angew. Chem. Int. Ed.* **2010**, *50*, 528-531.

Abstract:

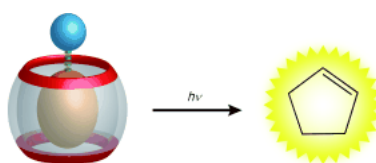




Under pressure: Carboxylic acid dimers enclosed in molecular capsules experience an internal pressure of about 5–10 kbar, which leads to compression of the hydrogen bonds (see scheme).

- Transition-Metal-Promoted Chemoselective Photoreactions at the Cucurbituril Rim  
Koner, A. L.; Márquez, C.; Dickman, M. H.; Nau, W. M. *Angew. Chem. Int. Ed.* **2010**, *50*, 545-548.

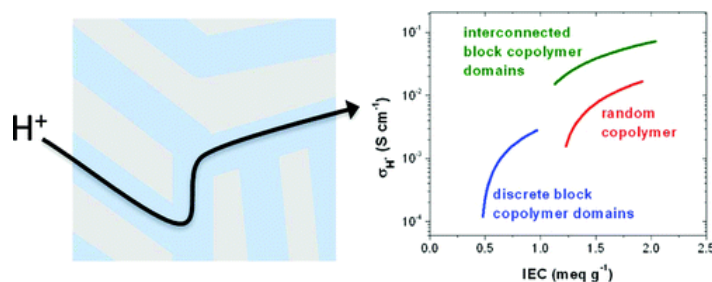
Abstract:



When included in a supramolecular barrel with transition-metal ions as lids, bicyclic azoalkanes undergo phase-selective photolysis to afford new photoproducts and photoproduct distributions. In the presence of the macrocycle cucurbit[7]uril and  $\text{Ag}^+$  ions, 2,3-diazabicyclo[2.2.1]hept-2-ene forms a ternary host-guest inclusion complex in which the cations are coordinated to the carbonyl rims of the host. Direct photolysis of this ternary complex provides cyclopentene as a new photoproduct.

- Block Copolymers for Fuel Cells  
Elabd, Y. A.; Hickner, M. A. *Macromolecules* **2011**, *44*, 1–11.

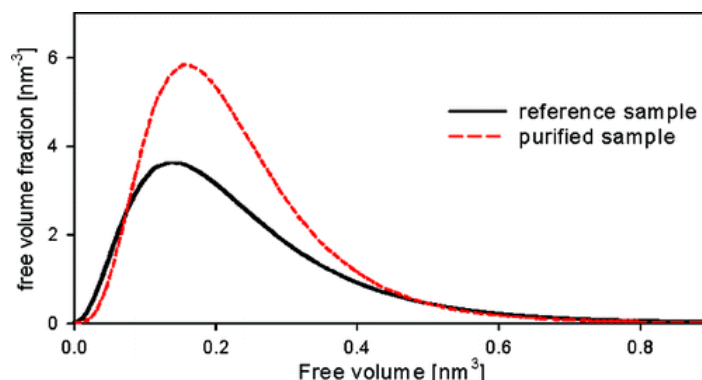
Abstract:



Ion-containing block copolymers hold promise as next-generation proton exchange membranes in hydrogen and methanol fuel cells. These materials' self-assembled ordered nanostructures facilitate proton transport over a wide range of conditions, a requirement for robust fuel cell performance. In this perspective, we will present an overview of the morphology and transport properties of ion-containing block copolymers that have been studied to gain insight into the fundamental behavior of these materials and, in some cases, are targeted toward applications in fuel cells and other electrochemical devices. We will discuss the challenges associated with predicting and obtaining well-ordered morphologies in block copolymers with high ion content, particularly those with chemistries that can withstand the chemical and mechanical stresses of the fuel cell, such as aromatic backbone block copolymers. New opportunities for ion-containing block copolymers in alkaline membrane fuel cells will also be reviewed.

- Initiation of Cavitation of Polypropylene during Tensile Drawing  
Rozanski, A.; Galeski, A.; Debowska, M. *Macromolecules* **2011**, *44*, 20–28.

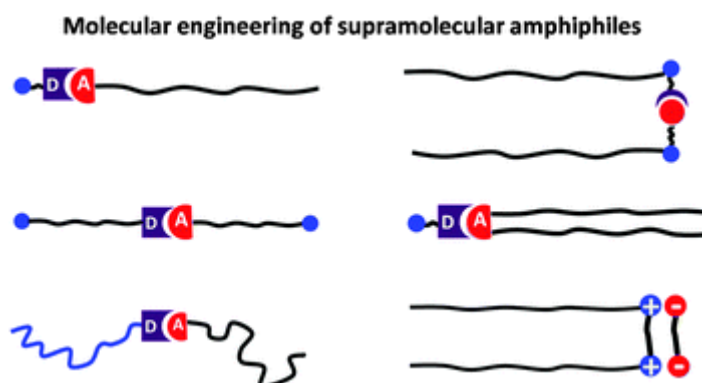
Abstract:



The effect of stabilizers, additives, and low molecular weight fractions on cavitation during tensile drawing was studied in polypropylene. The additives were extracted from compression molded samples by critical CO<sub>2</sub> and also by a mixture of nonsolvents. The extract was an oily liquid composed of antioxidant, processing stabilizer, and a spectrum of low molecular weight fractions of polypropylene. Purified polypropylene exhibited surprisingly more intense cavitation than pristine polypropylene as it was determined by small-angle X-ray scattering and volume strain measurements. Intensification of the cavitation process in the purified samples was explained by the changes in the amorphous phase, namely, the changes in free volume by eliminating low fractions and soluble additives. An increase in free volume was probed with positron annihilation lifetime spectroscopy. Intense formation of cavitation pores in purified polypropylene proves that initiation of cavitation in polypropylene has a homogeneous nature.

- Supramolecular amphiphiles  
Zhang, X.; Wang, C. *Chem. Soc. Rev.* **2011**, *40*, 94-101.

Abstract:

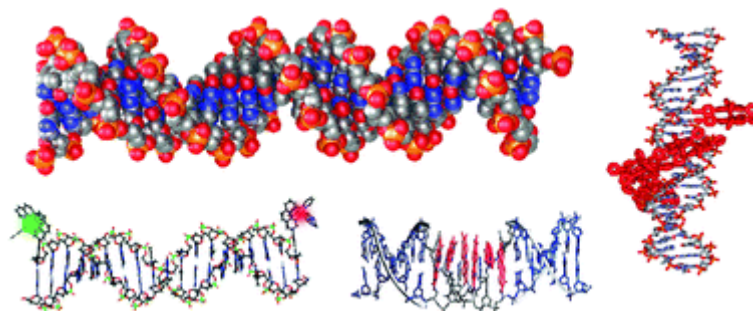


Supramolecular amphiphiles (SA), also named superamphiphiles, refer to amphiphiles that are formed by non-covalent interactions. This *tutorial review* focuses on the molecular architectures of SAs, including diversified topologies such as single chain, double chain, bolaform, gemini and rotaxane types. Non-covalent syntheses that have been employed to fabricate SAs are driven by hydrogen bonding, electrostatic attraction, host–guest recognition, charge transfer interaction, metal coordination and so on. It should be noted that SAs can be either small organic molecules or polymers. SAs allow for tuning of their amphiphilicity in a reversible fashion, leading to controlled self-assembly and disassembly. This line of research has been enriching traditional colloid chemistry

and current supramolecular chemistry, and the application of SAs in the field of functional supramolecular materials is keenly anticipated.

- DNA as supramolecular scaffold for functional molecules: progress in DNA nanotechnology  
Bandy, T. J.; Brewer, A.; Burns, J. R.; Marth, G.; Nguyen Nguyen, T.; Stulz, E. *Chem. Soc. Rev.* **2011**, *40*, 138-148.

Abstract:



Oligonucleotides have recently gained increased attraction as a supramolecular scaffold for the design and synthesis of functional molecules on the nanometre scale. This *tutorial review* focuses on the recent progress in this highly active field of research with an emphasis on covalent modifications of DNA; non-covalent interactions of DNA with molecules such as groove binders or intercalators are not part of this review. Both terminal and internal modifications are covered, and the various points of attachment (nucleobase, sugar moiety or phosphodiester backbone) are compared. Using selected examples of the recent literature, the diversity of the functionalities that have been incorporated into DNA strands is discussed.