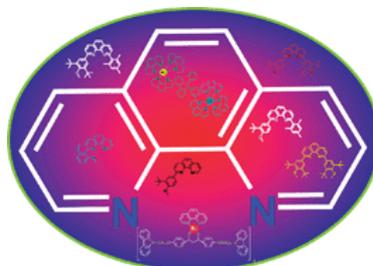


- 1,10-Phenanthrolines: versatile building blocks for luminescent molecules, materials and metal complexes

Accorsi, G.; Listorti, A.; Yoosaf, K.; Armaroli, N. *Chem. Soc. Rev.* **2009**, *38*, 1690 – 1700.

Abstract:

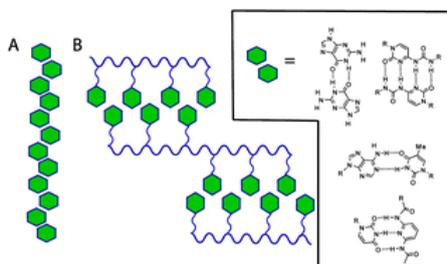


1,10-Phenanthroline entails several appealing structural and chemical properties: rigidity, planarity, aromaticity, basicity, chelating capability. This makes it a versatile starting material for synthetic organic, inorganic and supramolecular chemistry. In this *tutorial review* we examine how the chemical versatility of pristine 1,10-phenanthroline, a weakly fluorescent molecule, has been exploited to design many UV-Vis-NIR luminescent organic derivatives and coordination compounds with transition-metal (Ru(II), Os(II), Rh(III), Cr(III), Pt(II), Zn(II), Cu(I), Ag(I)) and rare-earth (Eu(III), Tb(III), Yb(III), Nd(III), Er(III)) cations. They are utilized for many analytical and technological applications.

- Base-pairing mediated non-covalent polymers

Fathalla, M.; Lawrence, C. M.; Zhang, N.; Sessler, J. L.; Jayawickramarajah, J. *Chem. Soc. Rev.* **2009**, *38*, 1608 – 1620.

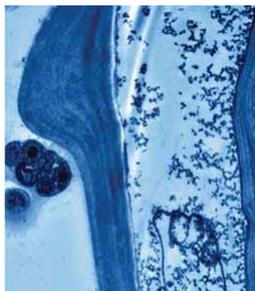
Abstract:



The naturally occurring nucleic acid bases (nucleobases) adenine, thymine (uracil), guanine, and cytosine are widely appreciated for their ability to stabilize canonical Watson–Crick base-pairing motifs, as well as a number of other well-characterized arrangements, such as Hoogsteen and wobble heterodimers, and a variety of homodimers. In this *tutorial review*, the use of these kinds of interactions to form synthetic polymeric and oligomeric ensembles is summarized. Particular emphasis will be placed on synthetic analogues of guanine that stabilize the formation of well-defined higher order aggregates, as well as *de novo* polymeric systems whose properties are modulated by the presence of nucleobase derivatives incorporated within or attached to the chain-defining backbone. In both cases, nucleobase–nucleobase interactions serve to underlie the chemistry, establish the structural morphology, and enable the development of bioinspired, environmentally responsive materials.

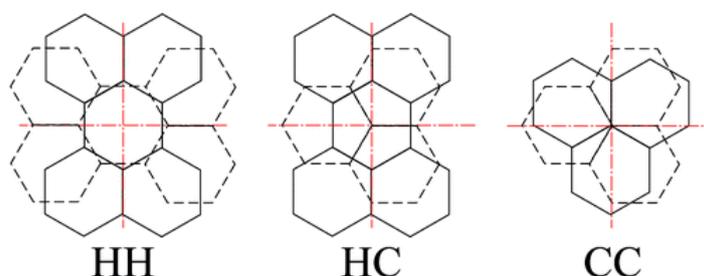
- Uptake, Translocation, and Transmission of Carbon Nanomaterials in Rice Plants

Lin, S.; Reppert, J.; Hu, Q.; Hudson, J. S.; Reid, M. L.; Ratnikova, T. A.; Rao, A. M.; Luo, H.; Ke, P. C. *Small* **2009**, *5*, 1128-1132.

Abstract:

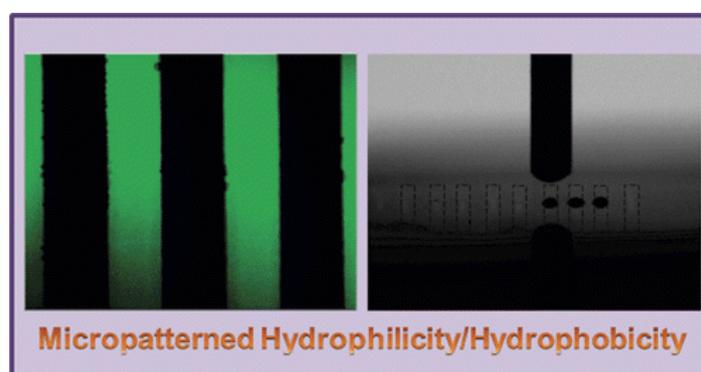
A transmission electron microscopy (TEM) image shows the significant uptake of  $C_{70}$  particles by a plant leaf cell. The  $C_{70}$  particles appear as numerous small aggregates in the vacuole and the cell walls of the leaf cell are shown as dark layered structures in the image. Scale of image:  $5 \times 6 \mu\text{m}$ .

- Contact Geometry and Conductance of Crossed Nanotube Junctions under Pressure  
Bulat, F. A.; Couchman, L.; Yang, W. *Nano Lett.* **2009**, *9*, 1759–1763.

Abstract:

We explored the relative stability, structure, and conductance of crossed nanotube junctions with dispersion corrected density functional theory. We found that the most stable junction geometry, not studied before, displays the smallest conductance. While the conductance increases as force is applied, it levels off very rapidly. This behavior contrasts with a less stable junction geometry that show steady increase of the conductance as force is applied. Electromechanical sensing devices based on this effect should exploit the conductance changes close to equilibrium.

- Microscale Patterning of Hydrophobic/Hydrophilic Surfaces by Spatially Controlled Galvanic Displacement Reactions  
Rizzello, L.; Shankar, S. S.; Fragouli, D.; Athanassiou, A.; Cingolani, R.; Pompa, P. P. *Langmuir* **2009**, *25*, 6019–6023.

Abstract:

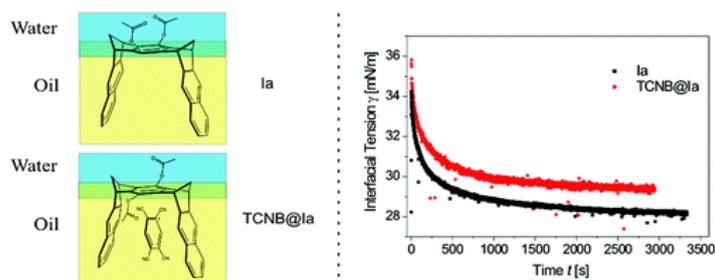
In this letter, we report the design and fabrication of different metal patterns for the realization of spatially controlled hydrophobic/hydrophilic regions with micrometer resolution. The fabrication

procedure, based on a combination of lithographic techniques and wet-chemistry reactions (namely, spontaneous Galvanic displacement reactions) is reliable, undemanding, and highly versatile, allowing the achievement of precise spatial control along with the use of a wide variety of different materials.

- Gemini-like Molecular Clips and Tweezers: The Influence of Structure and Guest Binding on Interfacial Tension

Degen, P.; Leick, S.; Rehage, H.; Polkowska, J.; Klärner, F.-G. *Langmuir* **2009**, *25*, 6094–6099.

Abstract:

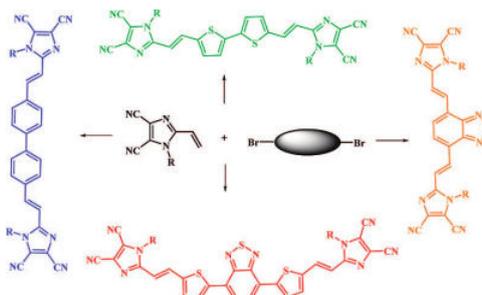


In a series of experiments, we studied the interfacial activity of aromatic aliphatic molecules with rigid geminilike structures at the interface between toluene and water. These molecules, called clips and tweezers, have rigid central benzene or naphthalene spacer-units, each substituted with two polar groups as well as two rigid aromatic side walls. They can serve as host molecules and selectively bind a variety of electron-deficient aromatic and aliphatic guest molecules. In different experiments, we compared the interfacial tensions with the calculated hydrophilic-lipid-balance (HLB) values of these molecules. The measured interfacial tensions depend as much on the HLB values as on the geometric structure of the water insoluble molecules. The concentration dependence of the surface tension gave evidence for the formation of inverse micellar aggregates, which were formed in the oil phase above a well-defined value of the bulk concentration. The presence of aggregates in the organic liquid could also be investigated by dynamic light scattering measurements. We observed typical diameters of the inverse micellar aggregates in the order of 5.6 nm, and the critical micelle concentrations (cmc's) coincided well with the results of interfacial tension measurements. From the surface excess in the vicinity of the cmc, we calculated the space occupied by a single clip molecule on the self-assembled monolayer. The observed molecular surface area was in agreement with the effective molecular diameters of the molecules. In additional experiments, we could also show that complexes with aromatic guest molecules such as 1,2-4,5-tetracyanobenzene (TCNB) led to a reduction of the amphiphilic clip properties.

- Electron-Accepting Conjugated Materials Based on 2-Vinyl-4,5-dicyanoimidazoles for Application in Organic Electronics

Shin, R. Y. C.; Sonar, P.; Siew, P. S.; Chen, Z.-K.; Sellinger, A. *J. Org. Chem.* **2009**, *74*, 3293–3298.

Abstract:

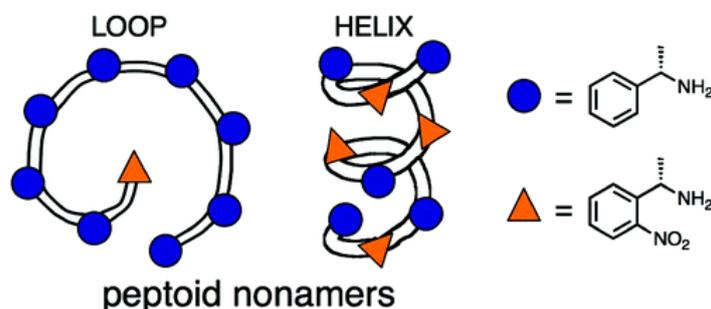


We report the Heck coupling of 2-vinyl-4,5-dicyanoimidazole (vinazene) with selected di- and trihalo aromatics in an effort to prepare linear and branched electron-accepting conjugated materials for application in organic electronics. By selecting the suitable halo-aromatic moiety, it is possible to tune the HOMO–LUMO energy levels, absorption, and emission properties for a specific application. In this regard, materials with strong photoluminescence from blue → green → red are reported that may have potential application in organic light-emitting diodes (OLEDs). Furthermore, derivatives with strong absorption in the visible spectrum, coupled with favorable HOMO–LUMO levels, have been used to prepare promising organic photovoltaic devices (OPVs) when combined with commercially available semiconducting donor polymers.

- Synthesis and Characterization of Nitroaromatic Peptoids: Fine Tuning Peptoid Secondary Structure through Monomer Position and Functionality

Fowler, S. A.; Luechapanichkul, R.; Blackwell, H. E. *J. Org. Chem.* **2009**, *74*, 1440–1449.

Abstract :



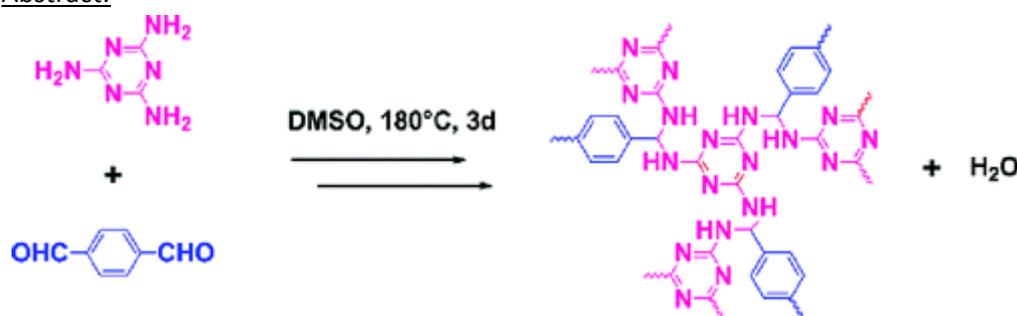
*N*-Substituted glycine oligomers, or peptoids, have emerged as an important class of foldamers for the study of biomolecular interactions and for potential use as therapeutic agents. However, the design of peptoids with well-defined conformations a priori remains a formidable challenge. New approaches are required to address this problem, and the systematic study of the role of individual monomer units in the global peptoid folding process represents one strategy. Here, we report our efforts toward this approach through the design, synthesis, and characterization of peptoids containing nitroaromatic monomer units. This work required the synthesis of a new chiral amine building block, (*S*)-1-(2-nitrophenyl)ethanamine (*s2ne*), which could be readily installed into peptoids using standard solid-phase peptoid synthesis techniques. We designed a series of peptoid nonamers that allowed us to probe the effects of this relatively electron-deficient and sterically encumbered  $\alpha$ -chiral side chain on peptoid structure, namely, the peptoid threaded loop and helix. Circular dichroism spectroscopy of the peptoids revealed that the nitroaromatic monomer has a significant effect on peptoid secondary structure. Specifically, the threaded loop structure was disrupted in a nonamer containing alternating *N*-(*S*)-1-phenylethylglycine (*Nspe*) and *Ns2ne* monomers, and the major conformation was helical instead. Indeed, placement of a single *Ns2ne* at the *N*-terminal position of (*Nspe*)<sub>9</sub> resulted in a destabilized form of the threaded loop structure relative to the

homonamer ( $Nspe$ )<sub>9</sub>. Conversely, we observed that incorporation of  $N$ -( $S$ )-1-(4-nitrophenyl)ethylglycine ( $Nsnp$ , a  $p$ -nitro monomer) at the  $N$ -terminal position *stabilized* the threaded loop structure relative to ( $Nspe$ )<sub>9</sub>. Additional experiments revealed that nitroaromatic side chains can influence peptoid nonamer folding by modulating the strength of key intramolecular hydrogen bonds in the peptoid threaded loop structure. Steric interactions were also implicated for the  $Ns2ne$  monomer. Overall, this study provides further evidence that aromatic side-chain structure, even if perturbed in a single monomer unit, can strongly influence local peptoid backbone conformation.

- Catalyst-free Preparation of Melamine-Based Microporous Polymer Networks through Schiff Base Chemistry

Schwab, M. G.; Fassbender, B.; Spiess, H. W.; Thomas, A.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2009**, *131*, 7216–7217.

Abstract:

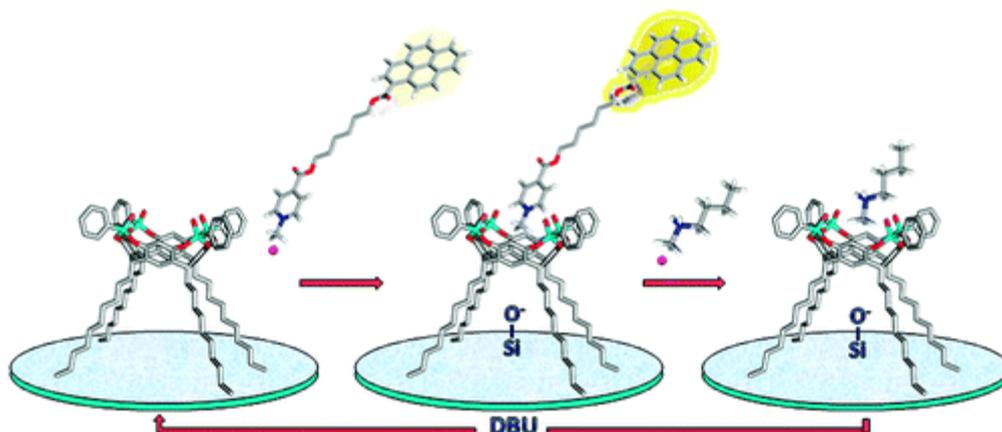


Recently, the synthesis of organic materials with high porosity has received considerable scientific interest, and various chemical approaches have been applied to the build-up of microporous polymer networks. In a novel catalyst-free process using Schiff base chemistry, melamine has been reacted with various di- and trivalent aldehydes to form a series of highly cross-linked microporous aminal networks with BET surface areas as high as 1377 m<sup>2</sup>/g and a NLDFT micropore volume of up to 0.41 cm<sup>3</sup>/g. It was shown that through the proper choice of the starting compounds the porosity of the final material can be fine-tuned. The materials contain up to 40 wt % of nitrogen and were also found to exhibit high thermal stability. Owing to the cheap and abundant monomers used in this study these networks are promising candidates for large-scale applications in gas storage, gas separation, catalysis, and sensing.

- Molecular Recognition on a Cavitand-Functionalized Silicon Surface

Biavardi, E.; Favazza, M.; Motta, A.; Fragalà, I. L.; Massera, C.; Prodi, L.; Montalti, M.; Melegari, M.; Condorelli, G. G.; Dalcanale, E. *J. Am. Chem. Soc.* **2009**, *131*, 7447–7455.

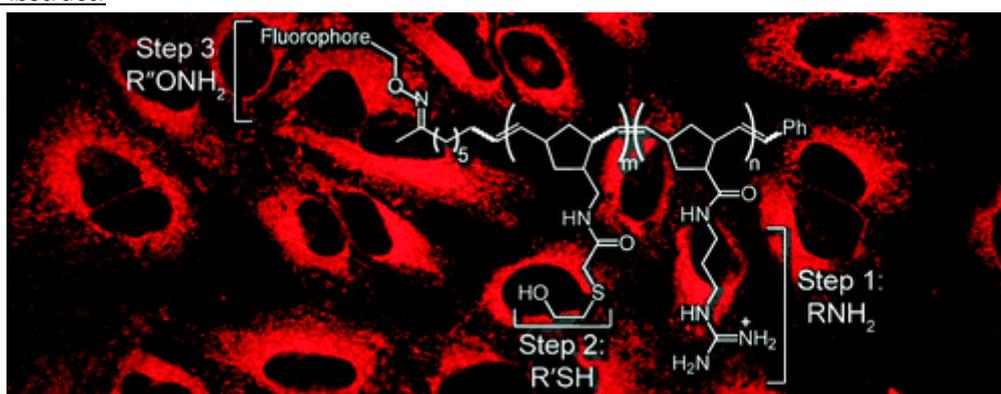
Abstract:



A Si(100) surface featuring molecular recognition properties was obtained by covalent functionalization with a tetraphosphonate cavitant (Tiiii), able to complex positively charged species. Tiiii cavitant was grafted onto the Si by photochemical hydrosilylation together with 1-octene as a spatial spectator. The recognition properties of the Si-Tiiii surface were demonstrated through two independent analytical techniques, namely XPS and fluorescence spectroscopy, during the course of reversible complexation–guest exchange–decomplexation cycles with specifically designed ammonium and pyridinium salts. Control experiments employing a Si(100) surface functionalized with a structurally similar, but complexation inactive, tetrathiosphosphonate cavitant (TSiiii) demonstrated no recognition events. This provides evidence for the complexation properties of the Si-Tiiii surface, ruling out the possibility of nonspecific interactions between the substrate and the guests. The residual Si–O<sup>−</sup> terminations on the surface replace the guests' original counterions, thus stabilizing the complex ion pairs. These results represent a further step toward the control of self-assembly of complex supramolecular architectures on surfaces.

- General Synthetic Route to Cell-Permeable Block Copolymers via ROMP  
Kolonko, E. M.; Pontrello, J. K.; Mangold, S. L.; Kiessling, L. L. *J. Am. Chem. Soc.*, **2009**, *131*, 7327–7333.

Abstract:



The applications of block copolymers are myriad, ranging from electronics to functionalized resins to therapeutics. The ring-opening metathesis polymerization (ROMP) is an especially valuable reaction for block copolymer assembly because each block can be generated with length control. We sought to use this polymerization to expand the repertoire of block copolymers by implementing a strategy that involves postpolymerization modification of a backbone bearing selectively reactive groups. To this end, we demonstrate that ROMP can be used to synthesize a block copolymer scaffold that possesses three types of functional groups—a succinimidyl ester, an  $\alpha$ -chloroacetamide group, and a

ketone—each of which can be modified independently. Thus, a single scaffold can be elaborated to afford a wide range of block copolymers. Exploiting this synthetic approach and the length control offered by ROMP, we assemble block copolymers capable of traversing the membrane and entering mammalian cells.

7

- Coordination-Assisted Assembly of 1-D Nanostructured Light-Harvesting Antenna  
Zhang, X.; Chen, Z.-K.; Loh, K. P. *J. Am. Chem. Soc.* **2009**, *131*, 7210–7211.

Abstract:

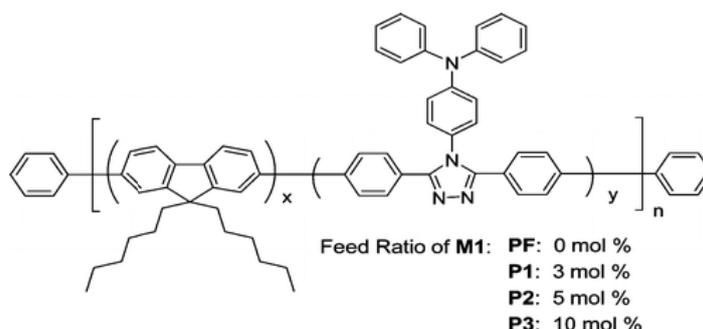


An efficient light-harvesting antenna was achieved via self-assembly of two distinct chromophores into nanoscale supramolecular coordination polymers (NSCPs). Efficient fluorescence resonance energy transfer is favorable in the self-assembled 1-D nanostructure as a result of fast and efficient exciton migration in the ordered architecture.

- Copolyfluorenes Containing Bipolar Groups: Synthesis and Application To Enhance Electroluminescence of MEH-PPV.

Wu, C.-S.; Chen, Y. *Macromolecules* **2009**, *42*, 3729-3737.

Abstract:



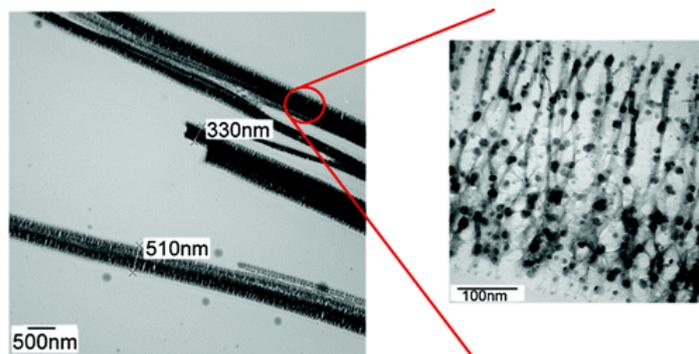
Enhancing electroluminescence of conventional MEH-PPV {poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]} is desirable due to its popularity in polymeric emitting materials. The enhancement is much readily attained by simple blending with functional polymers instead of tedious structural modification. In response to this, three copolyfluorenes (**P1-P3**) containing bipolar groups (3.1-11.2 mol %), directly linked hole-transporting triphenylamine and electron-transporting 1,2,4-triazole, are synthesized by Suzuki coupling reaction. The bipolar groups not only suppress undesirable green emission of polyfluorene under thermal annealing but also increase hole and electron affinity of the resulting copolyfluorenes. Blending the bipolar copolyfluorenes with MEH-PPV effectively improves the emission efficiency of its electroluminescent devices [ITO/PEDOT: PSS/polymer blend/Ca(50 nm)/Al(100 nm)]. The maximum luminance and maximum luminance efficiency are significantly enhanced from 3120 cd/m<sup>2</sup> and 0.49 cd/A (MEH-PPV device) to 19 560

cd/m<sup>2</sup> and 1.08 cd/A (blend device with ca. 0.5 wt % of bipolar groups), respectively. Our results demonstrate the efficacy of the bipolar copolyfluorenes in enhancing electroluminescence of MEH-PPV.

- Fabrication and Characterization of Self-Assembled  $\beta$ -Cyclodextrin Threaded Monomers and Induced Helical Polymers.

Liu, J.-H.; Chiu, Y.-H.; Chiu, T.-H. *Macromolecules* **2009**, *42*, 3715-3720.

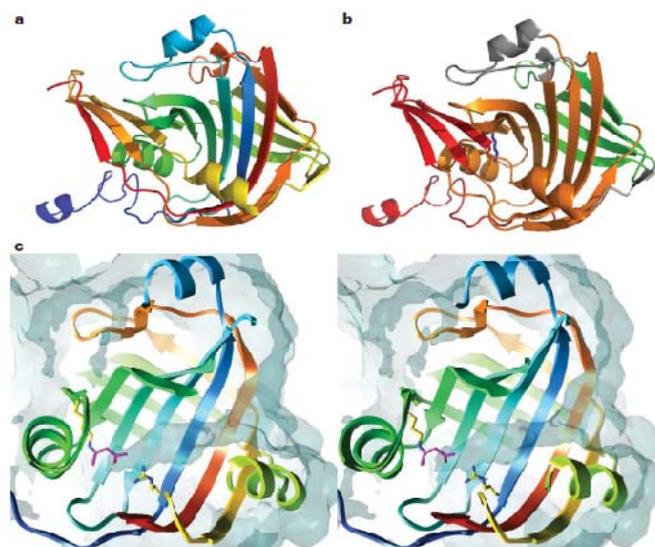
Abstract:



A novel chiral monomer end-capped with a cholesteryl group and threaded with  $\beta$ -cyclodextrin was synthesized in order to induce the formation of a helical polymer. <sup>1</sup>H NMR studies revealed that one or two cyclodextrin molecules were threaded onto the synthesized chiral monomer, leading to the formation of a helical construction of self-assembled inclusion complexes. The formation of a self-assembled inclusion complex was identified using SEM and TEM. The monomeric self-assembled inclusion complex was further polymerized using benzoyl peroxide as a photoinitiator. Both the highly ordered alignment and the helical structure of self-assembled supramolecules were confirmed using polarized optical microscopy and circular dichroism spectroscopy, respectively. We have first demonstrated an easy process for the fabrication of helical polymers via self-assembled monomers threaded with a  $\beta$ -cyclodextrin end and capped with a chiral moiety.

- Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions  
Powner, M. W.; Gerland, B.; Sutherland, J. D. *Nature* **2009**, *459*, 393-397.

Abstract:



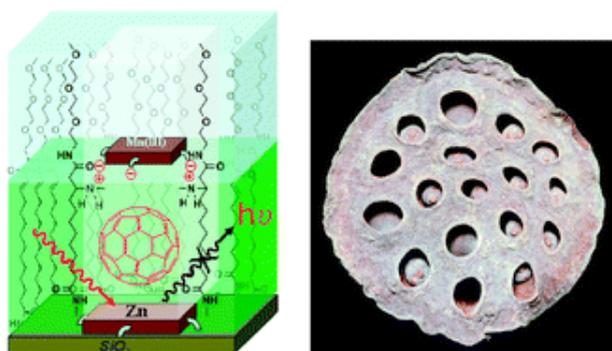


and of the enamine adduct with the substrate analogue 2,4-pentanedione. Surprisingly, the shift of the pKa of Lys 115 is not due to the proximity of Lys 116, the side chain of which is oriented away from the active site. Instead, Lys 116 participates in the structural anchoring of Lys 115 in a long, hydrophobic funnel provided by the novel fold of the enzyme. Thus, AADase perturbs the pKa of the nucleophile by means of a desolvation effect by placement of the side chain into the protein core while enforcing the proximity of polar residues, which facilitate decarboxylation through electrostatic and steric effects.

- Construction of trimeric porphyrin-fullerene-porphyrin stacks within surface-derived pores of nano-scale dimensions.

Bhosale, S. V.; Langford S. J.; Krsta, D. *Chem. Commun.* **2009**, 3166 - 3168.

Abstract:

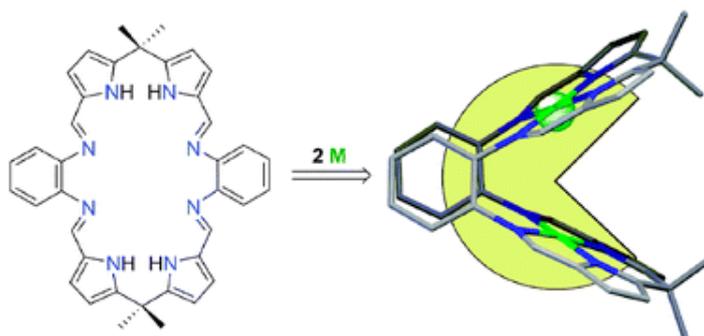


A new efficient strategy of a zinc porphyrin based yocowell cavity as a receptor for the formation of stable inclusion complexes of fullerenes via-electronic donor–acceptor and hydrophobic interactions, and finally anionic porphyrin used as a cover to the wells.

- A macrocyclic approach to transition metal and uranyl Pacman complexes.

Love, J. B. *Chem. Commun.* **2009**, 3154 – 3165.

Abstract:



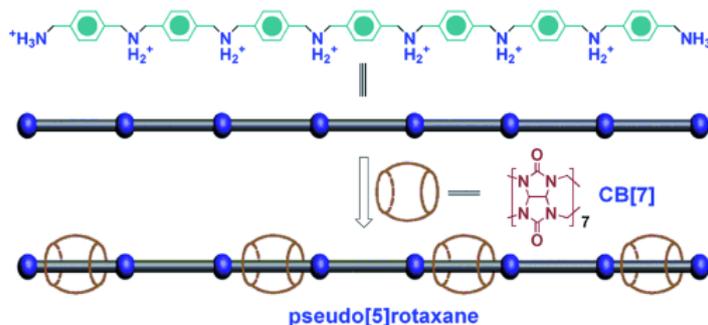
Multielectron redox chemistry involving small molecules such as O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> is intrinsic to the chemical challenges surrounding sustainable, low-carbon energy generation and exploitation. Compounds with more than one metal reaction site facilitate this chemistry by providing both unique binding environments and combined redox equivalents. However, controlling the aggregation of metal cations is problematic, as both the primary coordination spheres of the metals and the metal–metal separations have to be defined carefully. We described recently a series of pyrrole-based macrocyclic ligands designed to manage metal aggregation and form molecular multimetallic complexes. In particular, we have shown that these compartmentalised Schiff-base calixpyrroles generally form rigid Pacman complexes that prescribe well-defined, metallo microenvironments

within the molecular cleft. This article will review the development of this chemistry and its context, and will highlight structural facets and reaction chemistry of metal complexes from across the periodic table.

- Efficient Preparation of Separable Pseudo[*n*]rotaxanes by Selective Threading of Oligoalkylammonium Salts with Cucurbit[7]uril

Yin, J.; Chi, C.; Wu, J. *Chem. Eur. J.* **2009**, *24*, 6050-6057.

Abstract:



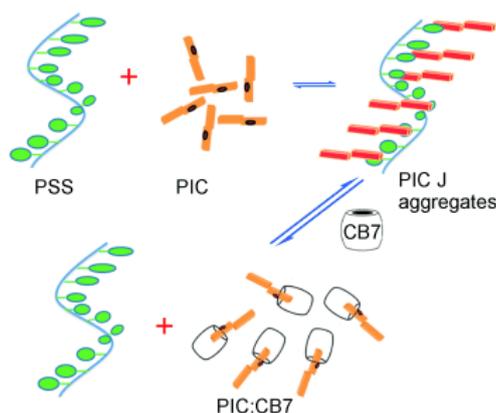
**A salty solution:** Well-defined pseudo[*n*]rotaxanes (*n*=2, 3, 4, 5) were prepared as pure compounds through threading of oligoalkylammonium salts with cucurbit[7]uril (CB[7]) and by subsequent counterion exchange. A unique self-assembling mode was observed (see graphic).

We describe the efficient preparation of well-defined, homogeneous pseudo[*n*]rotaxanes (*n*=2, 3, 4, 5) by the selective threading of oligoalkylammonium salts with cucurbit[7]uril (CB[7]) and the subsequent simple separation of the pure pseudo[*n*]rotaxanes from the complicated system. A series of well-defined oligoalkylammonium salts were prepared by stepwise synthesis and their molecular recognition and self-assembly with a solution of CB[7] in CF<sub>3</sub>CO<sub>2</sub>D/D<sub>2</sub>O (1:1 v/v) were investigated. As a result of the high affinity of CB[7] to the *p*-xylylene diammonium units (-NH<sub>2</sub><sup>+</sup>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>-) in the oligoalkylammonium salts, the CB[7] rings threaded onto these cationic threads to form pseudorotaxane structures. Interestingly, due to the repulsive dipole-dipole electrostatic interactions between the CB[7] units and steric hindrance, the threading process exhibited a high selectivity and a unique self-assembling mode was discovered in which two CB[7] units cannot bind the same ammonium site. The as-formed well-defined pseudo[*n*]rotaxanes can be easily separated as pure compounds from the mixture by simple counterion exchange with NH<sub>4</sub>PF<sub>6</sub> and the pure pseudo[*n*]rotaxanes are stable and partially soluble in normal organic solvents. Such facile preparation and separation are mainly ascribed to the high binding constant between CB[7] and the oligoalkylammonium salts and the unique solubility of CB[7] in protonic acid. As most pseudorotaxanes reported in the literature exist as a dynamic mixture and their separation is usually difficult, our research represents one good example in which pure pseudo[*n*]rotaxanes (*n*=2, 3, 4, 5) can be obtained by a simple “threading-followed-by-precipitation” method.

- Controlling the Formation of Cyanine Dye H- and J-Aggregates with Cucurbituril Hosts in the Presence of Anionic Polyelectrolytes

Gadde, S.; Batchelor, E. K.; Kaifer, A. E. *Chem. Eur. J.* **2009**, *24*, 6025-6031.

Abstract:



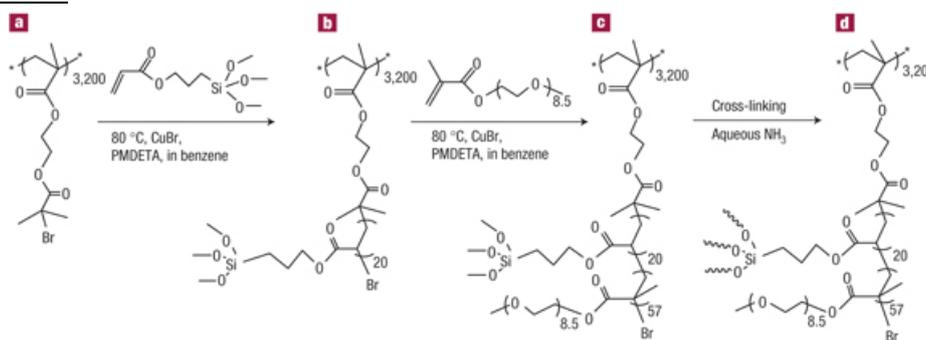
**Controlling aggregation:** The formation of H- and J-aggregates by cyanine dyes can be significantly enhanced by poly(styrenesulfonate) and further controlled through host-guest complexation with the cucurbit[7]uril host (see picture).

The presence of anionic polyelectrolytes enhances the tendency of cationic cyanine dyes to form aggregates in aqueous media. In this work we investigate the interactions between two cyanine dyes, pseudoisocyanine (PIC) and pinacyanol (PIN), with polystyrenesulfonate (PSS) as the key additive to develop J- and H-aggregates. We also take advantage of the binding properties of the cucurbit[7]uril (CB7) host to control formation of these aggregates through its host-guest interactions with the dye molecules. UV/Vis absorption spectroscopic studies clearly demonstrate the PSS-enhanced formation of J-aggregates in the case of PIC and H-aggregates in the case of PIN. Electrostatic interactions between the cyanine dye molecules and the polyelectrolyte chains assist the formation of J- or H-aggregates at very low dye concentrations (ca.  $10^{-6}$  M). Optimum development of dye aggregates was observed at a sulfonate/dye molar ratio of about 3:1. Departures from this stoichiometric ratio seem to perturb the optimal aggregate structure. Furthermore, the presence of CB7 was found to effectively disrupt the interactions responsible for dye aggregation. Thus, CB7 completely disrupts the J-aggregates formed by PIC and the H-aggregates (as well as lower concentrations of J-aggregates) formed by PIN. UV/Vis and emission spectroscopic studies clearly indicate that binding of CB7 to both dye molecules removes them from the aggregate structures. Our spectroscopic data clearly indicate that regulation of the relative molar ratios of dye, CB7 host, and polyelectrolyte sulfonate groups leads to a quantitative control of dye aggregation, yielding variable amounts of PIC J- and PIN H-aggregates in these solutions.

- Water-soluble organo-silica hybrid nanowires

Yuan, J.; Xu, Y.; Walther, A.; Bolisetty, S.; Schumacher, M.; Schmalz, H.; Ballauff, M.; Müller, A. H. E. *Nature Materials* **2008**, *7*, 718-722.

Abstract:

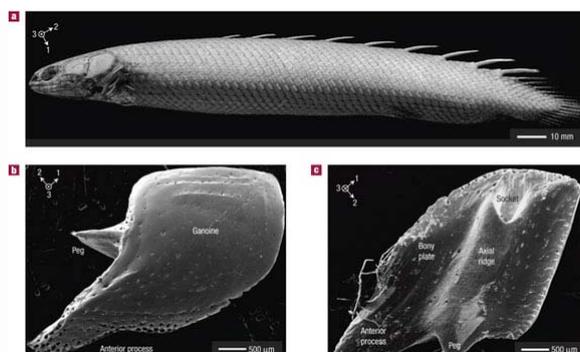


There has been growing interest in the past decade in one-dimensional (1D) nanostructures, such as nanowires, nanotubes or nanorods, owing to their size-dependent optical and electronic properties and their potential application as building blocks, interconnects and functional components for assembling nanodevices. Significant progress has been made; however, the strict control of the distinctive geometry at extremely small size for 1D structures remains a great challenge in this field. The anisotropic nature of cylindrical polymer brushes has been applied to template 1D nanostructured materials, such as metal, semiconductor or magnetic nanowires. Here, by constructing the cylindrical polymer brushes themselves with a precursor-containing monomer, we successfully synthesized hybrid nanowires with a silsesquioxane core and a shell made up from oligo(ethylene glycol) methacrylate units, which are soluble in water and many organic solvents. The length and diameter of these rigid wires are tunable by the degrees of polymerization of both the backbone and the side chain. They show lyotropic liquid-crystalline behaviour and can be pyrolysed to silica nanowires. This approach provides a route to the controlled fabrication of inorganic or hybrid silica nanostructures by living polymerization techniques.

- Materials design principles of ancient fish armour

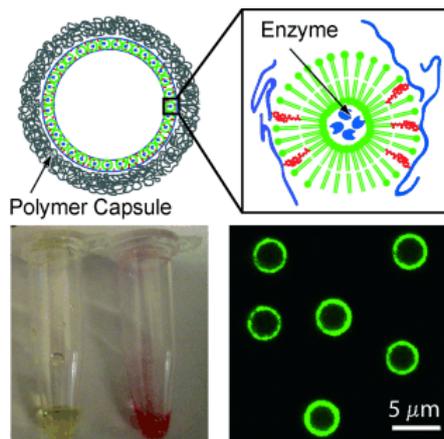
Bruet, B. J. F.; Song, J.; Boyce, M. C.; Ortiz, C. *Nature Materials* **2008**, *7*, 748-756.

Abstract:



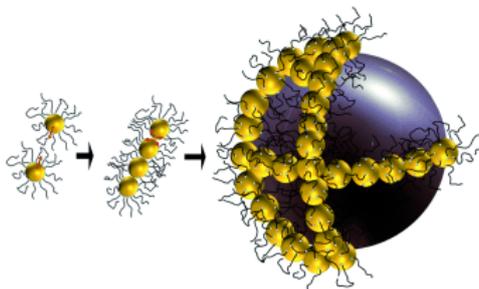
Knowledge of the structure–property–function relationships of dermal scales of armoured fish could enable pathways to improved bioinspired human body armour, and may provide clues to the evolutionary origins of mineralized tissues. Here, we present a multiscale experimental and computational approach that reveals the materials design principles present within individual ganoid scales from the 'living fossil' *Polypterus senegalus*. This fish belongs to the ancient family Polypteridae, which first appeared 96 million years ago during the Cretaceous period and still retains many of their characteristics. The mechanistic origins of penetration resistance (approximating a biting attack) were investigated and found to include the juxtaposition of multiple distinct reinforcing composite layers that each undergo their own unique deformation mechanisms, a unique spatial functional form of mechanical properties with regions of differing levels of gradation within and between material layers, and layers with an undetectable gradation, load-dependent effective material properties, circumferential surface cracking, orthogonal microcracking in laminated sublayers and geometrically corrugated junctions between layers.

- A Microreactor with Thousands of Subcompartments: Enzyme-Loaded Liposomes within Polymer Capsules  
Städler, B.; Chandrawati, R.; Price, A. D.; Chong, S.-F.; Breheney, K.; Postma, A.; Connal, L. A.; Zelikin, A. N.; Caruso, F. *Angew. Chem. Int. Ed.* **2009**, *48*, 4359–4362.

Abstract:

**Fully loaded:** Noncovalent anchoring of liposomes into polymer multilayered films with cholesterol-modified polymers allows the preparation of capsosomes - liposome-compartmentalized polymer capsules (see picture). A quantitative enzymatic reaction confirmed the presence of active cargo within the capsosomes and was used to determine the number of subcompartments within this novel biomedical carrier system.

- Self-Assembly of Amphiphilic Nanocrystals  
Carbone, L.; Manna, L.; Sönnichsen, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 4282 – 4283.

Abstract:

**Amphiphilic hybrid materials** are formed from polymer-coated semiconductor nanoparticles that simulate a surfactant-like response (see picture). The strength and density of the surface coating are the key assembling forces driving a transition from single particles to cylindrical or vesicular superstructures.