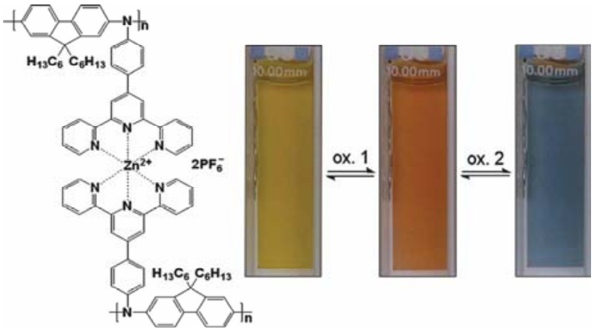
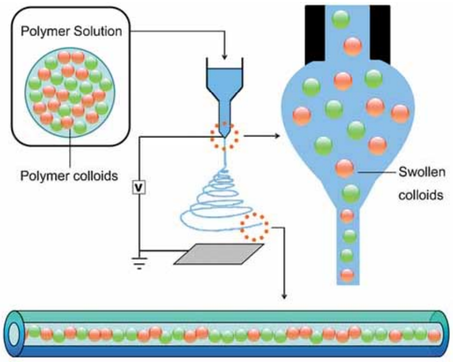
- Fast-Switching Electrochromic Films of Zinc Polyiminofluorene-Terpyridine Prepared Upon Coordinative Supramolecular Assembly
  Maier, A.; Rabindranath, R.; Tieke, B. *Adv. Mater*. **2009**, *21*, 959-963.
  Abstract :



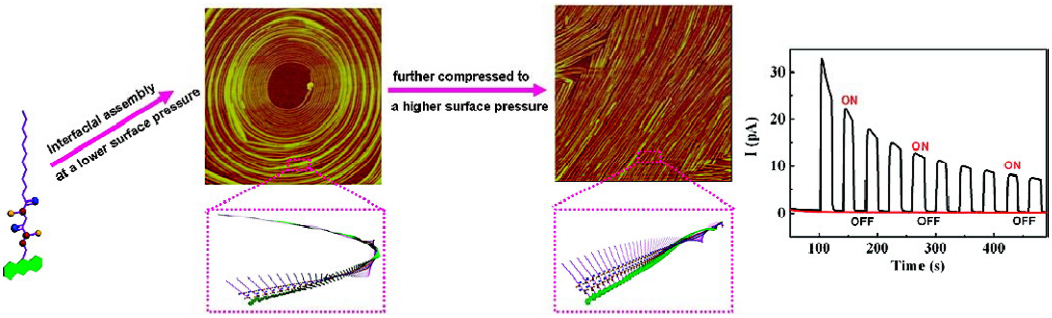
Coordinative self-assembly of zinc(II) ions and polytopic polyiminofluorene-tpy ligands is used to prepare electrochromic films with thickness in the nanometer range. The films can be switched between yellow, red, and blue, and exhibit switching times of 500 ms, high contrast, and high stability.

- Core-Sheath Nanofibers Containing Colloidal Arrays in the Core for Programmable Multi-Agent Delivery
  Jo, E.; Lee, S.; Kim, K. T.; Won, Y. S.; Kim, H.-S.; Cho, E. C.; Jeong, U. *Adv. Mater*. **2009**, *21*, 968-972.
  Abstract:



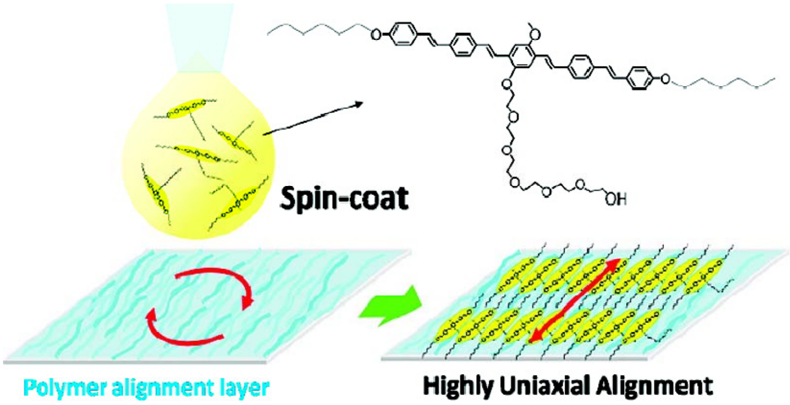
Polymeric core-sheath nanofibers consisting of polymeric sheath and arrays of colloids in the core are produced by one-step single-nozzle electrospinning. Loading different species of active agents in each colloid provides control over the release of each of the agents independently, which enables a programmed release pattern for multiple agents.

- Controllable Fabrication of Supramolecular Nanocoils and Nanoribbons and Their Morphology-Dependent Photoswitching
  Zhang, Y.; Chen, P.; Jiang, L.; Hu, W.; Liu, M. *J. Am. Chem. Soc.* **2009**, *131*, 2756–2757.
  Abstract:



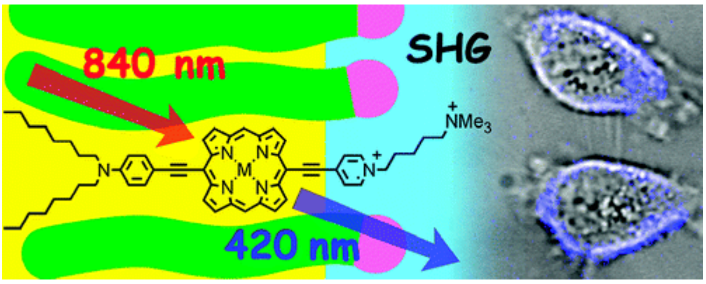
Nanocoils and straight nanoribbons have been controllably fabricated through the interfacial organization of an anthracene derivative. A morphology-dependent photoswitching has been observed. While the nanocoils show no photocurrent response, the straight nanoribbons display a switchable photocurrent upon an on/off illumination.

- Highly Uniaxial Orientation in Oligo(p-phenylenevinylene) Films Induced During Wet-Coating Process
  Nishizawa, T.; Lim, H. K.; Tajima, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2009**, *131*, 2464–2465.
  <u>Abstract:</u>



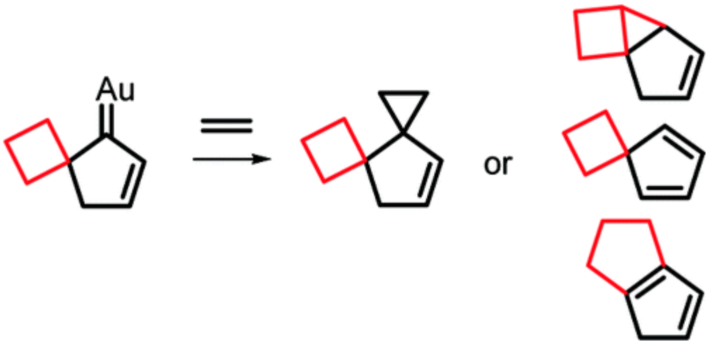
Highly uniaxial alignment of π-conjugated oligo(p-phenylenevinylene)s was spontaneously achieved in the as-cast films by simply spin-coating the solution onto mechanically rubbed polymer alignment layers such as poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid) (PEDOT:PSS) film, resulting in a high dichroic ratio ($A_{//}/A_{\perp}$) of 41.0 and an order parameter ($[A_{//} - A_{\perp}]/[A_{//} + 2A_{\perp}]$) of 0.93 estimated from the polarized absorption spectra of the films, and its application to organic photovoltaic devices was also demonstrated to achieve a high anisotropy in photosensitivity.

- Amphiphilic Porphyrins for Second Harmonic Generation Imaging
  Reeve, J. E.; Collins, H. A.; De Mey, K.; Kohl, M. M.; Thorley, K. J.; Paulsen, O.; Clays, K.; Anderson, H. L. *J. Am. Chem. Soc.* **2009**, *131*, 2758–2759.
  <u>Abstract :</u>



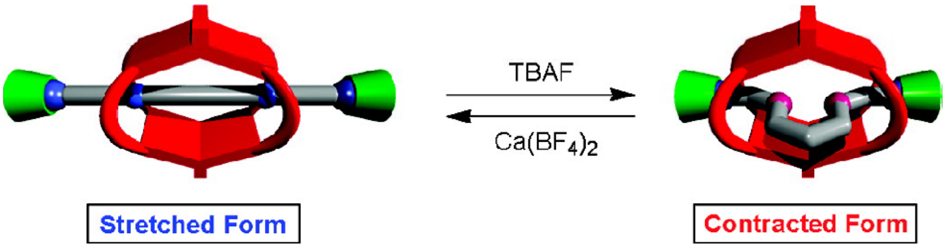
Amphiphilic donor−acceptor *meso*-ethynyl porphyrins with polar pyridinium electron-acceptor head groups and hydrophobic dialkyl-aniline electron donors have high molecular hyperpolarizabilities (as measured by hyper-Rayleigh scattering) and high affinities for biological membranes. When bound to water droplets in dodecane, or to the plasma membranes of living cells, they can be used for second harmonic generation (SHG) microscopy; an incident light of wavelength 840 nm generates a strong frequency-doubled signal at 420 nm. Copper(II) and nickel(II) porphyrin complexes give similar SHG signals to those of the free-base porphyrins, while exhibiting no detectable two-photon excited fluorescence.

- Generation and Trapping of Cyclopentenylidene Gold Species: Four Pathways to Polycyclic Compounds
  Lemière, G.; Gandon, V.; Cariou, K.; Hours, A.; Fukuyama, T.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **2009**, *131*, 2993–3006.
  Abstract:



Cyclopentenylidene gold complexes can easily be formed from vinyl allenes through a Nazarov-like mechanism. Such carbenes may transform in four different ways into polycyclic frameworks: electrophilic cyclopropanation, C−H insertion, C−C migration, or proton shift. We have studied the selectivity of these different pathways and used our findings for the expedient preparation of valuable complex molecules. An application to the total synthesis of a natural product, $\Delta^{9(12)}$-capnellene, is presented. DFT computations were carried out to shed light on the mechanisms.

- A Molecular Cage-Based [2]Rotaxane That Behaves as a Molecular Muscle
  Chuang C.-J.; Li W.-S.; Lai C.-C.; Liu Y.-H.; Peng S.-M.; Chao I.; Chiu S.-H. *Org. Lett*. **2009**, *11*, 385-388.
  Abstract :

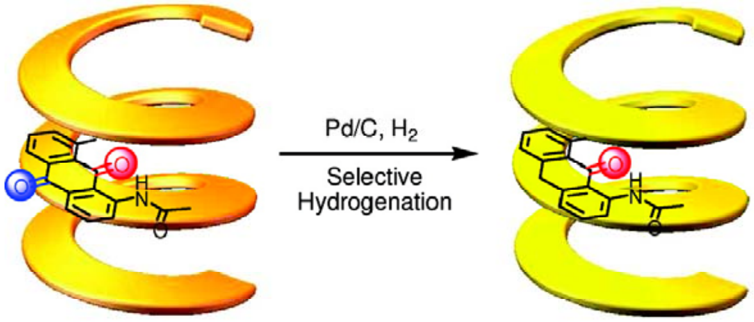


We report a molecular cage-based [2]rotaxane that functions as an artificial molecular muscle through the control of the addition and removal of fluoride anions. The percentage change in molecular length of the [2]rotaxane is about 36% between the stretched and contracted states, which is larger than the percentage change (~27%) in human muscle.

- Folding-Induced Selective Hydrogenation of Helical 9,10-Anthraquinone Analogues

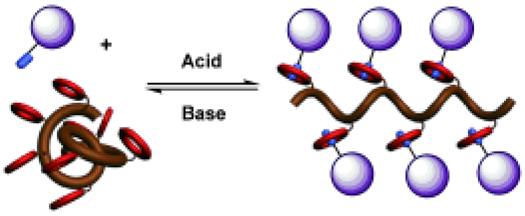
Hu H.-Y.; Xiang J.-F.; Cao J.; Chen C.-F. *Org. Lett*. **2008**, *10*, 5035-5038.

Abstract :



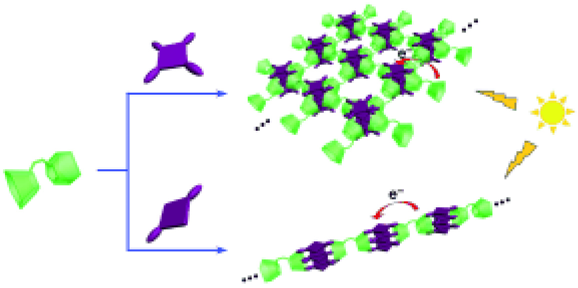
The first selective catalytic hydrogenation induced by the artificial helix based on oligo(phenanthroline dicarboxamide)s containing a 9,10-anthraquinone subunit is described. Due to the steric hindrance within the helically folded oligomers, the selective reductions of the anthraquinone units were completely different from those of model substrates, which subsequently mimicked the enzyme catalysis for preventing some reactions from occurring.

- pH-Controllable Supramolecular Systems
  Leung, K. C. F.; Chak, C. F.; Lo, C. F.; Wong, W.; Xuan, S.; and Cheng, C. H. K. *Chem. Asian J.* **2009**, 4, 364 – 381.
  Abstract:



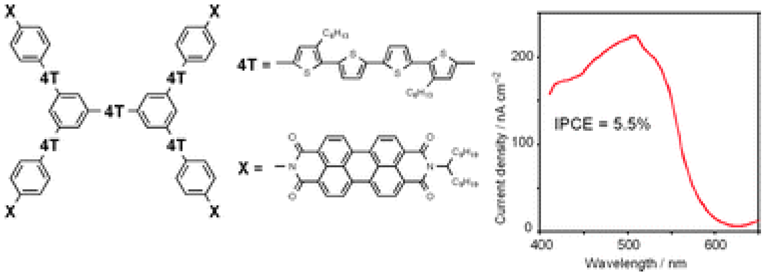
This Focus Review surveys representative examples of pH-controllable supramolecular systems with interesting features and state-of-the-art applications such as 1) conformational changes within individual molecules; 2) folding/unfolding of polymers; 3) simultaneous binding of cations and anions; 4) logic function; 5) ON–OFF switchable colorimetric sensing; 6) translocation of macrocycle-in-rotaxane molecules; 7) large-scale movement within molecules; and 8) regulation of the substrate flow in nanocontainers. In particular, systems will be discussed that involve: pH-induced conformational changes of a resorcinarene cavitand and a bis(iron porphyrin) complex; pH control in assembly and disassembly of supramolecular systems stabilized with different major noncovalent interactions; pH-driven movements of interlocked molecules involving rotaxanes, molecular elevators, and molecular muscles; and, finally, multicomponent supramolecular systems immobilized on solid supports as pH-responsive nanovalves for the controlled release of specific substrates. Recent advances in the understanding of pH-controllable supramolecular systems have led to the construction of meaningful molecular machines for electronic and biological applications that are amenable to control by simple perturbation with acids and bases.

- Nano-Supramolecular Assemblies Constructed from Water-Soluble Bis(calix[5]arenes) with Porphyrins and Their Photoinduced Electron Transfer Properties
  Guo, D. S.; Chen, K.; Zhang, H. Q.; and Liu, Y. *Chem. Asian J.* **2009**, 4, 436 – 445.
  Abstract:



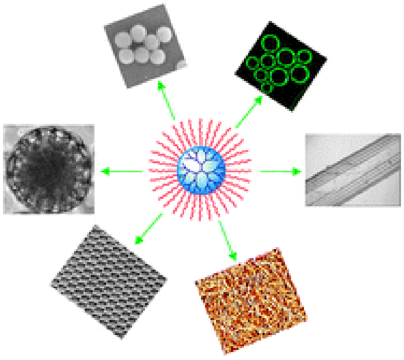
Possessing 2D netlike and 1D linear morphologies, two nanosupramolecular architectures A1 and A2 are constructed by tetracationic porphyrin (G1) and dicationic porphyrin (G2), respectively, upon complexation with the novel water-soluble bis(psulfonatocalix[5]arenes) bridged at the lower rim (H2). Corresponding to the molecular design, the aggregation morphologies are well manipulated by the inherent binding sites of the building blocks through host–guest interactions as well as charge interactions. In comparison to the simple p- sulfonatocalix[5]arene H1 which can only form particle-type complexes C1 and C2 with porphyrin guests, H2 provides excellent pre-organized structure to construct highly complex nano-supramolecular assemblies. The exhibited electron-transfer process of the supramolecular systems is further investigated by steady-state and time-resolved fluorescence spectroscopy, electrochemical measurements, and transient absorption spectroscopy. The results obtained show that calixarenes are also effective electron donors in PET besides acting as significant building blocks, which gives them many advantages in constructing well-ordered nanomaterials with the capability of electron and energy transport.

- Dendritic oligothiophene bearing perylene bis(dicarboximide) groups as an active material for photovoltaic device
  Ie, Y.; Uto, T.; Yamamoto, N.; Aso, Y. *Chem. Commun*. **2009**, 1213 – 1215.
  <u>Abstract :</u>



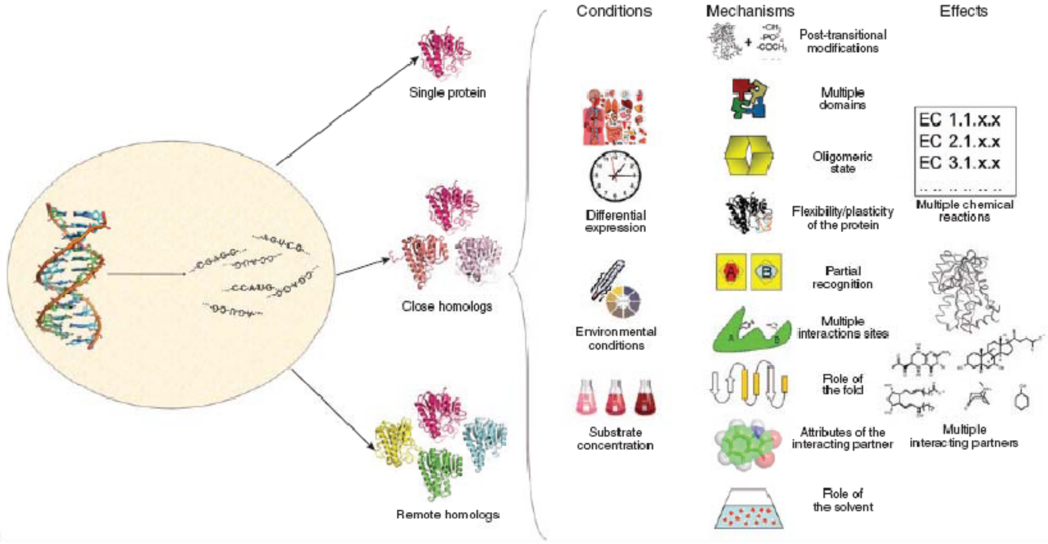
A dendritic oligothiophene containing perylene bis(dicarboximide) units was synthesized and its electronic properties and photovoltaic performance were investigated.

- Supramolecular self-assembly of amphiphilic hyperbranched polymers at all scales and dimensions: progress, characteristics and perspectives.
  Zhou, Y.; Yan, D. *Chem.* Commun. **2009,** 1172 – 1188.
  <u>Abstract :</u>



This feature article describes the supramolecular self-assembly of hyperbranched polymers (HBPs), including the progress, unique characteristics and future perspectives. HBPs are irregular in molecular structure compared with that of linear block copolymers and dendrimers. However, similar to these well-defined polymer tectons, HBPs have displayed great potential to be excellent precursors in solution self-assembly, interfacial self-assembly and hybrid self-assembly. Many impressive supramolecular aggregates and hybrids at all scales and dimensions, such as macroscopic tubes, micro- or nano-vesicles, fibers, spherical micelles and honeycomb films, have been generated. In addition, HBPs also demonstrate unique characteristics or advantages in supramolecular self-assembly behaviours, including controllable morphologies and structures, special properties, characteristic self-assembly mechanism and facile functionalization process. Although still being at the early stage, self-assembly of HBPs has provided a new avenue for the development of supramolecular chemistry.

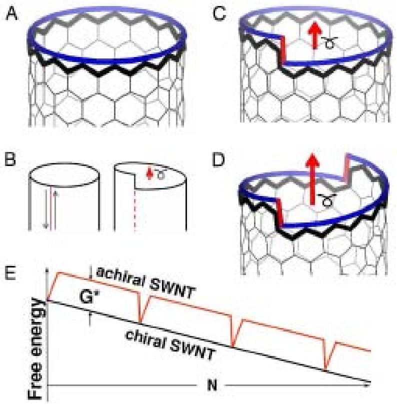
- Protein promiscuity and its implications for biotechnology
  Nobeli, I.; Favia, A. D.; Thornton, J. M. *Nature biotechnology* **2009**, *27*, 159-160.
  Abstract:

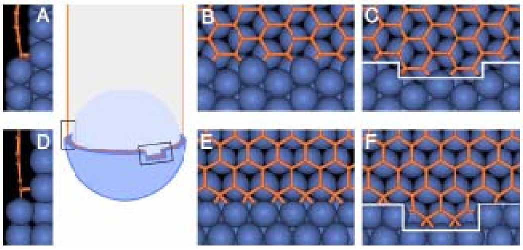


Molecular recognition between proteins and their interacting partners underlies the biochemistry of living organisms. Specificity in this recognition is thought to be essential, whereas promiscuity is often associated with unwanted side effects, poor catalytic properties and errors in biological function. Recent experimental evidence suggests that promiscuity, not only in interactions but also in the actual function of proteins, is not as rare as was previously thought. This has implications not

only for our fundamental understanding of molecular recognition and how protein function has evolved over time but also in the realm of biotechnology.
Understanding protein promiscuity is becoming increasingly important not only to optimize protein engineering applications in areas as diverse as synthetic biology and metagenomics but also to lower attrition rates in drug discovery programs, identify drug interaction surfaces less susceptible to escape mutations and potentiate the power of polypharmacology.

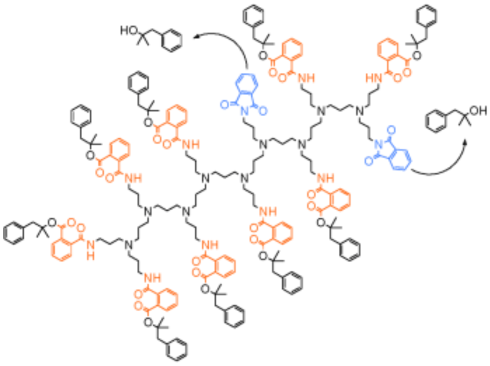
- Dislocation theory of chirality-controlled nanotube growth
  Ding, F.; Harutyunyan, A. R.; Yakobson, B. I. *Proc. Nat. Acad. Sci.* **2009**, *106*, 2506–2509.
  Abstract:





The periodic makeup of carbon nanotubes suggests that their formation should obey the principles established for crystals. Nevertheless, this important connection remained elusive for decades and no theoretical regularities in the rates and product type distribution have been found. Here we contend that any nanotube can be viewed as having a screw dislocation along the axis. Consequently, its growth rate is shown to be proportional to the Burgers vector of such dislocation and therefore to the chiral angle of the tube. This is corroborated by the ab initio energy calculations, and agrees surprisingly well with diverse experimental measurements, which shows that the revealed kinetic mechanism and the deduced predictions are remarkably robust across the broad base of factual data.

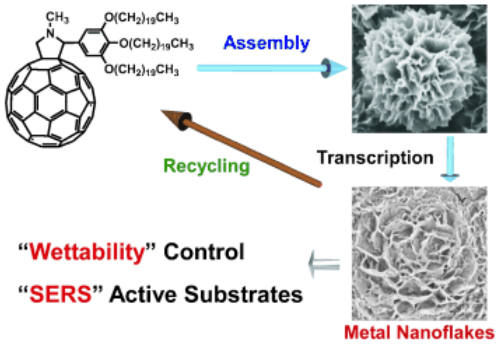
- Parameters Influencing the Release of Tertiary Alcohols from the Surface of “Spherical” Dendrimers and “Linear” Stylomers by Neighbouring-Group-Assisted Hydrolysis of 2-Carbamoylbenzoates
  Trachsel, A.; de Saint Laumer, J.-Y.; Haefliger, O. P.; Herrmann, A. *Chem. Eur. J.* **2009**, *15,* 2846-2860.
  Abstract:



Size is not all! Investigation of the controlled release of tertiary alcohols from the surface of dendrimers and “stylomers” as polymer model systems (see scheme) showed that the polarity of the conjugates and structural modifications in close proximity to the release unit have a stronger influence on the rates of hydrolysis than the size (generation) or shape (linear or spherical) of the macromolecules.

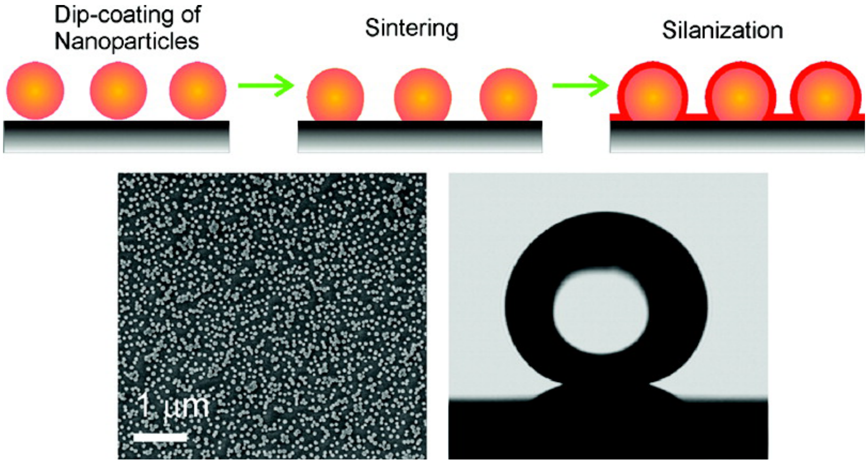
The influence of structural and physico-chemical parameters on the release of a volatile tertiary alcohol (2-methyl-1-phenyl-2-propanol) by neighbouring-group-assisted cyclisation of 2-carbamoylbenzoates at neutral pH was investigated by comparing the covalent-bond cleavage from the surface of linear, comblike poly(propylene imine) “stylomers” and their corresponding spherical, globular dendrimers. Determination of the kinetic rate constants for the stepwise intramolecular cyclisation of the 2-carbamoylbenzoate moiety by using HPLC showed that the polarity of the conjugates, and thus their solubility in the aqueous reaction medium, has a stronger influence on the rates of hydrolysis than the size (generation) or shape (linear or spherical) of the macromolecules. Furthermore, structural modifications in close proximity to the release unit, such as the presence of functionalities with catalytic activity, have a strong impact on the release efficiency of the active molecules. An understanding of the physico-chemical parameters determining the local environment of the covalent-bond cleavage site is therefore an important prerequisite to transfer the characteristics of small molecules to larger structures such as oligomers and polymers and thus to design efficient macromolecular conjugates for the controlled delivery of bioactive compounds.

- Supramolecular Templates for Nanoflake-Metal Surfaces
  Shen, Y.; Wang, J.; Kuhlmann, U.; Hildebrandt, P.; Ariga, K.; Möhwald, H.; Kurth, D. G.; Nakanishi, T. *Chem. Eur. J.* **2009**, *15*, 2763-2767.
  Abstract:



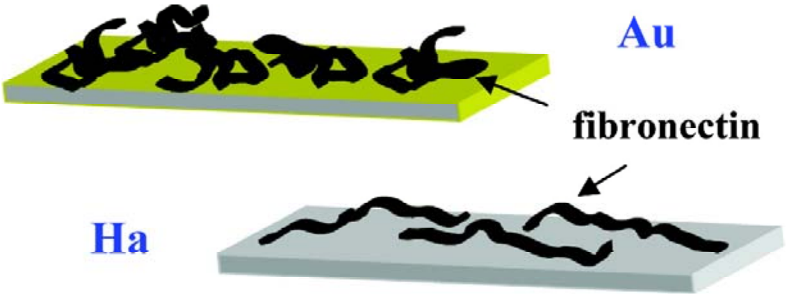
A sustainable method for the fabrication of metallic surfaces with flower-like fractal morphology was developed by using a three-dimensional supramolecular assembly as a template. Modifying Au nanoflakes with self-assembled monolayers or polymers allows the surface wettability to be adjusted from superhydrophobic to superhydrophilic (see figure). Furthermore, Au nanoflakes present excellent substrates for surface-enhanced Raman spectroscopy (SERS).

- Stable and Transparent Superhydrophobic Nanoparticle Films
  Ling, X. Y.; Phang, I. Y.; Vancso, G. J.; Huskens, J.; Reinhoudt, D. N. *Langmuir* **2009**, *25*, 3260-3263.
  Abstract:



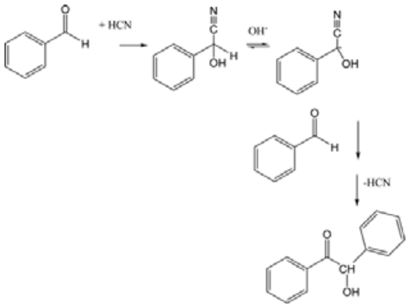
A superhydrophobic surface with a static water contact angle (θ_w) > 150° was created by a simple "dip-coating" method of 60-nm SiO_2 nanoparticles onto an amine-terminated (NH_2) self-assembled monolayer (SAM) glass/silicon oxide substrate, followed by chemical vapor deposition of a fluorinated adsorbate. For comparison, a close-packed nanoparticle film, formed by convective assembly, gave θ_w ~120°. The stability of the superhydrophobic coating was enhanced by sintering of the nanoparticles in an O_2 environment at high temperature (1100 °C). A sliding angle of <5° indicated the self-cleaning properties of the surface. The dip-coating method can be applied to glass substrates to prepare surfaces that are superhydrophobic and transparent.

- Enhanced Surface Activation of Fibronectin upon Adsorption on Hydroxyapatite
  Dolatshahi-Pirouz, A.; Jensen, T.; Foss, M.; Chevallier, J.; Besenbacher, F. *Langmuir* **2009**, *25*, 2971-2978.
  Abstract:



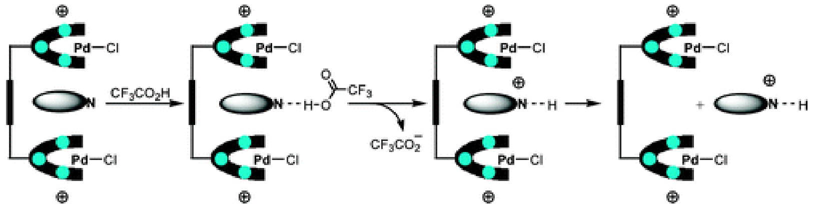
In this study the adsorption characteristics and the structure of fibronectin adsorped on hydroxyapatite (Ha) and a reference gold substrate (Au) is examined by quartz crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM) at the following concentrations: 20 μg/mL, 30 μg/mL, 40 μg/mL, 100 μg/mL, 200 μg/mL, and 500 μg/mL. The conformational changes of the fibronectin molecules upon surface binding were examined as well with monoclonal antibody directed against the cell binding-domain (CB domain) of fibronectin. The QCM-D and AFM results show that the fibronectin uptake is larger on Au as compared with Ha regardless of the protein bulk concentration used in the experiment, suggesting that the individual fibronectin molecules in general attach to the surfaces in a more unfolded configuration on Ha. Moreover the dissipation values obtained with QCM-D indicate that the individual fibronectin molecules bind in a more compact and rigid configuration on Au compared to the Ha surface. In particular the monoclonal antibody data show that the CB domain on fibronectin is more available on Ha, where such cell-recognizing abilities are more pronounced at low fibronectin surface coverage. The results demonstrate that the detailed molecular structure of fibronectin and its functional activity depend significantly on both the underlying surface chemistry as well as the fibronectin surface coverage.

- Thiamin Diphosphate Catalysis: Enzymic and Nonenzymic Covalent Intermediates.
  Kluger, R.; Tittmann, K. *Chem. Rev.* **2008***, 108,* 1797-1833.
  Abstract:



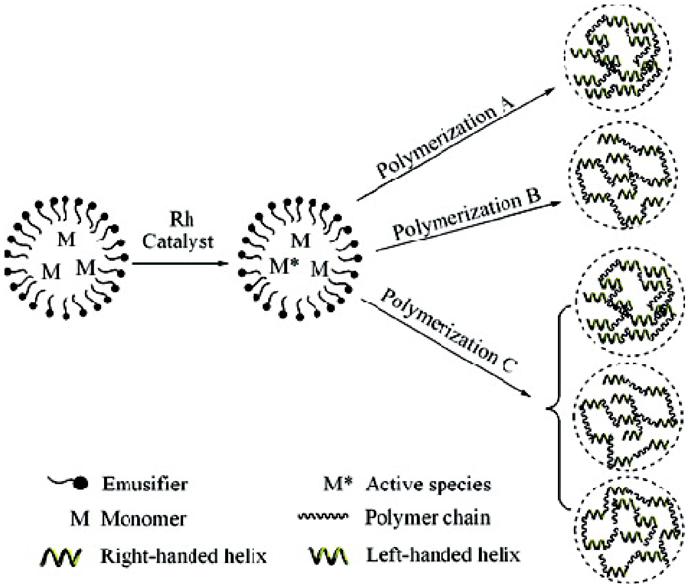
The idea of "reasonableness" of organic reactions is based on recorded evidence of reaction patterns. The logical patterns are organized based on structural and functional group relationships. Thermal decarboxylation ordinarily requires that the departing carboxyl group be in conjugation with an unsaturated functional group, permitting transition state stabilization of the incipient delocalized carbanion which becomes protonated. (In practical terms of synthesis, decarboxylation in the absence of conjugation requires a procedure involving silver salts, halogens, and free radical mechanisms.) Biochemical pathways are understood as direct analogies to organic chemical reactions, with enzymes serving as effective catalysts in reducing the energies of transition states. Decarboxylation of pyruvate is a common primary metabolic process whose outcome amounts to electrophilic substitution at an acyl carbon. The early discovery of this reaction was the source of extensive chemical speculation since it is outside the established pattern of spontaneous decarboxylation processes. If such a reaction were to occur by a simple exchange of electrophiles, the intermediate would be an acyl carbanion, a species that is too high in energy to exist as an intermediate. While enzymes may stabilize high energy species they also utilize indirect pathways that involve stabilized conjugates and associated transition states. In the case of the decarboxylation of pyruvate, addition of enzyme-bound thiamin diphosphate (TDP) to the carbonyl group of the substrate provides an intermediate whose decarboxylation produces a stabilized intermediate

- Square-Planar Pd(II), Pt(II), and Au(III) Terpyridine Complexes: Their Syntheses, Physical Properties, Supramolecular Constructs, and Biomedical Activities.
  Eryazici, I.; Moorefield, C. N. Newkome G. R. *Chem. Rev.* **2008***, 108,* 1834-1895.
  Abstract:



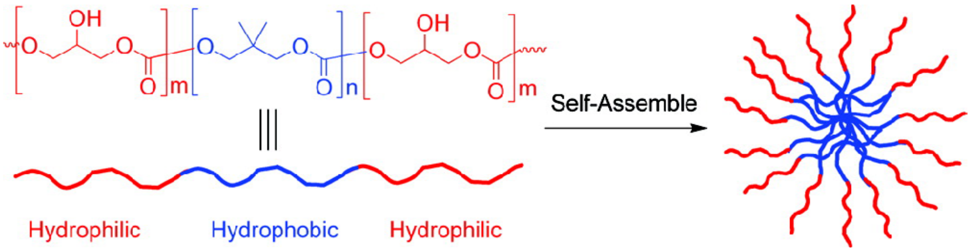
Metal–ligand interactions are inherent in a succession of important self-assembly strategies used in supramolecular chemistry. To this extent, the development of chelating ligands and their transition metal complexes has been of increasing interest. Since the 1980s, terpyridine ligands have been intensely studied specifically for their octahedral complexes with various transition metals, for example, Fe(II), Ru(II), Zn(II), and so forth, in order to capitalize their unique photophysical, electrochemical, magnetic, and optical properties. In the 1970s, terpyridines were also found to form stable square-planar complexes with d8 late transition metal ions, such as Pt(II), Pd(II), and Au(III). Later in the 1990s, the Pt(II), as opposed to Pd(II) and Au(III), terpyridine complexes were extensively investigated due to their unique luminescent properties offering potential applications in chemosensing for solvents and metal ions, photocatalysis and biological activities, such as DNA intercalation and covalent binding to biomolecules with potential applications, as antitumor, radiotherapy, antiprotozoal agents and protein probes. In turn, Pd(II) terpyridine complexes have been utilized as supramolecular recognition centers and the Au(III) complexes have been demonstrated to possess antitumor activity. Whereas octahedral terpyridine complexes have been surveyed, this review is directed at syntheses, physical and structural properties, supramolecular chemistry, and biomedical applications of the interesting square-planar terpyridine complexes.

- Synthesis of Nano-Latex Particles of Optically Active Helical Substituted Polyacetylenes via Catalytic Microemulsion Polymerization in Aqueous Systems.
  Deng, J.; Chen, B.; Luo, X.; Yang, W. *Macromolecules* **2009**, *42*, 933-938.
  Abstract:



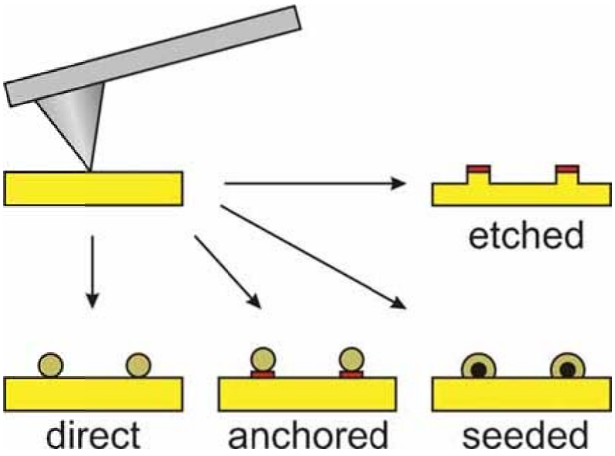
This article reports on the first catalytic microemulsion polymerizations of substituted acetylenes in aqueous medium, providing nanoscale particles exhibiting optical activities and consisting of helical polymers. Three types of substituted acetylenessone achiral *N*-propargylamide, two chiral *N*-propargylsulfamides, and chiral *N*-propaygylureas were polymerized in the presence of hydrophobic Rh-based catalyst and with SDS as emulsifier and DMF as coemulsifier. Such microemulsion polymerizations led to nanoscale particles (70-110 nm in diameter) of polymers adopting helical conformations. The particles derived from the chiral monomers showed large specific rotations and intense circular dichroism (CD) signals. The obtained polymer dispersions demonstrated high stability. The thus-prepared polymers after removing the emulsifier and coemulsifier showed much stronger CD signals, and the helices were found to have higher thermal stability when compared with the corresponding polymers synthesized via catalytic polymerizations in organic solvents. The microemulsion polymerizations enable the polymers to form predominantly one-handed helical structures. The possible mechanisms were proposed for the formation of optically active polymer particles, for the formation of predominantly one-handed helices, and for the increased thermal stability of the helices formed in the polymers.

- Amphiphilic Triblock Copolycarbonates with Poly(glycerol carbonate) as Hydrophilic Blocks.
  Zhang, X.; Mei, H.; Hu, C.; Zhong, Z.; Zhuo, R. *Macromolecules* **2009**, *42*, 1010-1016.
  Abstract:



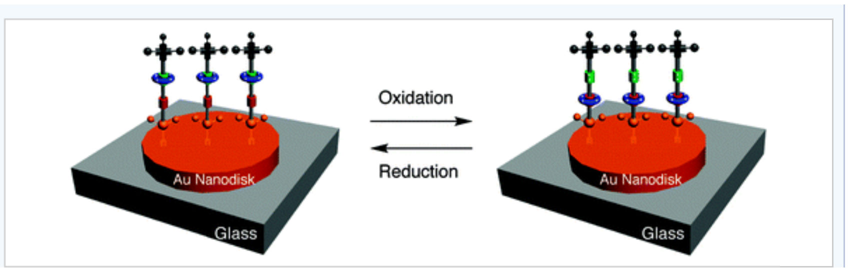
Amphiphilic triblock copolycarbonates poly(glycerol carbonate-*b*-DTC-*b*-glycerol carbonate) with poly(glycerol carbonate) chains as the hydrophilic blocks were designed and synthesized. In the first step, the PDTC diol macroinitiators were synthesized via bulk polymerization of DTC with 1,6-hexanediol as an initiator and Sn(Oct)2 as a catalyst. Then the amphiphilic triblock copolycarbonates were synthesized via cationic ringopening polymerization of 2-benzyloxytrimethylene carbonate (BTMC) with PDTC diol as a macroinitiator and fumaric acid as a catalyst, followed by a hydrogenolytic deprotection reaction with Pd-C as a catalyst in an autoclave. The amphiphilic triblock copolymers were characterized by 1H NMR, 13C NMR, GPC, DSC, and water contact angle. The self-assemble behavior of the amphiphilic triblock copolycarbonate in deuterated solvents monitored by 1H NMR showed a strong incompatibility of the two segments. Stable micelle solution of the amphiphilic triblock copolycarbonate in water was prepared by adding water to a THF solution of the polymer followed by removal of the organic solvent by rota-evaporation. Dynamic light scattering measurement showed that the micelle had a narrow unimodal size distribution. Drug-loading properties of the copolycarbonate micelles were tested with prednisone acetate as a model drug.

- Dip-Pen-Nanolithographic Patterning of Metallic, Semiconductor, and Metal Oxide Nanostructures on Surfaces
  Basnar, B.; Willner, I. *Small* **2009**, *5*, 28-44.
  Abstract:



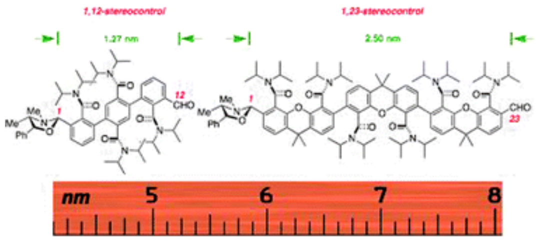
Dip-pen nanolithography (DPN) is a powerful method to pattern nanostructures on surfaces by the controlled delivery of an "ink" coating the tip of an atomic force microscope upon scanning and contacting with surfaces. The growing interest in the use of nanoparticles as structural and functional elements for the fabrication of nanodevices suggests that the DPN-stimulated patterning of nanoparticles on surfaces might be a useful technique to assemble hierarchical architectures of nanoparticles that could pave methodologies for functional nanocircuits or nanodevices. This Review presents different methodologies for the nanolithographic patterning of metallic, semiconductor, and metal oxide nanostructures on surfaces. The mechanisms involved in the formation of the nanostructures are discussed and the effects that control the dimensions of the resulting patterns are reviewed. The possible applications of the nanostructures are also addressed.

- Active Molecular Plasmonics: Controlling Plasmon Resonances with Molecular Switches
  Zheng, Y. B.; Yang, Y.-W.; Jensen, L.; Fang, L.; Juluri, B. K.; Flood, A. H.; Weiss, P. S.; Stoddart, J. F.; Huang, T. J. *Nano Lett.* 2009, *9*, 819–825.
  Abstract:



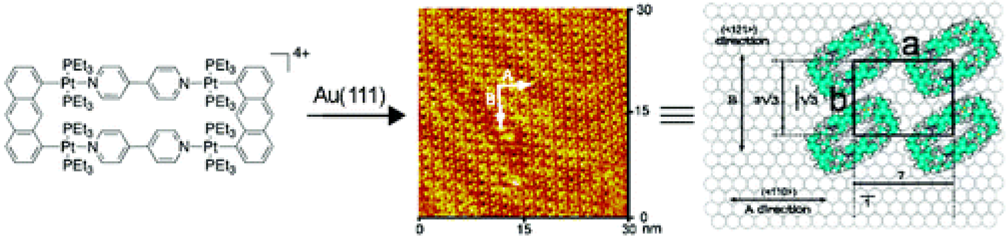
A gold nanodisk array, coated with bistable, redox-controllable [2]rotaxane molecules, when exposed to chemical oxidants and reductants, undergoes switching of its plasmonic properties reversibly. By contrast, (i) bare gold nanodisks and (ii) disks coated with a redox-active, but mechanically inert, control compound do not display surface-plasmon-based switching. Along with calculations based on time-dependent density functional theory, these experimental observations suggest that the nanoscale movements within surface-bound "molecular machines" can be used as the active components in plasmonic devices.

- Transmission of stereochemical information over nanometre distances in chemical reactions
  Clayden, J. *Chem. Soc. Rev.* **2009**, *38*, 817 – 829.
  Abstract:



By exploiting intramolecular interactions such as dipole repulsion, and by incorporating a terminal chiral controlling feature, the global conformation of a molecule may be governed. In such an environment, stereoselective reactions can occur at considerable distances from the source of stereochemical information, providing a simple method for information relay over scales of >1 nm (or about seven bond lengths). This *tutorial review* discusses the development of this idea, and describes examples which depend on relayed dipole repulsion and on the absolute control of helicity. Future prospects in the area employing control over extended helical foldamers are elaborated.

- Surface Confined Metallosupramolecular Architectures: Formation and Scanning Tunneling Microscopy Characterization
  Li, S.-S.; Northrop, B. H.; Yuan, Q.-H.; Wan, L.-J.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 249–259.
  Abstract:



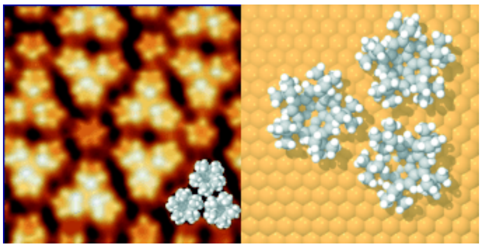
Metallosupramolecular compounds have attracted a great deal of attention over the past two decades largely because of their unique, highly complex structural characteristics and their potential electronic, magnetic, optical, and catalytic properties. These molecules can be prepared with relative ease using coordination-driven self-assembly techniques. In particular, the use of electron-poor square-planar Pt(II) transition metals in conjunction with rigid, electron-rich pyridyl donors has enabled the spontaneous self-assembly of a rich library of 2D metallacyclic and 3D metallacage assemblies via the directional-bonding approach. With this progress in the preparation and characterization of metallosupramolecules, researchers have now turned their attention toward fully exploring and developing their materials properties.

Assembling metallosupramolecular compounds on solid supports represents a vitally important step toward developing their materials properties. Surfaces provide a means of uniformly aligning and orienting these highly symmetric metallacycles and metallacages. This uniformity increases the level of coherence between molecules above that which can be achieved in the solution phase and provides a way to integrate adsorbed layers, or adlayers, into a solid-state materials setting. The dynamic nature of kinetically labile Pt(II)−N coordination bonds requires us to adjust deposition and imaging conditions to retain the assemblies' stability. Toward these aims, we have used scanning tunneling microscopy (STM) to image these adlayers and to understand the factors that govern surface self-assembly and the interactions that influence their structure and stability.

This Account describes our efforts to deposit 2D rectangular and square metallacycles and 3D trigonal bipyramidal and chiral trigonal prism metallacages on highly oriented pyrolytic graphite

(HOPG) and Au(111) substrates to give intact assemblies and ordered adlayers. We have investigated the effects of varying the size, symmetry, and dimensionality of supramolecular adsorbates, the choice of substrate, the use of a molecular template, and the effects of chirality. Our systematic investigations provide insights into the various adsorbate−adsorbate and substrate−adsorbate interactions that largely determine the architecture of each assembly and affect their performance in a materials setting. Rational control over adlayer formation and structure will greatly enhance the potential of these supramolecules to be used in a variety of applications such as host−guest sensing/diagnostic systems, molecular electronic devices, and heterogeneous stereoselective synthesis and catalysis.

- Self-Assembly of Fivefold-Symmetric Molecules on a Threefold-Symmetric Surface
  Guillermet, O.; Niemi, E.; Nagarajan, S.; Bouju, X.; Martrou, D.; Gourdon, A.; Gauthier, S. *Angew. Chem. Int. Ed.* **2009**, 48, 1970 –1973.
  Abstract:



Buckybowls: The adsorption of penta-*tert*-butylcorannulene, a molecule with fivefold symmetry, on Cu(111), a surface with threefold symmetry, is investigated by scanning tunneling microscopy complemented by structure calculations. The symmetry mismatch is resolved by the formation of threefold-symmetric subunits consisting of three molecules, which combine with single molecules to form a nearly perfect filling of the plane (see picture).