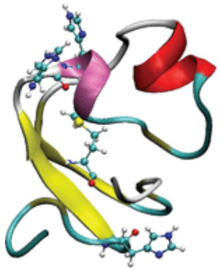
- The chemistry of Alzheimer's disease
  Rauk, A. *Chem. Soc. Rev.* **2009**, *38*, 2698 – 2715.
  Abstract:

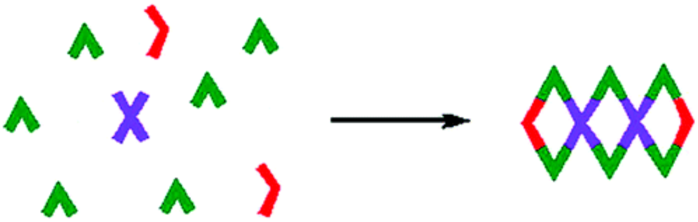


The chemistry of Alzheimer's disease is largely centred on the amyloid β-peptide, its formation, structure, and interactions with metals, membranes, proteins and other species. This *critical review* summarizes the current state of knowledge (252 references).

- Combining transition metal catalysis and organocatalysis: a broad new concept for catalysis
  Shao, Z.; Zhang, H. *Chem. Soc. Rev.* **2009**, *38*, 2745 – 2755.
  Abstract:

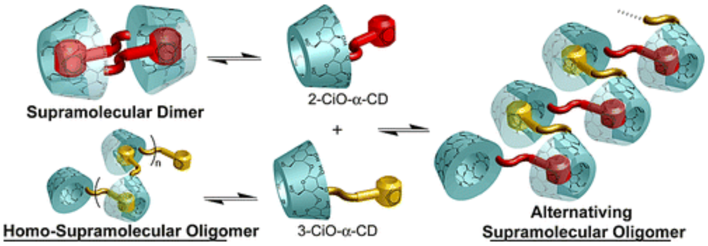
In recent years, the concept of combining transition metal catalysis and organocatalysis has emerged as a promising strategy for developing new and valuable reactions, and has attracted considerable attention as it could potentially enable unprecedented transformations not currently possible by use of the transition metal complex or the organocatalyst alone. In this *critical review*, this strategy is illustrated with several recent outstanding examples, with the aim of shedding light on the synthetic utilities and potentials of this concept as a novel tool in organic synthesis (118 references).

- Stoichiometric Control of Multiple Different Tectons in Coordination-Driven Self-Assembly: Preparation of Fused Metallacyclic Polygons
  Lee, J.; Ghosh, K.; Stang, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 12028–12029.
  Abstract:



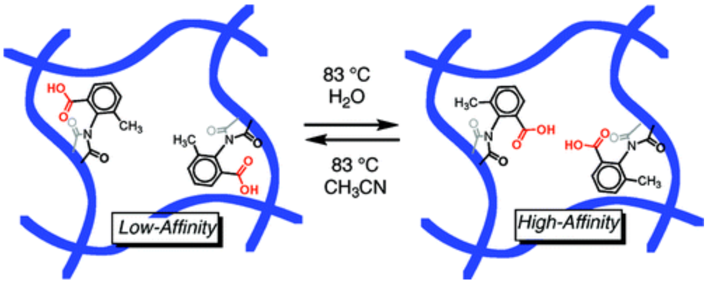
We present a general strategy for the synthesis of stable, multicomponent fused polygon complexes in which coordination-driven self-assembly allows for single supramolecular species to be formed from multicomponent self-assembly and the shape of the obtained polygons can be controlled simply by changing the ratio of individual components. The compounds have been characterized by multinuclear NMR spectroscopy and electrospray ionization mass spectrometry.

- Social Self-Sorting: Alternating Supramolecular Oligomer Consisting of Isomers
  Tomimasu, N.; Kanaya, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2009**, *131*, 12339–12343.
  Abstract:



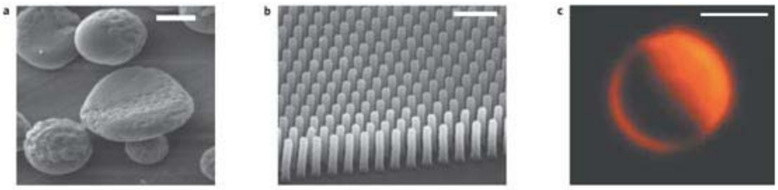
The isomers of cinnamoyl α-CDs (2-CiO-α-CD and 3-CiO-α-CD) organize by themselves to give different types of supramolecular complexes in aqueous solutions. 2-CiO-α-CD was found to form a double-threaded dimer, which was characterized by single crystal X-ray analysis. The molecular sizes of supramolecular complexes consisting of CiO-α-CDs were estimated by pulsed field gradient spin−echo NMR, which gives the diffusion coefficient (D). D of 2-CiO-α-CD was found to be 2.3 × 10−10 m^2/s at concentrations over 10 mM and D was saturated. It should be noted that the hydrodynamic radius derived from D of 2-CiO-α-CD was found to be 9.6 Å, which closely matched the result from the single crystal X-ray analysis. D of 3-CiO-α-CD, however, was smaller than that of 2-CiO-α-CD at concentrations over 32 mM, indicating that 3-CiO-α-CD formed a supramolecular oligomer. Two-dimensional (2D)-ROESY spectra of the mixture of 2-CiO-α-CD and 3-CiO-α-CD did not show a correlation between the same species; rather, correlation peaks between 2-CiO-α-CD and 3-CiO-α-CD were observed. D’s of a mixture of 2-CiO-α-CD and 3-CiO-α-CD were found to be larger than those of 2-CiO-α-CD and 3-CiO-α-CD, respectively, indicating that the mixture of 2-CiO-α-CD and 3-CiO-α-CD formed an alternative supramolecular oligomer and not a self- or random- supramolecular complex. CDs recognize a guest molecule and the substitutional position of a guest molecule on CD, suggesting that CDs have social self-sorting capability.

- Solvent Programmable Polymers Based on Restricted Rotation
  Zhang, Y.; Lavin, J. M.; Shimizu, K. D. *J. Am. Chem. Soc.* **2009**, *131*, 12062–12063.
  Abstract:



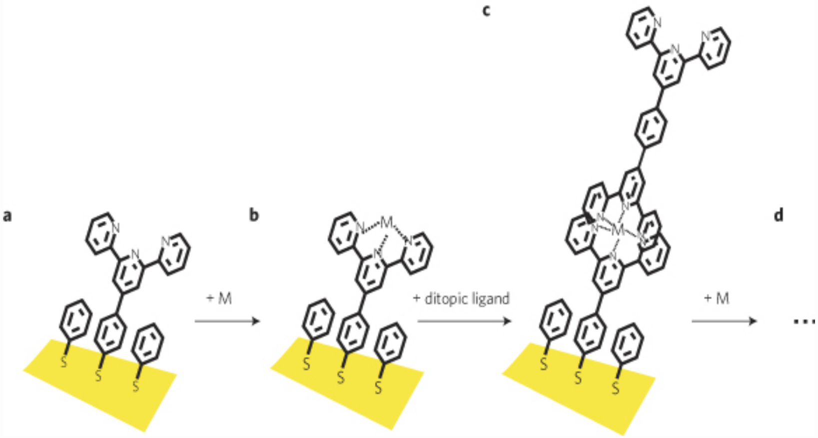
Solvent programmable polymers (SPPs) were developed that can modulate their recognition properties by heating in different solvents. These highly cross-linked polymer gels were able to respond to differences in solvent polarity at elevated temperatures via rotation about a C_{aryl}−N_{imide} bond of a carboxylic acid monomer. When heated in polar solvents such as water, the number of solvent accessible carboxylic acids in the polymers increases. When heated in nonpolar solvents such as toluene, the number of solvent accessible carboxylic acids decreases. On cooling to rt, these changes are preserved and maintained even when the polymer is removed from the solvent imprinting environment. The solvent memory is due to the reestablishement of restricted rotation around that C_{aryl}–N_{imide} bond, which locks the carboxylic acid recognition groups into either a solvent accessible or inaccessible orientation. The solvent programmability was also shown to be reversible. The fidelity of the SPP switching process did not decrease after five cycles of heating in polar and nonpolar solvents.

- Physical approaches to biomaterial design
  Mitragotri, S.; Lahann, J. *Nature Materials* **2009**, *8*, 15-23.
  Abstract:



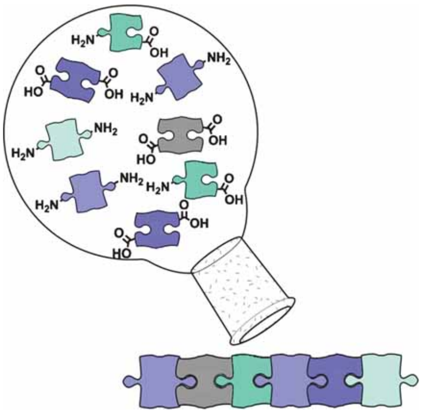
The development of biomaterials for drug delivery, tissue engineering and medical diagnostics has traditionally been based on new chemistries. However, there is growing recognition that the physical as well as the chemical properties of materials can regulate biological responses. Here, we review this transition with regard to selected physical properties including size, shape, mechanical properties, surface texture and compartmentalization. In each case, we present examples demonstrating the significance of these properties in biology. We also discuss synthesis methods and biological applications for designer biomaterials, which offer unique physical properties.

- Highly conductive ~40-nm-long molecular wires assembled by stepwise incorporation of metal centres
  Tuccitto, N.; Ferri, V.; Cavazzini, M.; Quici, S.; Zhavnerko, G.; Licciardello, A.; Rampi, M. A. *Nature Materials* **2009**, *8*, 41-46.
  Abstract:



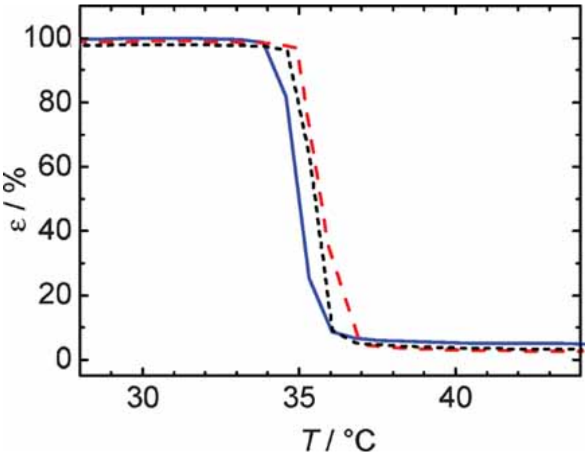
One of the main goals of molecular electronics is to achieve electronic functions from devices consisting of tailored organic molecules connecting two metal electrodes. The fabrication of nanometre-scale spaced electrodes still results in expensive, and often scarcely reproducible, devices. On the other hand, the 'conductance' of long organic molecules—generally dominated by the tunnelling mechanism—is very poor. Here, we show that by incorporating a large number of metal centres into rigid molecular backbones we can obtain very long (up to 40 nm) and highly 'conductive' molecular wires. The metal-centre molecular wires are assembled in situ on metal surfaces via a sequential stepwise coordination of metal ions by terpyridine-based ligands. They form highly ordered molecular films of elevated mechanical robustness. The electrical properties, characterized by a junction based on Hg electrodes, indicate that the 'conductance' of these metal-centre molecular wires does not decrease significantly even for very long molecular wires, and depends on the nature of the incorporated redox centre. The outstanding electrical and mechanical characteristics of these easy-to-assemble molecular systems open the door to a new generation of molecular wires, able to bridge large-gap electrodes, and to form robust films for organic electronics.

- Precision Polymers: Monodisperse, Monomer-Sequence-Defined Segments to Target Future Demands of Polymers in Medicine
  Hartmann, L.; Börnerm H.G. *Adv. Mater.* **2009,** 3425-3431.
  Abstract:



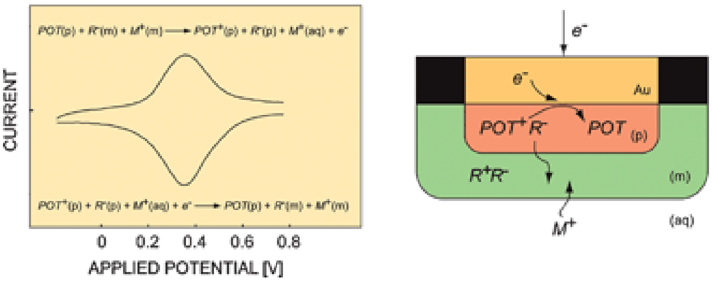
The sequential assembly of synthetic monomers from a library of building blocks leads to monodisperse polymer platforms. Such precision polymers allow for the accurate correlation of monomer sequence and (bio)properties, providing precisely adaptable model systems to deepen insight into interactions of polymers and biosystems.

- Polymer Networks Combining Controlled Drug Release, Biodegradation, and Shape Memory Capability
  Neffe, A.T.; Hanh, B.D.; Steuer, S.; Lendleinm, A. *Adv. Mater.* **2009,** 3394-3398.
  Abstract:



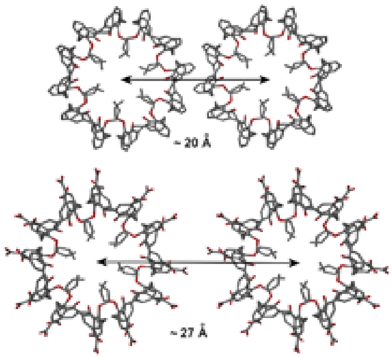
A triple functional polymer network system that combines shape-memory capability, biodegradability, and drug release is developed. The choice of network structure and switching segment prevent that drug incorporation substantially changes the thermal and mechanical properties as well as the shape-memory functionality (see recovery curves). A diffusion-controlled release that is independent from biodegradation is enabled.

- Thin layer electrochemical extraction of non-redoxactive cations with an anion-exchanging conducting polymer overlaid with a selective membrane.
  Si, P.; Bakker, E. *Chem. Commun.* **2009**, 5260 – 5262.
  <u>Abstract :</u>



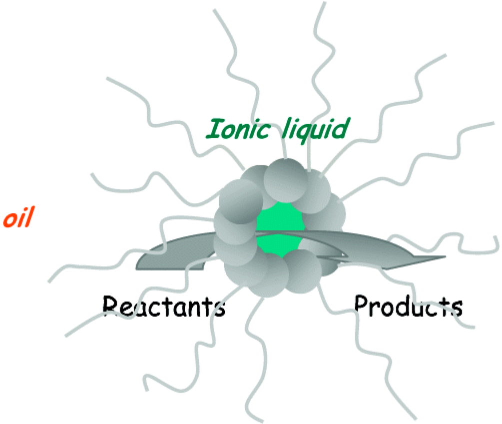
We report here on the selective voltammetric cation transfer into a polymeric thin layer film that is back side contacted with an anion-exchanging conducting polymer, poly(3-octylthiophene).

- Modulation of nanotube packing through the controlled self-assembly of tris-p-carboxylatocalix[4]arenes.
  Kennedy, S.; Dalgarno, S. J. *Chem. Commun.* **2009**, 5275 – 5277.
  <u>Abstract :</u>



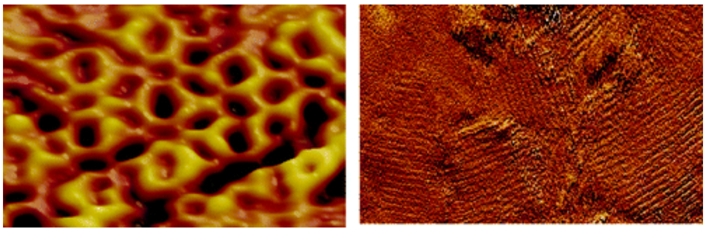
Crystallisation of tris-carboxylatocalix[4]arenes from pyridine affords self-assembled layered and triply helical nanotubular arrays; the latter of these represents a modulation of nanotubule spacing in a persistent self-assembly motif.

- Ionic Liquid/Oil Microemulsions as Chemical Nanoreactors
  Gayet, F.; El Kalamouni, C.; Lavedan, P.; Marty, J.-D.; Brûlet, A.; Lauth-de Viguerie, N. *Langmuir* **2009**, *25*, 9741–9750.
  <u>Abstract:</u>



The phase diagram and microstructure of the ternary system ionic, liquid benzylpyridinium bis(trifluoromethanesulfonyl) imide)/nonionic surfactant (octylphenol ethoxylate)/toluene, were studied by using conductivity measurements, dynamic light scattering, pulse field gradient spin-echo NMR, and small-angle neutron scattering. Three microregions were identified by conductivity measurements according to the percolation theory. The sizes of ILin- oil microemulsions with various IL fractions were then determined by NMR and DLS and were found to be in accordance with the radii of gyration (approximately 2 or 3 nm) determined by SANS. The reverse IL-in-oil microemulsions were used as nanoreactors to perform a Matsuda-Heck reaction between p-methoxyphenyl diazonium salt and 2,3-dihydrofurane in the presence of a palladium catalyst. The reaction yields obtained were greater in microemulsions (67%) than in bulk IL (33%), highlighting a strong effect of confinement. Moreover, a direct correlation between the quantity of IL and the reaction yield was observed.

- In Vivo Imaging of S-Layer Nanoarrays on Corynebacterium glutamicum
  Dupres, V.; Alsteens, D.; Pauwels, K.; Dufrêne, Y. F. *Langmuir* **2009**, *25*, 9653–9655.
  Abstract:



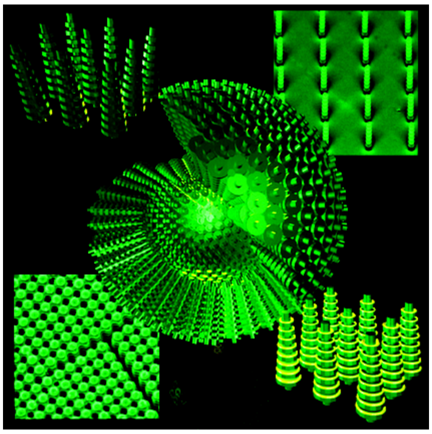
Crystalline bacterial cell surface layers (S-layers) are monomolecular arrays of (glyco)proteins that have recently produced a wealth of new opportunities in nanotechnology. Whereas the in vitro imaging of isolated S-layers is well established, their direct imaging on live cells remains very challenging. Here we use atomic force microscopy (AFM) to visualize S-layer nanoarrays on living Corynebacterium glutamicum bacteria. We demonstrate the presence of two highly ordered surface layers. The most external layer represents the hexagonal S-layer, and the inner layer displays regular patterns of nanogrooves that could act as a biomolecular template promoting the 2-D assembly of S-layer monomers.

These nanoscale analyses open new avenues for understanding the structure of protein monomolecular arrays, which is a crucial challenge in current nanoscience and life science research.

- Highly Ordered Conjugated Polymer Nanoarchitectures with Three-Dimensional Structural Control

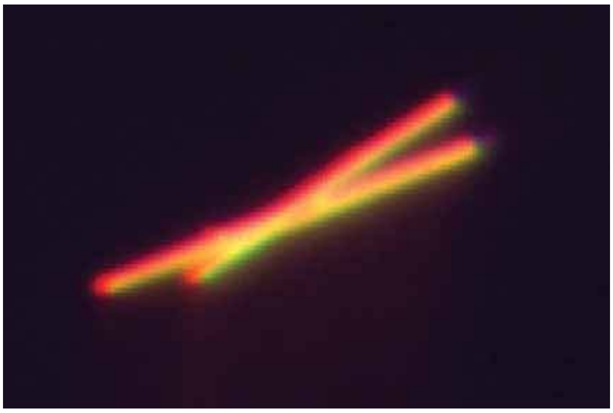
Vlad, A.; Dutu, C. A.; Guillet, P.; Jedrasik, P.; Fustin, C.-A.; Södervall, U.; Gohy, J.-F.; Melinte, S. *Nano Lett.* **2009**, *9,* 2838–2843.

Abstract:



Conductive polymers are a class of materials with vast potential for tomorrow's ultra-large-scale technologies as they combine structural and functional diversity with flexible synthesis and processing approaches. A missing component, with their subtle chemical structure, is reliable building at nanoscale. Here we report on the patterning of polyaniline, a prototypical conjugated polymer, with an unprecedented areal patterning order and density exceeding 0.25 teradot/inch^2. With template-confined growth, through platinum-surface-catalyzed polymerization of aniline, highly ordered arrays of distinct polyaniline nanowires are produced with a typical diameter ≤15 nm and aspect ratio higher than 20. Up-scaling is straightforward. Complex three-dimensional structural control is achieved through a direct pattern transfer via resist- and dose-modulated electron beam lithography. The morphology-modulated nanowires self-assemble in key−lock type architectures induced by the structure asymmetry and nonuniformity of the capillary forces associated with the re-entrant features.

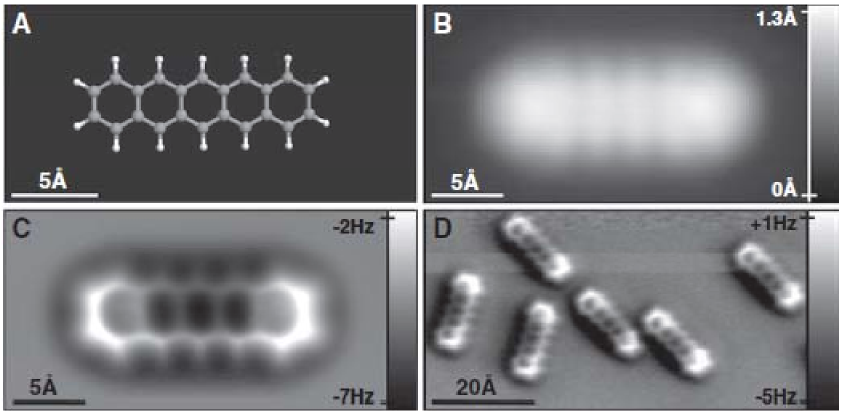
- Nanoscale Ampoule Fabrication by Capillary Autoclosing
  Bae, C.; Kim, H.; Han, D.; Yoo, H.; Kim, J.; Shin, H. *Small* **2009**, *5*, 1936-1941.
  Abstract:



The open ends of oxide nanotubes (NTs) can be sealed with silica at room temperature and pressure after incorporation of desired materials into the NTs, the payload volume of which is adjustable (see picture for the case of fluorophores). This process originates from a synergetic reaction of capillary-condensed water and silicon reactants, which rapidly produces silica at the ends of the NTs.

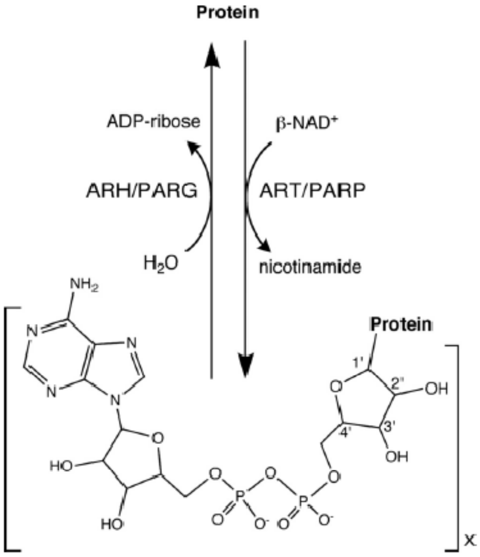
- The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy

Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G. *Science* **2009**, *325*, 1110-1114.
Abstract:



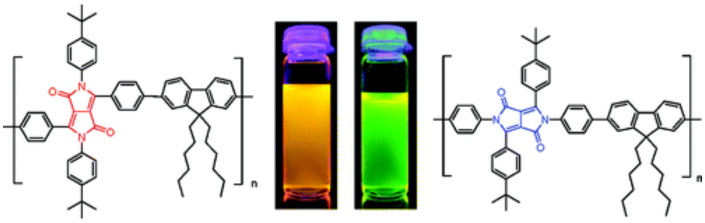
Resolving individual atoms has always been the ultimate goal of surface microscopy. The scanning tunneling microscope images atomic-scale features on surfaces, but resolving single atoms within an adsorbed molecule remains a great challenge because the tunneling current is primarily sensitive to the local electron density of states close to the Fermi level. We demonstrate imaging of molecules with unprecedented atomic resolution by probing the short-range chemical forces with use of noncontact atomic force microscopy. The key step is functionalizing the microscope's tip apex with suitable, atomically well-defined terminations, such as CO molecules. Our experimental findings are corroborated by ab initio density functional theory calculations. Comparison with theory shows that Pauli repulsion is the source of the atomic resolution, whereas van der Waals and electrostatic forces only add a diffuse attractive background.

- Mechanism of ADP-ribosylation removal revealed by the structure and ligand complexes of the dimanganese mono-ADP-ribosylhydrolase DraG
  Berthold, C. L.; Wang, H.; Nordlund, S.; Högbom, M. *Proc. Nat. Acad. Sci.* **2009**, *106*, 14247–14252.
  Abstract:



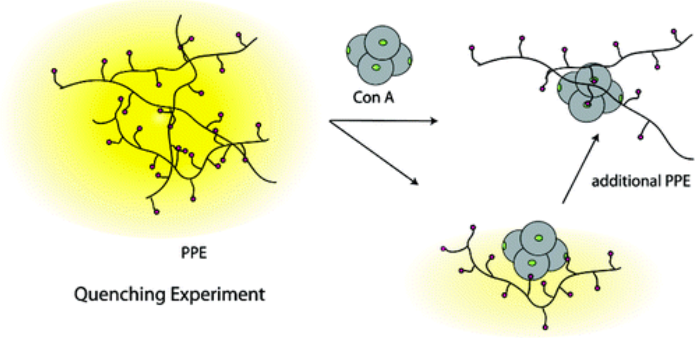
ADP-ribosylation is a ubiquitous regulatory posttranslational modification involved in numerous key processes such as DNA repair, transcription, cell differentiation, apoptosis, and the pathogenic mechanism of certain bacterial toxins. Despite the importance of this reversible process, very little is known about the structure and mechanism of the hydrolases that catalyze removal of the ADP-ribose moiety. In the phototrophic bacterium *Rhodospirillum rubrum*, dinitrogenase reductase-activating glycohydrolase (DraG), a dimanganese enzyme that reversibly associates with the cell membrane, is a key player in the regulation of nitrogenase activity. DraG has long served as a model protein for ADP-ribosylhydrolases. Here, we present the crystal structure of DraG in the holo and ADP-ribose bound forms.Wealso present the structure of a reaction intermediate analogue and propose a detailed catalytic mechanism for protein de-ADP-ribosylation involving ring opening of the substrate ribose. In addition, the particular manganese coordination in DraG suggests a rationale for the enzyme's preference for manganese over magnesium, although not requiring a redox active metal for the reaction.

- Highly Luminescent Polymers Containing the 2,3,5,6-Tetraarylated Pyrrolo[3,4-*c*]pyrrole-1,4-dione (*N*-Aryl DPP) Chromophore in the Main Chain.
  Zhang, K.; Tieke, B. *Macromolecules* **2008**, *41*, 7287-7295.
  Abstract:



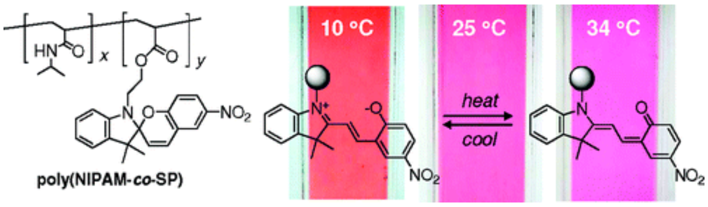
Synthesis and characteristic properties of polymers P-1-P-3 are described containing the 2,3,5,6-tetraarylated pyrrolo[3,4-*c*]pyrrole-1,4-dione unit in the main chain. P-1 is prepared from 2,5-bis(4-*t*-butylphenyl)-3,6-bis(4′-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP1) and 9,9-di-*n*-hexylfluorene-2,7′-bispinacolatoboronester **3**, P-2 from 2,5-bis(4′-bromo-phenyl)-3,6-bis(4-*t*-butylphenyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (D2) and **3**, and P-3 from DPP1, **3**, and 2,5-bis(*n*-hexyloxybenzene)-1,4-bispinacolatoboronester **4** via Pd-catalyzed Suzuki coupling. Molecular weights of the polymers are about 8000-10 000 Da. All polymers are soluble in common organic solvents such as toluene, chloroform, dichloromethane, tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) and exhibit a strong fluorescence with Stokes shift up to 56 nm (P-3) and quantum yield up to 81% (P-1). Although P-1 and P-2 are isomers, their optical and electrochemical properties are very different. P-1 with a polyconjugated carbon backbone exhibits absorption and fluorescence maxima of 516 and 569 nm, respectively, which are bathochromically shifted by 15-25 nm with regard to monomer DPP1. In P-2, the π-conjugation of the backbone is interrupted by the lactam N-atoms, so that absorption and fluorescence are similar to those of monomer DPP2 (498 and 531 nm, respectively). Properties of polyconjugated copolymer P-3 are similar to those of P-1. Band gaps of P-1 and P-2 are 2 and 2.3 eV, respectively. Cyclovoltammetric studies indicate irreversible oxidation and reduction cycles.

- Sugar-Substituted Poly(*p*-phenyleneethynylene)s: Sensitivity Enhancement toward Lectins and Bacteria.
  Phillips, R. L.; Kim, I.-B.; Carson, B. E.; Tidbeck, B.; Bai Y.; Lowary, T. L.; Tolbert, L. M.; Bunz, U. H. F. *Macromolecules* **2008**, *41*, 7316-7320.
  Abstract:



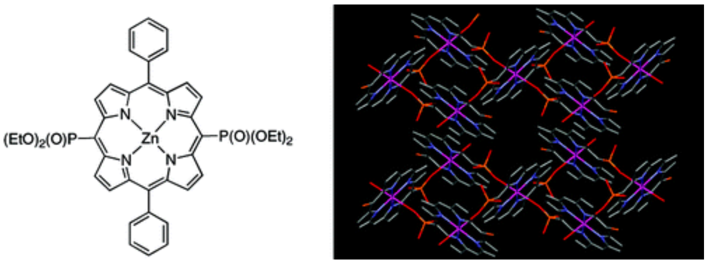
The synthesis of two novel, water-soluble, sugar-substituted poly(*p*-phenyleneethynylene)s and their interactions with concanavalin A (Con A) and bacteria (*Escherichia coli*) are reported, and the issue of sensitivity enhancement is investigated. Both sugar-substituted PPEs (**P5** and **P7**) exhibited strong interactions with Con A with *K*SV values exceeding 108 M-1. The binding constants between the sugar-substituted polymers and Con A were also quantitatively calculated using isothermal titration calorimetry (ITC) resulting in association constants as high as 106 M-1. **P5** and **P7** strongly interact with mannose-binding *E. coli*, which led to their aggregation.

- Spiropyran-Conjugated Thermoresponsive Copolymer as a Colorimetric Thermometer with Linear and Reversible Color Change
  Shiraishi, Y.; Miyamoto, R.; Hirai, T. *Org. Lett.* **2009**, *11*, 1571–1574.
  Abstract:



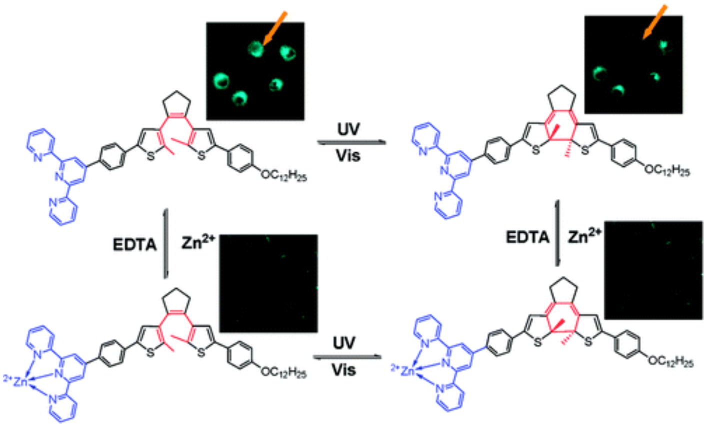
A simple copolymer, poly(NIPAM-*co*-SP), consisting of *N*-isopropylacrylamide and spiropyran units, behaves as a colorimetric thermometer exhibiting temperature-responsive linear and reversible bathochromic/hypsochromic shift of the absorption spectra under UV irradiation.

- Synthesis of *meso*-Polyphosphorylporphyrins and Example of Self-Assembling
  Enakieva, Y. Y.; Bessmertnykh, A. G.; Gorbunova, Y. G.; Stern, C.; Rousselin, Y.; Tsivadze, A. Y.; Guilard, R. *Org. Lett.* **2009**, *11*, 3842–3845.
  Abstract:



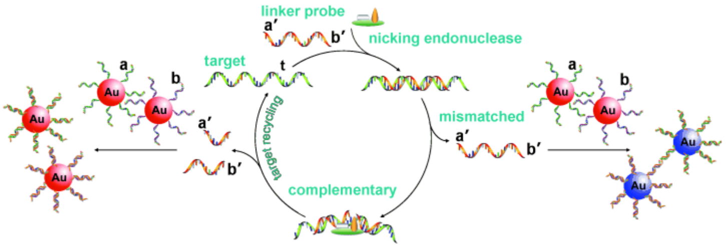
Pd-catalyzed coupling reactions have been used to prepare *meso*-phosphorylporphyrins. A 2D metal–organic network formed via P═O···Zn axial supramolecular coordination of 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyrin is the first example of a 2D framework based on phosphorylporphyrin derivatives.

- Multiresponsive Switchable Diarylethene and Its Application in Bioimaging
  Piao, X.; Zou, Y.; Wu, J.; Li, C.; Yi, T. *Org. Lett.* **2009**, *11*, 3818–3821.
  Abstract:



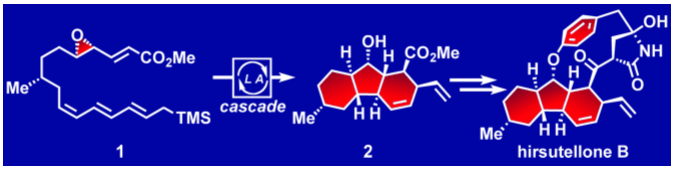
A multiresponsive fluorescent switch based on diarylethene and terpyridine units was developed. It exhibits effective switchable fluorescence which can be controlled by UV/visible light or metal ion/EDTA in solution. More importantly, having low toxicity, it can enter live cells as a fluorescent probe and can also serve as a detector for the biological process of metal ion transmembrane transport.

- Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease Assisted Nanoparticle Amplification
  Xu, W.; Xue, X.; Li, T., Zeng, H., Liu, X. *Angew. Chem. Int. Ed.* **2009**, *48*, 6849 – 6852.
  Abstract :



One-two punch: Single stranded DNA sequences can be detected by nicking endonuclease assisted nanoparticle amplification (see picture). The detection system offers a colorimetric detection limit of 0.5 fmol within hours for selected oligonucleotides. Detection of DNA sequences with a single base mismatch or different lengths is also demonstrated.

- Total Synthesis of Hirsutellone B
  Nicolaou, K. C.; Sarlah, D.; Wu, T. R.; Zhan, W. *Angew. Chem. Int. Ed.* **2009**, *48*, 6870 – 6874.
  Abstract :



Cascading reactions, including the conversion of a TMS-epoxy tetraene **1** into the hirsutellone tricyclic core **2**, feature heavily in the first total synthesis of the antituberculosis fungal metabolite hirsutellone B. TMS=trimethylsilyl, LA=Lewis acid.