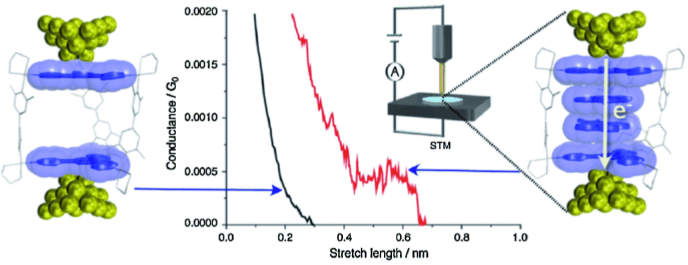
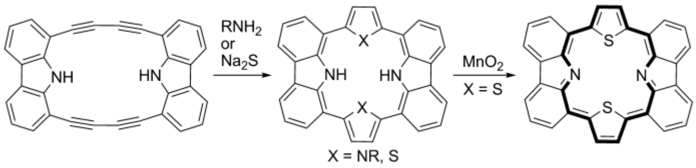
- Electron Transport through Single Molecules Comprising Aromatic Stacks Enclosed in Self-Assembled Cages
  Kiguchi, M.; Takahashi, T.; Takahashi, Y.; Yamauchi, Y.; Murase, T.; Fujita, M.; Tada, T.; Watanabe, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 5708–5711.
  Abstract:



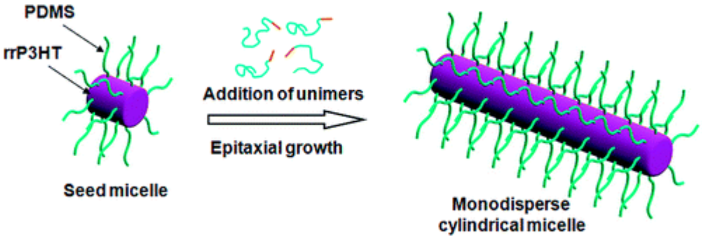
Face-to-face communication: Electron transport through single-molecule π stacks was directly measured between gold nanogap electrodes by using STM (see scheme). Self-assembled coordination cages containing π-stacked aromatic molecules are conductive (right), whereas the empty cage is not (left).

- Synthesis of Carbazole-Containing Porphyrinoids by a Multiple Annulation Strategy: A Core-Modified and π-Expanded Porphyrin
  Maeda, C.; Yoneda, T.; Aratani, N.; Yoon, M.-C.; Lim, J. M.; Kim, D.; Yoshioka, N.; Osuka, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 5691–5694.
  Abstract:



Going around in circles: The copper(I)-mediated annulation of a doubly 1,3-butadiyne-bridged carbazole dimer with amines or Na_2S provides isophlorins containing carbazole or thiophene-carbazole moieties, respectively (see scheme). Oxidization of the thiophene-containing isophlorin with MnO_2 gives the corresponding porphyrin, which displays distinct aromaticity and remarkably intensified and red-shifted absorption bands in the near IR region.

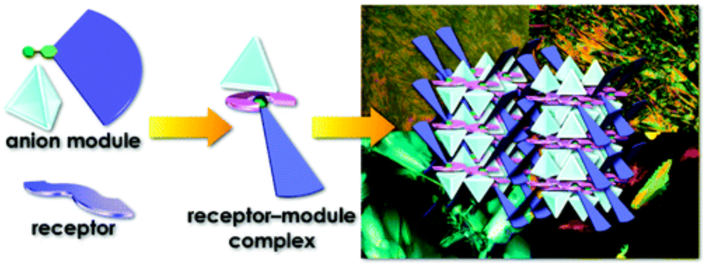
- Cylindrical Micelles of Controlled Length with a π-Conjugated Polythiophene Core via Crystallization-Driven Self-Assembly
  Patra, S. K.; Ahmed, R.; Whittell, G. R.; Lunn, D. J.; Dunphy, E. L.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2011**, *133*, 8842–8845.
  Abstract:



Solution self-assembly of the regioregular polythiophene-based block copolymer poly(3-hexylthiophene)-*b*-poly(dimethylsiloxane) yields cylindrical micelles with a crystalline P3HT core.

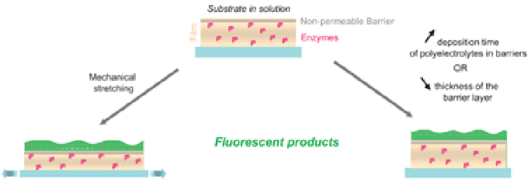
Monodisperse nanocylinders of controlled length have been prepared via crystallization-driven self-assembly using seed micelles as initiators.

- Anion Modules: Building Blocks of Supramolecular Assemblies by Combination with π-Conjugated Anion Receptors
  Maeda, H.; Naritani, K.; Honsho, Y.; Seki, S. *J. Am. Chem. Soc.* **2011**, *133*, 8896–8899.
  Abstract:



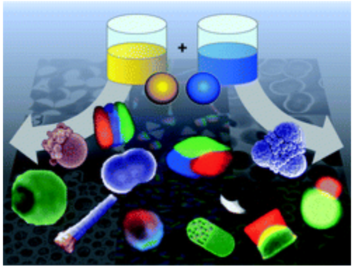
Dipyrrolyldiketone boron complexes, as π-conjugated acyclic anion receptors, act as building subunits of various assemblies through noncovalent interactions in the form of receptor–anion complexes. Instead of, or in addition to, the modification of receptor structures, the introduction of *anion modules* as building blocks for the assemblies was found to be useful in forming various soft materials. Gallic carboxylate derivatives **3-*n*** (*n* = 16, 18, 20), as tetrabutylammonium (TBA) salts, form receptor–anion-module complexes that can be used to fabricate supramolecular assemblies. Combinations of aliphatic anion modules **3-*n*** and receptors **1a**,**b** along with a TBA cation afforded products with mesophases, which were indicated by differential scanning calorimetry and polarized optical microscopy. X-ray diffraction measurements of the solid states and mesophases of **1a**·**3-*n***·TBA and **1b**·**3-*n***·TBA revealed highly ordered structures including lamellar structures, which could be modulated by the lengths of the alkyl chains of the modules. Functional materials exhibiting electrical conductivity were fabricated by using combinations of anionic building blocks that form assemblies by themselves and π-conjugated acyclic receptors.

- Tailored design of mechanically sensitive biocatalytic assemblies based on polyelectrolyte multilayers
  Mertz, D.; Vogt, C.; Hemmerlé, J.; Debry, C.; Voegel, J.-C.; Schaaf, P.; Lavalle, P. *J. Mater. Chem.* **2011**, *21*, 8324-8331.
  Abstract:



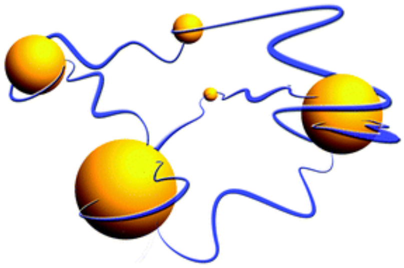
Mechanically sensitive surfaces responding to mechanical forces constitute an attractive emerging field of research. This requires the engineering of complex surfaces with finely controlled properties, especially regarding the permeability behaviour towards specific molecules. Here we designed such surfaces using polyelectrolyte multilayer nanostructures. Polylysine/hyaluronic acid multilayer films were used as a micro-container of enzymes and denser multilayers deposited on top of the reservoir were tailored to control their permeability. We find that permeability towards fluorescein diphosphate (FDP) not only depends on the number of bilayers constituting the barrier but more surprisingly on the deposition time of the polyelectrolytes during the barrier buildup, a long contact time (10 min) leading to porous barriers. This effect is explained by diffusion and exchange processes taking place in the reservoir during the buildup process. For films composed of a non-permeable barrier towards enzymatic substrate FDP, we tested the enzymatic activity when mechanical stretching was applied to the architecture. Under stretch and in the presence of FDP on top of the film, the catalytic activity was switched on. These biologically inspired surfaces constitute a first step to the development of novel platforms able to trigger and to modulate chemical reactions under a mechanical stimulus.

- Multifunctional polymer particles with distinct compartments
  Yoon, J.; Lee, K. J.; Lahann, J. *J. Mater. Chem.* **2011**, *21*, 8502-8510.
  Abstract:



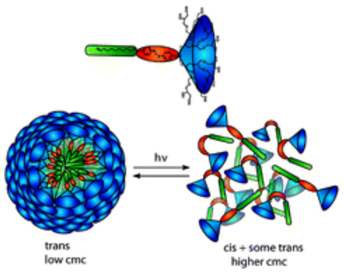
Polymer particles with controlled internal architecture are currently under development for a number of emerging applications. In compartmentalized particles, well-defined pockets of distinct materials can be designed that can give rise to a set of orthogonal (*i.e.*, dissimilar) properties within the same particle. While this aspect appears crucial, when multifunctional particles for sensing, imaging or drug delivery are sought after, their experimental realization has only recently been explored in broader terms. In this review, we highlight current progress related to the design and fabrication of multicompartmental particles and discuss potential benefits and experimental challenges associated with different synthetic routes.

- Guest-controlled aggregation of cavitand gold nanoparticles and *N*-methyl pyridinium-terminated PEG
  Dionisio, M.; Maffei, F.; Rampazzo, E.; Prodi, L.; Pucci, A.; Ruggeri, G.; Dalcanale, E. *Chem. Commun.* **2011**, *47*, 6596-6598.
  Abstract:



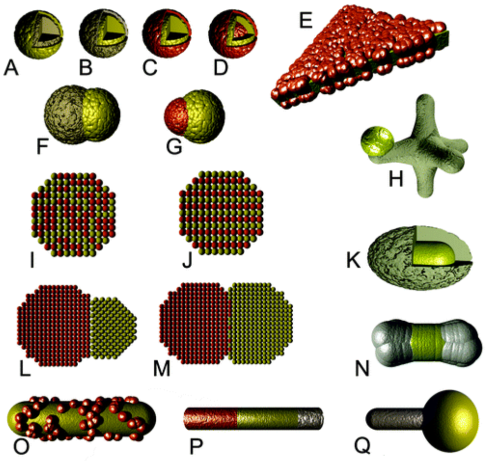
The introduction of a disulfide functionalized tetraphosphonate cavitand on Au nanoparticles promotes the reversible assembly of a network upon addition of a suitable polymeric ditopic guest.

- Photoresponsive amphiphiles based on azobenzene-dendritic glycerol conjugates show switchable transport behavior
  Kördel, C.; Popeney, C. S.; Haag, R. *Chem. Commun.* **2011**, *47*, 6584-6586.
  Abstract:



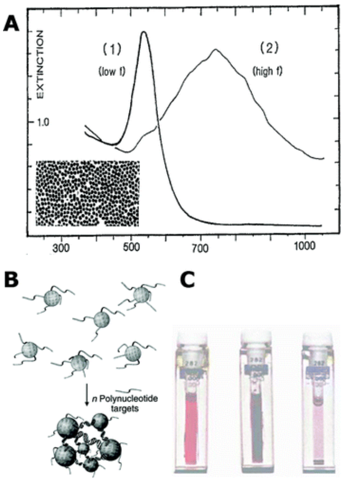
Non-ionic switchable amphiphiles were synthesized and their aggregation behavior characterized for the two different states.

- Synthesis and Optical Properties of Hybrid and Alloy Plasmonic Nanoparticles
  Cortie, M. B.; McDonagh, A. M. *Chem. Rev.* **2011**, *111*, 3713–3735.
  Abstract:



The plasmon resonances and other optical properties of elemental noble and alkali metal nanoparticles have generated enormous scientific interest. There are numerous applications for plasmon-active nanoparticles, especially in areas such as biological microscopy, medicine, and sensors. The various applications exploit some aspect of the plasmon resonance, which include particle–particle plasmon interactions, the unusual coloring or dichroic effects in isolated particles, light-induced plasmonic heating, light scattering, or two-photon phenomena.(Hybrid or multifunctional nanoparticles constructed from more than one component phase have also been attracting increasing interest due to their additional functionalities. In this review, we consider specifically the *optical* properties of *solid* nanoparticles composed of more than one phase or compound. Alloyed nanoparticles (solid solutions or intermetallic compounds of the metallic elements) are also included because these intergrade with the two-phase hybrids. The primary focus here is the optical properties related to plasmonic phenomena. We exclude nanoparticle hybrids between solid cores and organic ligands, or between solid cores and proteins and other large organic molecules, from the scope of the review because, in most cases, the only effect the organic substance has on the optical properties is to impart a small bathochromic shift (“red-shift”) to the plasmon resonance.

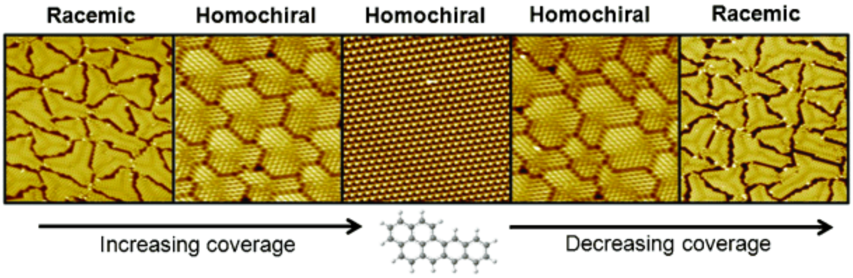
- Plasmons in Strongly Coupled Metallic Nanostructures
  Halas, N. J.; Lal, S.; Chang, W.-S.; Link, S.; Nordlander, P. *Chem. Rev.* **2011**, *111*, 3913–3961.
  Abstract:



The vivid optical properties of noble metal nanoparticles have been an object of fascination since ancient times. The ruby red of stained glass windows arises from gold nanoparticles, formed by the reduction of metallic ions in the glass-forming process. While these properties have been known and used for centuries, our scientific understanding of these properties has emerged far more recently, beginning with the development of classical electromagnetic theory. Gustav Mie's application of Maxwell's equations to explain the strong absorption of green light by a subwavelength gold sphere under plane wave illumination established the rigorous scientific foundation for our understanding of this phenomenon. The following decades saw increasing interest in the properties of light scattering by small particles, and in particular, the properties of small metallic nanoparticles, whose collective electronic resonances, known as plasmons, give rise to the strong optical absorption properties of this class of materials.

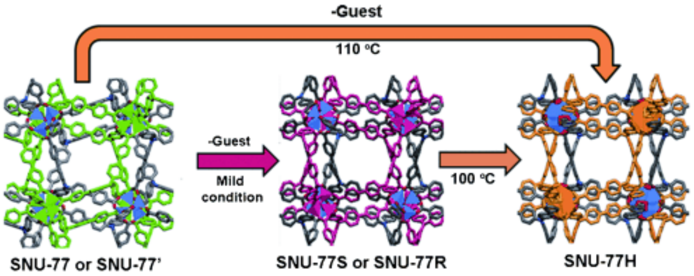
An even more dramatic optical property of metallic nanoparticles is their color change when a dilute suspension of nanoparticles aggregates. This can be seen when molecules or ions, such as a solution of NaCl, or molecular linkers, such as hemoglobin or DNA, are added to a suspension of noble metal nanoparticles. In the case of gold colloid, upon the onset of aggregation, a dramatic red-to-blue color change can easily be seen. When gold or silver nanoparticles begin to aggregate, they form pairs of nanoparticles and their optical spectrum acquires a new peak, red-shifted significantly from the spectral peak of the absorption for the isolated nanoparticle. For a fully aggregated solution, the red-shifted peak dominates the spectrum (Figure 1A). This phenomenon, commonly witnessed by colloidal chemists, requires an understanding of the electromagnetic properties of interacting metallic nanoparticles in close mutual proximity.

- Spontaneous Transmission of Chirality through Multiple Length Scales
  Iski, E. V. Tierney, H. L.; Jewell, A. D.; Sykes, E. C. H. *Chem. Eur. J.* **2011**, *17,* 7205–7212.
  <u>Abstract:</u>



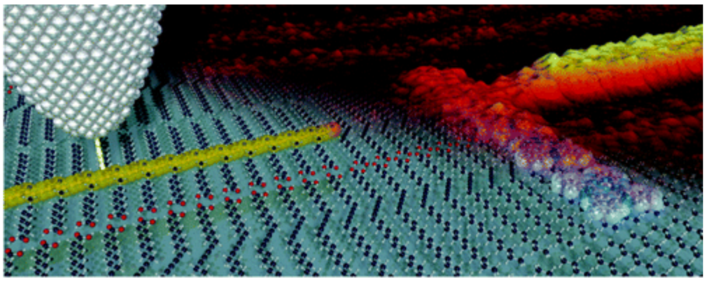
The hierarchical transfer of chirality in nature, from the nano-, to meso-, to macroscopic length scales, is very complex, and as of yet, not well understood. The advent of scanning probes has allowed chirality to be monitored at the single molecule or monolayer level and has opened up the possibility to track enantiospecific interactions and chiral self-assembly with molecular-scale detail. This paper describes the self-assembly of a simple, model molecule (naphtho[2,3-*a*]pyrene) that is achiral in the gas phase, but becomes chiral when adsorbed on a surface. This polyaromatic hydrocarbon forms a stable and reversibly ordered system on Cu(111) in which the transmission of chirality from single surface-bound molecules to complex 2D chiral architectures can be monitored as a function of molecular packing density and surface temperature. In addition to the point chirality of the surface-bound molecule, the unit cell of the molecular domains was also found to be chiral due to the incommensurate alignment of the molecular rows with respect to the underlying metal lattice. These molecular domains always aggregated in groups of three, all of the same chirality, but with different rotational orientations, forming homochiral “tri-lobe” ensembles. At a larger length scale, these tri-lobe ensembles associated with nearest-neighbor tri-lobe units of opposite chirality at lower packing densities before forming an extended array of homochiral tri-lobe ensembles at higher converges. This system displayed chirality at a variety of size scales from the molecular (≈1 nm) and domain (≈5 nm) to the tri-lobe ensemble (≈10 nm) and extended array (>25 nm) levels. The chirality of the tri-lobe ensembles dictated how the overall surface packing occurred and both homo- and heterochiral arrays could be reproducibly and reversibly formed and interchanged as a function of surface coverage. Finally, these chirally templated surfaces displayed remarkable enantiospecificity for naphtho[2,3-*a*]pyrene molecules adsorbed in the second layer. Given its simplicity, reversibility, and rich degree of order, this system represents an ideal test bed for the investigation of symmetry breaking and the hierarchical transmission of chirality through multiple length scales.

- A Highly Porous Metal–Organic Framework: Structural Transformations of a Guest-Free MOF Depending on Activation Method and Temperature
  Park, H. J.; Lim, D. W.; Yang, W. S.; Oh, T. R.; Suh, M. P. *Chem. Eur. J.* **2011**, *17,* 7251-7260.
  Abstract:



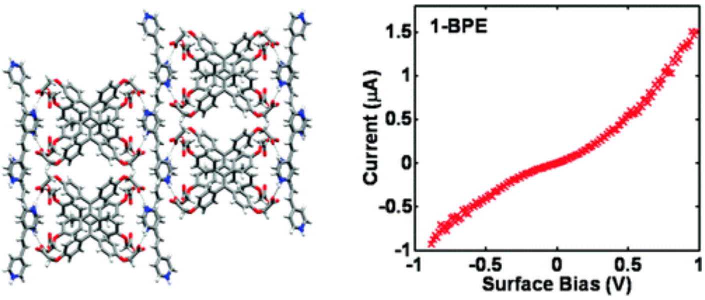
A doubly interpenetrating porous metal–organic framework (SNU-77) has been synthesized from the solvothermal reaction of the extended carboxylic acid tris(4′-carboxybiphenyl)amine (H3TCBPA) and $Zn(NO_3)_2$□$6H_2O$ in *N*,*N*-dimethylacetamide (DMA). SNU-77 undergoes single-crystal-to-single-crystal transformations during various activation processes, such as room-temperature evacuation, supercritical CO2 drying, and high temperature evacuation, to afford SNU-77R, SNU-77S, and SNU-77H, respectively. These guest-free MOFs exhibited different fine structures with different window shapes and different effective window sizes at room temperature. Variable-temperature synchrotron single-crystal X-ray analyses reveal that the guest-free structure is also affected by changes in temperature. Despite the different fine structures, SNU-77R, SNU-77S, and SNU-77H show similar gas sorption properties due to the nonbreathing nature of the framework and an additional structural change upon cooling to cryogenic gas sorption temperature. SNU-77H exhibits a large surface area (BET, 3670 m2□g−1), a large pore volume (1.52 cm3□g−1), and exceptionally high uptake capacities for N_2, H_2, O_2, CO_2, and CH_4 gases.

- Chemical Wiring and Soldering toward All-Molecule Electronic Circuitry
  Okawa, Y.; Mandal, S. K.; Hu, C.; Tateyama, Y.; Goedecker, S.; Tsukamoto, S.; Hasegawa, T.; Gimzewski, J. K.; Aono, M. *J. Am. Chem. Soc.* **2011**, *133*, 8227-8233.
  Abstract:



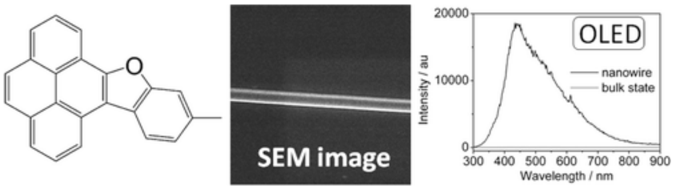
Key to single-molecule electronics is connecting functional molecules to each other using conductive nanowires. This involves two issues: how to create conductive nanowires at designated positions, and how to ensure chemical bonding between the nanowires and functional molecules. Here, we present a novel method that solves both issues. Relevant functional molecules are placed on a self-assembled monolayer of diacetylene compound. A probe tip of a scanning tunneling microscope is then positioned on the molecular row of the diacetylene compound to which the functional molecule is adsorbed, and a conductive polydiacetylene nanowire is fabricated by initiating chain polymerization by stimulation with the tip. Since the front edge of chain polymerization necessarily has a reactive chemical species, the created polymer nanowire forms chemical bonding with an encountered molecular element. We name this spontaneous reaction “chemical soldering”. First-principles theoretical calculations are used to investigate the structures and electronic properties of the connection. We demonstrate that two conductive polymer nanowires are connected to a single phthalocyanine molecule. A resonant tunneling diode formed by this method is discussed.

- Semiconducting Organic Assemblies Prepared from Tetraphenylethylene Tetracarboxylic Acid and Bis(pyridine)s via Charge-Assisted Hydrogen Bonding
  Kapadia, P P.; Ditzler, L. R.; Baltrusaitis, J.; Swenson, D. C.; Tivanski, A. V.; Pigge, F. C. *J. Am. Chem. Soc.* **2011**, *133*, 8490-8493.
  Abstract:



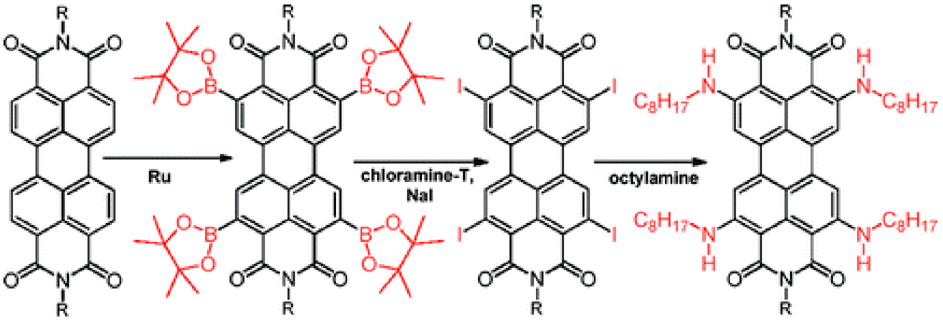
Principles of crystal engineering have been applied toward the construction of supramolecular assemblies between an acid-functionalized tetraphenylethylene derivative and three different bis(pyridine)s [4,4□-bis(pyridyl)ethylene, 4,4□-bis(pyridyl)ethane, and 4,4□-bipyridine]. Each assembly was structurally characterized, and charge transfer interactions within each sample were visually apparent. Quantum chemical calculations were used to determine crystal band structure and band gap magnitude, and electrical properties of the materials were measured using conducting probe atomic force microscopy (CP-AFM). The crystals displayed charge-carrier capability, and the magnitude of semiconductivity varied systematically as a function of conjugation in the bis(pyridine) component. Crystals incorporating 4,4′-bis(pyridyl)ethylene and 4,4′-bipyridine displayed conductivities comparable to those of established organic semiconductors (μ_{eff} = 0.38 and 1.7×10^{-2} $cm^2/V{\cdot}s$, respectively).

- Synthesis, Characterization, Self-Assembly, and Physical Properties of 11-Methylbenzo[*d*]pyreno[4,5-*b*]furan
  Xiao, J.; Yang, B.; Wong, J. I.; Liu, Y.; Wei, F.; Jie Tan, K.; Teng, X.; Wu, Y.; Huang, L.; Kloc, C.; Boey, F.; Ma, J.; Zhang, H.; Yang, H. Y.; Zhang, Q. *Org. Lett.* **2011**, *13*, 3004-3007.
  Abstract:



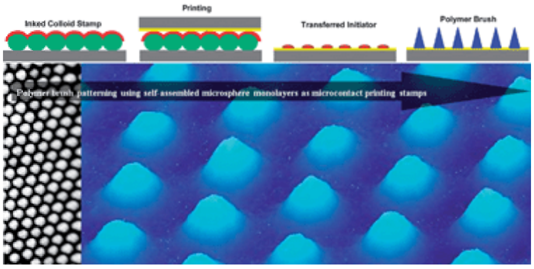
Synthesis, structure, and physical properties of a novel 11-methylbenzo[*d*]pyreno[4,5-*b*]furan (BPF) and its self-assembly in water have been reported. The performance of nanowire-based films in organic light-emitting diodes is much better than that of the thin film deposited by directly drop-coating BPF molecules in THF solution. SEM study indicates that the well-organized structure (nanowires) is an important factor in enhancing the performance of OLED devices.

- 2,5,8,11-Tetraboronic Ester Perylenediimides: A Next Generation Building Block for Dye-Stuff Synthesis
  Battagliarin, G.; Li, C.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2011**, *13*, 3012–3015.
  Abstract:



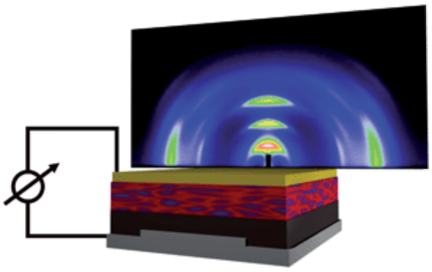
Via an unprecedentedly reported ruthenium catalyzed reaction, an efficient and straightforward method was developed for the synthesis of 2,5,8,11-tetraboronate perylenediimide derivatives. A possible reaction mechanism is proposed. The synthesis of 2,5,8,11-tetra-iodo and tetra-amino perylenediimides derivatives is also reported.

- Polymer brush patterning using self-assembled microsphere monolayers as microcontact printing stamps
  Chen, T.; Jordan, R.; Zauscher, S. *Soft Matter*, **2011**, *7*, 5532-5535.
  Abstract:



Self-assembled microsphere monolayers (SMMs) hold significant promise for micro- and nanopatterning. Here we exploit, for the first time, SMMs as stamps for microcontact printing (μCP) and demonstrate this to fabricate patterned initiator templates that can subsequently be amplified into polymer brushes by surface initiated atom transfer radical polymerization (SI-ATRP). SMM stamps avoid the need for expensive and sophisticated instrumentation in pattern generation, and provide a broad range of accessible surface chemistries and pitch size control.

- Morphology of polymer-based bulk heterojunction films for organic photovoltaics
  Ruderer, M.; Müller-Buschbaum, P. *Soft Matter*, **2011**, *7*, 5482-5493.
  Abstract:



In recent years organic photovoltaics have become one of the most increasing research areas due to their potential towards a cheap and broad applicability. Besides the chemical structure and the resulting electronic and absorption properties, the morphology of the active layer in such systems was found to be one of the most important issues to gain reasonable device performance. The development of tomography and advanced scattering techniques enables the detection of 3-dimensional morphologies in these materials. In this review we focus on the latest findings concerning the morphology and its control parameters in polymer-based bulk heterojunction systems and its importance for the development of high performance organic solar cells.