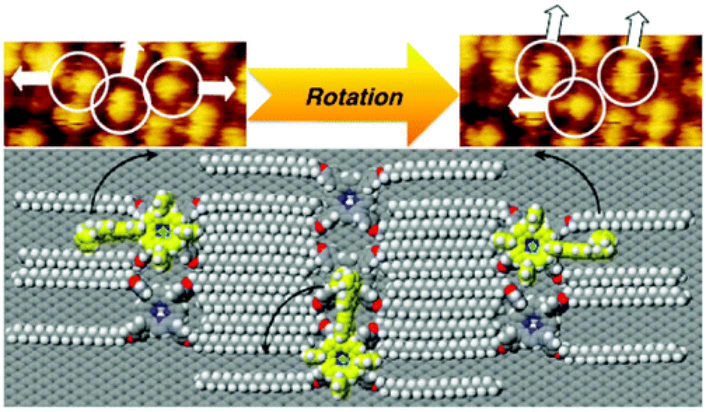
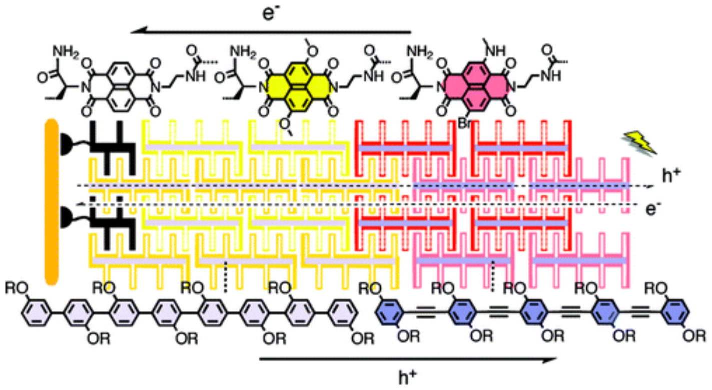
- Rotational Libration of a Double-Decker Porphyrin Visualized
  Otsuki, J.; Komatsu, Y.; Kobayashi, D.; Asakawa, M.; Miyake, K. *J. Am. Chem. Soc.* **2010**, *132*, 6870–6871.
  Abstract:



Scanning tunneling microscopy has revealed the reorientation of one of the macrocyclic rings of the double-decker porphyrin complex [Ce(TPP-Fc)(C_{22}OPP)] [TPP-Fc = 5-(4-(4-ferrocenylphenylethynyl)phenyl)-10,15,20-triphenylporphyrin; C_{22}OPP = 5,10,15,20-tetrakis(4-docosyloxyphenyl)porphyrin] by 90° between scans when the other ring is fixed on a surface. This libration was evidenced by monitoring the location of the appended ferrocene unit, which functioned as a molecular beacon signaling its position.

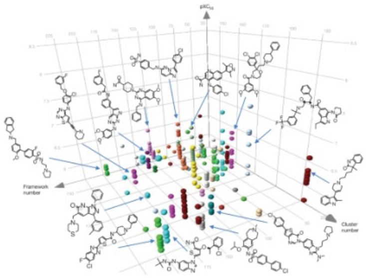
- Supramolecular n/p-Heterojunction Photosystems with Antiparallel Redox Gradients in Electron- and Hole-Transporting Pathways
  Sakai, N.; Bhosale, R.; Emery, D.; Mareda, J.; Matile, S. *J. Am. Chem. Soc.* **2010**, *132*, 6923–6925.
  Abstract:



Lessons from nature call for supramolecular n/p-heterojunctions with oriented multicolored antiparallel redox gradients (OMARG-SHJs) as “ideal” photosystems. Their design combines advantages of bilayer and bulk n/p-heterojunction (BHJ) solar cells for the directional separation of photogenerated charges before recombination can occur. Although conceptually attractive, OMARG-SHJs have remained beyond reach because of unresolved challenges in synthetic organic and supramolecular chemistry. Here we report the first OMARG-SHJs with two-component redox gradients in both the electron- and hole-transporting pathways. They were obtained by zipper assembly of stacks of red naphthalenediimide (NDI) electron donors along strings of oligophenylethynyl hole acceptors on top of yellow NDI electron acceptors along p-oligophenyl hole

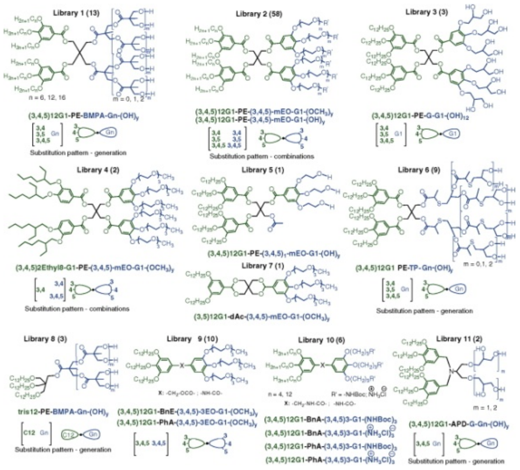
donors. The presence of both gradients is shown to be essential for achieving photoinduced charge separation over very long distances.

- Thousands of chemical starting points for antimalarial lead identification
  Gamo, F.-J. *et al. Nature* **2010,** *465*, 305–310.
  Abstract:



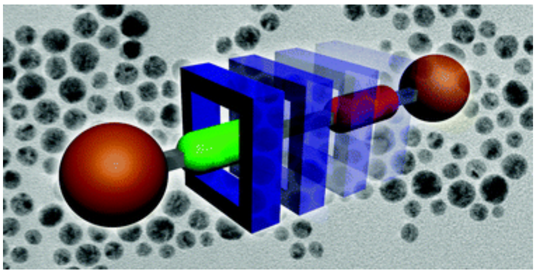
Malaria is a devastating infection caused by protozoa of the genus *Plasmodium*. Drug resistance is widespread, no new chemical class of antimalarials has been introduced into clinical practice since 1996 and there is a recent rise of parasite strains with reduced sensitivity to the newest drugs. We screened nearly 2 million compounds in GlaxoSmithKline's chemical library for inhibitors of *P. falciparum*, of which 13,533 were confirmed to inhibit parasite growth by at least 80% at 2 µM concentration. More than 8,000 also showed potent activity against the multidrug resistant strain Dd2. Most (82%) compounds originate from internal company projects and are new to the malaria community. Analyses using historic assay data suggest several novel mechanisms of antimalarial action, such as inhibition of protein kinases and host–pathogen interaction related targets. Chemical structures and associated data are hereby made public to encourage additional drug lead identification efforts and further research into this disease.

- Self-Assembly of Janus Dendrimers into Uniform Dendrimersomes and Other Complex Architectures
  Percec, V. *et al. Science* ***2010***, 328, 1009 – 1014.
  Abstract:



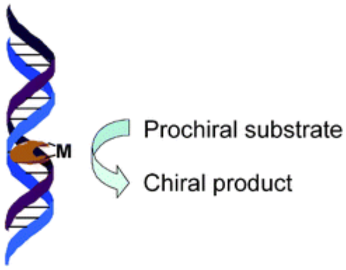
Self-assembled nanostructures obtained from natural and synthetic amphiphiles serve as mimics of biological membranes and enable the delivery of drugs, proteins, genes, and imaging agents. Yet the precise molecular arrangements demanded by these functions are difficult to achieve. Libraries of amphiphilic Janus dendrimers, prepared by facile coupling of tailored hydrophilic and hydrophobic branched segments, have been screened by cryogenic transmission electron microscopy, revealing a rich palette of morphologies in water, including vesicles, denoted dendrimersomes, cubosomes, disks, tubular vesicles, and helical ribbons. Dendrimersomes marry the stability and mechanical strength obtainable from polymersomes with the biological function of stabilized phospholipid liposomes, plus superior uniformity of size, ease of formation, and chemical functionalization. This modular synthesis strategy provides access to systematic tuning of molecular structure and of self-assembled architecture.

- Nanoparticles functionalised with reversible molecular and supramolecular switches
  Klajn, R.; Stoddart, J. F.; Grzybowski, B. A. *Chem. Soc. Rev.* **2010**, *39*, 2203 – 2237.
  Abstract:



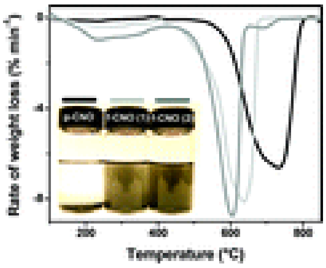
Nanoparticles (NPs) and molecular/supramolecular switches have attracted considerable interest during the past decade on account of their unique properties and prominent roles in the fields of organic chemistry and materials science. Materials derived from the combination of these two components are now emerging in the literature. This *critical review* evaluates materials which comprise NPs functionalised with well-defined self-assembled monolayers of molecular and supramolecular switches. We draw attention to the fact that immobilisation of switches on NPs does not, in general, hamper their switching ability, although it can impart new properties on the supporting particles. This premise leads us to the discussion of systems in which switching on the surfaces of NPs can be used to modulate reversibly a range of NP properties—optical, fluorescent, electrical, magnetic—as well as the controlled release of small molecules. Finally, we discuss examples in which molecular switches direct reversible self-assembly of NPs (308 references).

- DNA-based asymmetric catalysis
  Boersma, A. J.; Megens, R. P.; Feringa, B. L.; Roelfes, G. *Chem. Soc. Rev.* **2010**, *39*, 2083 – 2092.
  Abstract:



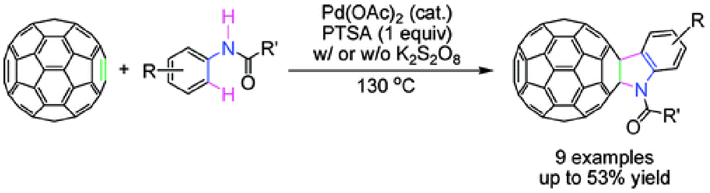
The unique chiral structure of DNA has been a source of inspiration for the development of a new class of bio-inspired catalysts. The novel concept of DNA-based asymmetric catalysis, which was introduced only five years ago, has been applied successfully in a variety of catalytic enantioselective reactions. In this *tutorial review*, the ideas behind this novel concept will be introduced, an overview of the catalytic chemistry available to date will be given and the role of DNA in catalysis will be discussed. Finally, an overview of new developments of potential interest for DNA-based asymmetric catalysis will be provided.

- Palladium-Catalyzed Heteroannulation of [60]Fullerene with Anilides via C–H Bond Activation
  Zhu, B.; Wang, G.-W. *Org. Lett.* **2009**, *11*, 4334–4337.
  Abstract:



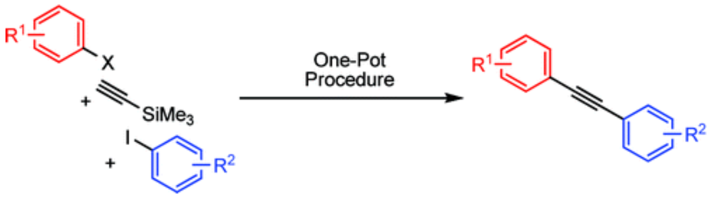
The palladium-catalyzed reaction of [60]fullerene with a variety of readily available anilides, initiated by C–H bond activation and followed by cyclization, afforded [60]fulleroindolines in a highly regioselective manner. A plausible reaction mechanism was proposed.

- Functionalization of MultilayerFullerenes (CarbonNano-Onions) using Diazonium Compounds and “Click” Chemistry
  Flavin, K.; Chaur, M. N.; Echegoyen, L.; Giordani, S. *Org. Lett.* **2010**, *12*, 840–843.
  Abstract:



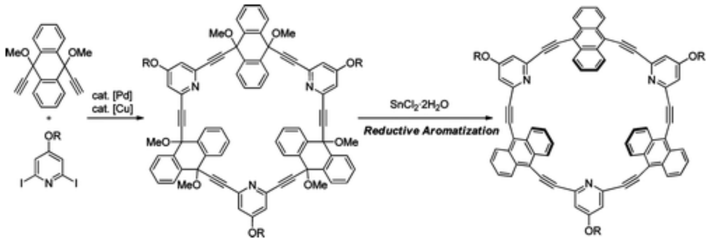
A novel versatile approach for the functionalization of multilayer fullerenes (carbonnano-onions) has been developed, which involves the facile introduction of a variety of simple functionalities onto their surface by treatment with in situ generated diazonium compounds. This approach is complemented by use of “click” chemistry which was used for the covalent introduction of more complex porphyrin molecules.

- One-Pot Procedure for the Synthesis of Unsymmetrical Diarylalkynes
  Severin, R.; Reimer, J.; Doye, S. *J. Org. Chem.* **2010**, *75*, 3518–3521.
  Abstract:



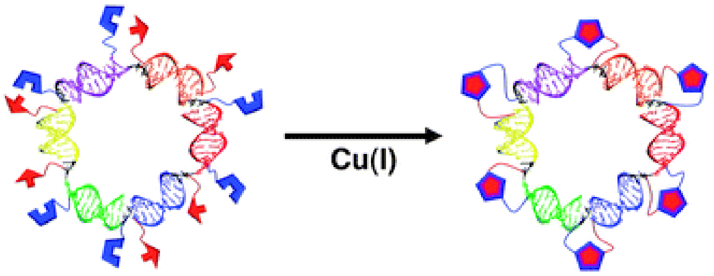
Unsymmetrical diarylalkynes are accessible by a one-pot procedure from two different aryl halides and (trimethylsilyl)acetylene. The three-component coupling is initialized by a Pd/Cu-catalyzed Sonogashira coupling of an aryl halide with (trimethylsilyl)acetylene. After subsequent desilylation of the formed aryl(trimethylsilyl)acetylene with aqueous potassium hydroxide, a second Sonogashira coupling with an aryl iodide that does not require any additional Pd/Cu-catalyst gives access to an unsymmetrical diarylalkyne.

- Synthesis of Strained Pyridine-Containing Cyclyne via Reductive Aromatization
  Miki, K.; Fujita, M.; Inoue, Y.; Senda, Y.; Kowada, T.; Ohe, K. *J. Org. Chem.* **2010**, *75*, 3537–3540.
  Abstract:



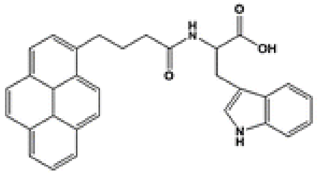
The Sonogashira–Hagihara coupling reactions of 2,6-diiodopyridine and *cis*-3,6-diethynyl-3,6-dimethoxycyclohexa-1,4-diene or *cis*-9,10-diethynyl-9,10-dimethoxy-9,10-dihydroanthracene gave macrocyclic compounds having alternating 2,6-diethynylpyridine and 3,6-dimethoxycyclohexa-1,4-diene segments. Transformation of the C_3-symmetric 2,6-diethynylpyridine-based cyclotrimer was efficiently achieved using tin-mediated reductive aromatization under mild conditions.

- A new fixation strategy for addressable nano-network building blocks
  Lundberg, E. P.; El-Sagheer, A. H.; Kocalka, P.; Wilhelmsson, L. M.; Brown, T.; Nordén, B. *Chem. Commun.* **2010**, *46*, 3714 – 3716.
  Abstract:

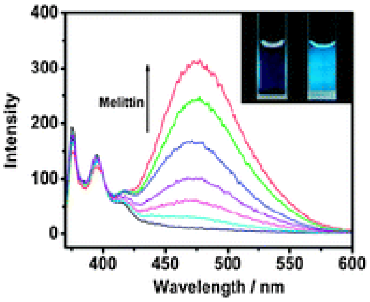


Rapid controlled self-assembly makes DNA ideal for building nanostructures. A problem using hybridized intermediates in hierarchic assembly is their thermodynamic lability. We demonstrate a click-fixation technology by which robust hexagonal DNA modules can be made. This principle is applicable to a wide variety of DNA nanoconstructs.

- A unique protein labeling system based on melittin and the non-covalent binding-induced pyrene excimer
  Li, Y.; Li, H. W.; Ma, L. J.; Dang, Y. Q.; Wu, Y. *Chem. Commun.* **2010**, *46*, 3768 – 3770.
  Abstract:

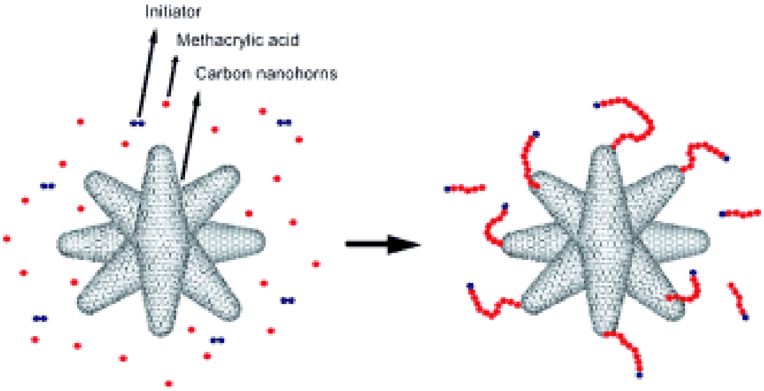


1



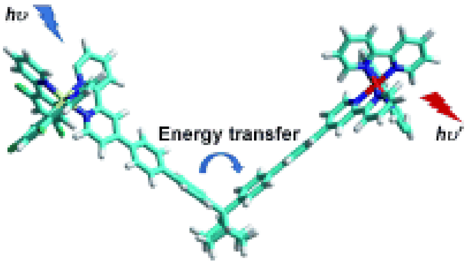
We report a unique protein labeling system based on melittin and a pyrene derivative (1). The specific region of the C-terminal in melittin efficiently induced the formation of the pyrene eximer, which can be used as a tag to target proteins and for further détection.

- Polymer Covalent Functionalization of Carbon Nanohorns Using Bulk Free Radical Polymerization
  Mountrichas, G.; Pispas, S.; Ichihasi, T.; Yudasaka, M.; Iijima, S.; Tagmatarchis, N. *Chem. Eur. J.* **2010**, *16*, 5927-5933.
  Abstract:



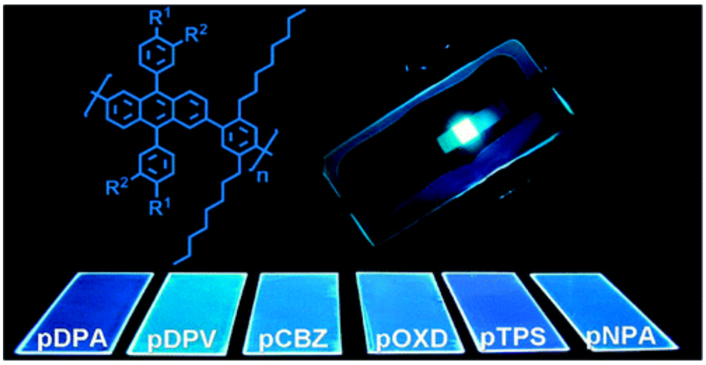
Herein, we report on a facile approach for the covalent functionalization of carbon nanohorns, using in situ bulk free radical polymerization of methacrylic acid. The obtained material is soluble in aqueous media, facilitating its processability and has been fully characterized by means of complementary spectroscopic techniques, electron microscopy, thermogravimetric analysis, and light scattering. Simultaneously, the material has been used as a template for the synthesis of gold nanoparticles on the surface of the polymer-decorated carbon nanohorns.

- Efficient Photoinduced Energy Transfer Mediated by Aromatic Homoconjugated Bridges
  Barcina, J. O.; Herrero-García, N.; Cucinotta, F.; De Cola, L.; Contreras-Carballada, P.; Williams, R. M.; Guerrero-Martínez, A. *Chem. Eur. J.* **2010**, *16*, 6033-6040.
  Abstract:



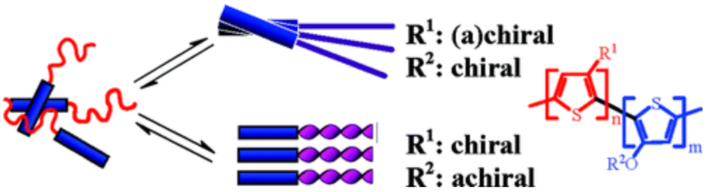
A new donor-bridge-acceptor (D-B-A) dyad consisting of ruthenium(II) and iridium(III) species separated by an homoconjugated bridge derived from 7,7-diphenylnorbornane [Ir-Nor-Ru]$^{3+}$ has been synthesised. The photophysical and electrochemical properties of the heterodinuclear complex have been compared with those of the analogous homodinuclear complexes [Ru-Nor-Ru]$^{4+}$ and [Ir-Nor- Ir]$^{2+}$. Transient absorption spectra on the nanosecond and sub-picosecond timescales show, for the first time, that an homoconjugated bridge can mediate efficiently in the photoinduced energy transfer from the iridium(III) to the ruthenium(II) centres according to a Dexter-type mechanism measurements.

- Synthesis and Characterization of a New Series of Blue Fluorescent 2,6-Linked 9,10-Diphenylanthrylenephenylene Copolymers and Their Application for Polymer Light-Emitting Diodes
  Chen, H.-Y.; Chen, C.-T.; Chen, C.-T. *Macromolecules* **2010**, *43*, 3613–3623.
  Abstract:



A series of new 9,10-diphenylanthracene-based, 2,6-linked blue-light-emitting copolymers bearing hole- or electron-transporter as well as bulky substituent were successfully synthesized. Photophysical, thermal, electrochemical, and electroluminescence (EL) properties of these copolymers were studied and characterized. Bright and efficient blue fluorescence in the solid state was achieved by incorporating bulky substituent into the copolymer backbone. Both hole- and electron-transport-substituted copolymers apparently enhanced the electroluminescent performance of their polymeric light-emitting diodes (PLEDs). A diphenylvinyl-bearing copolymer (pDPV) PLED exhibited sky-blue EL (λ_{max}^{EL} = 473 nm, CIE$_{x,y}$ = 0.16, 0.28) with peak luminous efficiency of 2.21 cd/A; a *N*-carbazole bearing copolymer (pCBZ) PLED displayed a blue EL (λ_{max}^{EL} = 469 nm, CIE$_{x,y}$ = 0.15, 0.22) with peak luminous efficiency of 2.15 cd/A. OXD-7 (1,3-bis(2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl)benzene) as an electron-transporting dopant was found to improve the performance of PLED significantly. A better balanced hole/electron charge carrier was ascribed to electron-transporting, 1,3,4-oxadiazole-bearing copolymer (pOXD) PLED. It showed a very mild efficiency rolls off: only 0.13 cd/A luminous efficiency drops from current densities of 10−100 mA/cm^2, corresponding to EL brightness of 169−1558 cd/m^2.

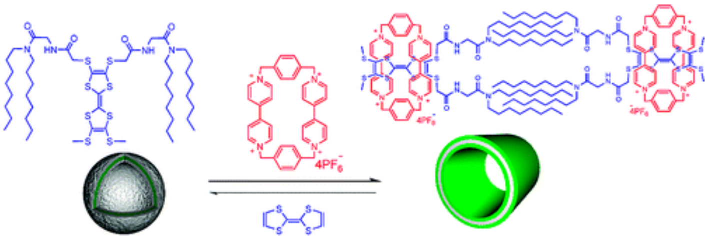
- Expression of Supramolecular Chirality in Block Copoly(thiophene)s
  Van den Bergh, K.; Cosemans, I.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2010**, *43*, 3794–3800.
  Abstract:



Three block copolymers, **P3AT(*S**)-*b*-P3AOT**, **P3AT(*R**)-*b*-P3AOT(*S**)**, and **P3AT(*S**)-*b*-P3AOT(*S**)**, composed of an alkyl- and an alkoxy-substituted poly(thiophene) block, were synthesized using the living chain-growth polymerization of poly(3-alkylthiophene)s. One or both of the blocks are equipped with a chiral side chain. The formation of the block copolymers was confirmed by GPC and ^{1}H NMR experiments. UV−vis, circular dichroism, and emission spectroscopy were used to study the conformational and supramolecular behavior of these block copolymers in solution. This revealed

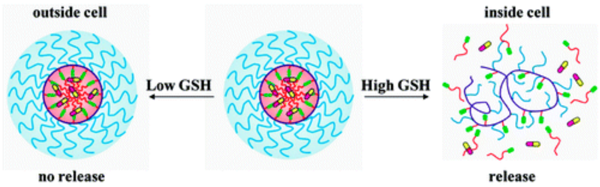
that the block aggregating first upon addition of nonsolvent has a major influence on the stacking and the chiroptical behavior of the other block.

- Vesicle Self-Assembly by Tetrathiafulvalene Derivatives in Both Polar and Nonpolar Solvents and Pseudo-Rotaxane Mediated Vesicle-to-Microtube Transformation
  Zhang, K.-D.; Wang, G.-T.; Zhao, X.; Jiang, X.-K., Li, Z.-T. *Langmuir* **2010**, *26,* 6878–6882.
  Abstract:



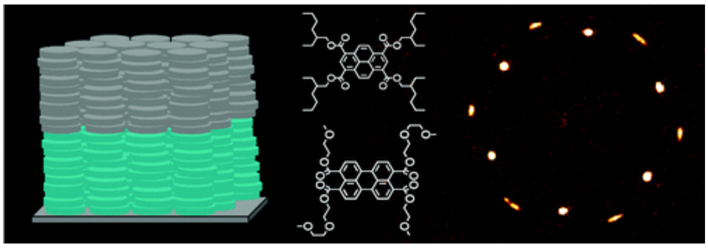
This paper reports the self-assemblies of vesicles from two tetrathiafulvalene (TTF) derivatives (**T1** and **T2**), that bear four or two amphiphilic side chains, in both polar and nonpolar solvents. The formation of vesicles is evidenced by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and dynamic light scattering (DLS) experiments, while the microstructural aspects of the vesicles are investigated by UV–vis, ^{1}H NMR, and high resolution TEM, which support a monolayer model for the vesicles. It is revealed that the formation of vesicles is driven by the combination of multiple noncovalent interactions, including π–π stacking, hydrogen-bonding, van der Waals force, and S···S interactions. It is also found that, in the presence of electron-deficient cyclobis(paraquat-*p*-phenylene) tetracation cyclophane, vesicles of **T2** can transform into microtubes as a result of the formation of the pseudo[2]rotaxane between the TTF unit of **T2** and the cyclophane. This process can be reversed by introducing pristine TTF into the solution of microtubes, due to release of **T2** from the pseudo[2]rotaxane through the formation of a more stable complex between pristine TTF and tetracation cyclophane.

- Redox-Sensitive Disassembly of Amphiphilic Copolymer Based Micelles
  Ryu, J.-H.; Roy, R.; Ventura, J.; Thayumanavan, S. *Langmuir* **2010**, *26*, 7086–7092.
  Abstract:



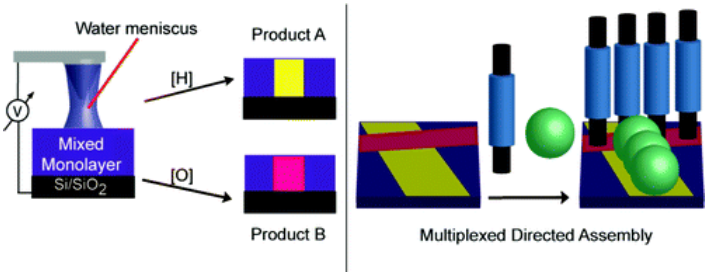
Amphiphilic polymers of different hydrophilic−lipophilic ratios were prepared by free radical polymerization using two monomers consisting of triethylene glycol as the hydrophilic part and an alkyl chain connected by disulfide bond as the hydrophobic part. These polymers form micelle-like nanoassemblies in aqueous media and can encapsulate hydrophobic drug molecules up to 14% of their mass. In a reducing environment, these polymeric micelles disassemble and dissolve in water, since the amphiphilic polymers are converted into hydrophilic polymers upon cleavage of the disulfide bond. This disassembly event results in the release of hydrophobic molecules that had been encapsulated inside the micelle, the rate of which was found to be dependent on the concentration of the reducing agent, glutathione (GSH). In vitro experiments also show that the GSH-dependent release of the doxorubicin can be used to effect cytotoxicity in MCF-7 cells.

- Face-on Oriented Bilayer of Two Discotic Columnar Liquid Crystals for Organic Donor−Acceptor Heterojunction
  Thiebaut, O.; Bock, H.; Grelet, E. *J. Am. Chem. Soc.* **2010**, *132*, 6886–6887.
  Abstract:



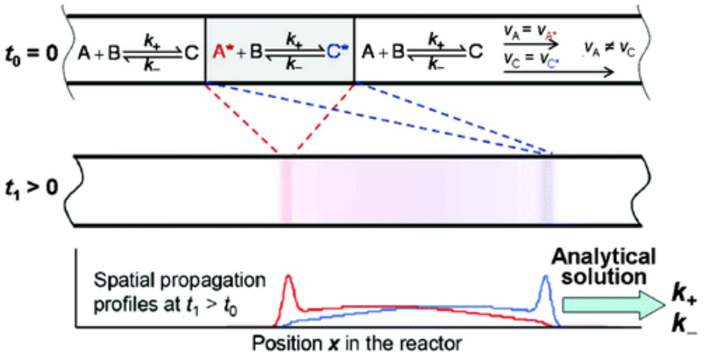
In this work, we report the achievement of a homeotropically (or face-on) oriented bilayer formed by a pair of discotic materials designed with specific properties: selective solubility, adjusted transition temperatures, and room temperature hexagonal columnar liquid-crystalline phase. The homeotropic orientation of the bilayer which is only a few hundred nanometers thick is performed by solution-processed deposition followed by thermal annealing in the geometry of open supported films and is evidenced by X-ray scattering. This represents the first proof of principle of an organic heterojunction based on two oriented columnar liquid crystal layers.

- Bifunctional Patterning of Mixed Monolayer Surfaces Using Scanning Probe Lithography for Multiplexed Directed Assembly
  Unruh, D. A.; Mauldin, C.; Pastine, S. J.; Rolandi, M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 6890–6891.
  Abstract:



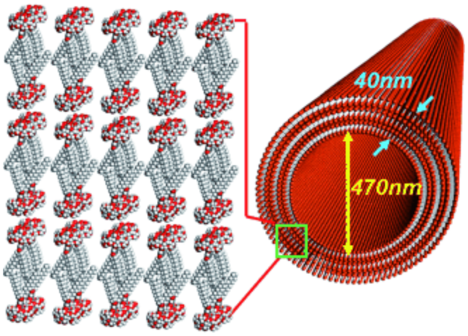
The patterning of a surface with more than one type of functionality in spatially resolved fashion is described. A scanning probe was used to create patterns composed of two orthogonal types of functionality within a dense, electrochemically active mixed monolayer via a simple modulation of the applied surface bias. One reductive pathway produces surface-bound amine moieties while the other creates an oxidized surface. The two newly created surface functionalities can each be used independently to locally deposit complementary materials such as electron- or hole-transporting molecules via self-assembly.

- MASKE: Macroscopic Approach to Studying Kinetics at Equilibrium
  Okhonin, V.; Berezovski, M. V.; Krylov, S. N. *J. Am. Chem. Soc.* **2010**, *132*, 7062–7068.
  Abstract:



The kinetics of biomolecular interactions at equilibrium is typically studied by “microscopic” methods that monitor concentration fluctuations of molecules in an “observation” volume in which the number of molecules is so small that the equilibrium is statistically impossible. Here, we introduce a “macroscopic” method for studying kinetics of biomolecular interactions at equilibrium which does not rely on monitoring the fluctuation of concentrations. We termed this method MASKE: a “macroscopic approach to studying kinetics at equilibrium”. Conceptually, in MASKE, two equilibrium reaction mixtures, “unlabeled” and “labeled”, are both prepared with two reactants and their complex; in the labeled mixture, one reactant is labeled for detection. A “macroscopic” amount of the labeled mixture is introduced into a long and narrow reactor filled with the unlabeled mixture, and a differential mobility of the reactant versus the complex is then induced by an external action along the reactor. The kinetics of complex formation and dissociation is then studied from the label-propagation pattern. In this work, we developed the theory of MASKE and experimentally proved it with a capillary as a reactor, a fluorophore as a label, and an electric field as a differential mobility inducer. Two pairs of molecules interacting with significantly different rate constants were used in this proof-of-principle work.

- Giant Nanotubes Loaded with Artificial Peroxidase Centers: Self-Assembly of Supramolecular Amphiphiles as a Tool To Functionalize Nanotubes
  Tang, Y.; Zhou, L.; Li, J.; Luo, Q.; Huang, X.; Wu, P.; Wang, Y.; Xu, J.; Shen, J.; Liu, J. *Angew. Chem. Int. Ed*. **2010**, *49*, 3920 –3924.
  Abstract:

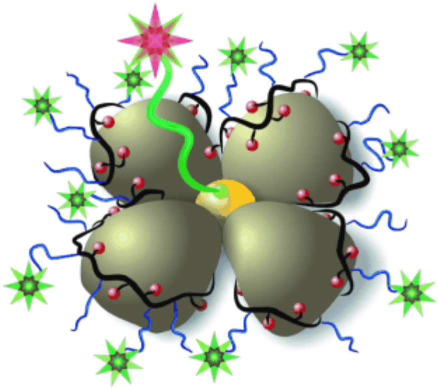


Test tubes: Large-diameter nanotubes have been obtained by direct self-assembly of cyclodextrin-based host-guest superamphiphiles (see picture). By manipulating the surface of the nanotubes with a combination of a molecular-imprinting strategy and self-assembly, the main catalytic components of glutathione peroxidase were fabricated on the nanotube scaffold.

- Au@MnO Nanoflowers: Hybrid Nanocomposites for Selective Dual Functionalization and Imaging

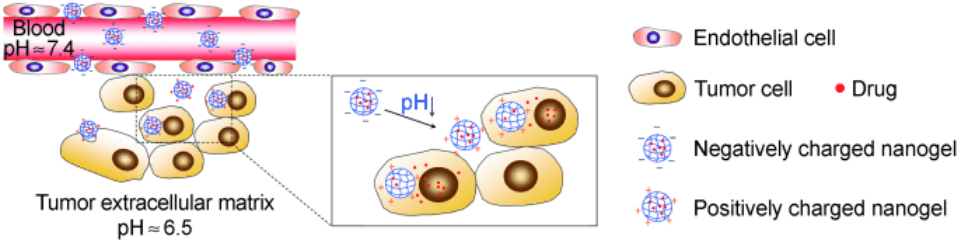
Schladt, T. D.; Shukoor, M. I.; Schneider, K.; Tahir, M. N.; Natalio, F.; Ament, I.; Becker, J.; Jochum, F. D.; Weber, S.; Köhler, O.; Theato, P.; Schreiber, L. M.; S_nnichsen, C.; Schroder, H. C.; Müller, W. E. G.; Tremel, W. *Angew. Chem. Int. Ed*. **2010**, *49*, 3976 –3980.

Abstract:



Flower power: A convenient strategy for preparing core-tunable multicomponent Au@MnO nanocrystals has been developed. The magnetic nanoflowers are not only efficient as cargo-specific carriers but also have excellent fluorescent properties resulting from fluorophors bound to the Au and MnO domains.

- A Tumor-Acidity-Activated Charge-Conversional Nanogel as an Intelligent Vehicle for Promoted Tumoral-Cell Uptake and Drug Delivery
  Du, J.-Z.; Sun, T.-M.; Song, W.-J.; Wu, J.; Wang, J. *Angew. Chem. Int. Ed***. 2010,** *49*, 3621 – 3626.
  Abstract:



A positive (or negative) chameleon: A nanogel that is negatively charged at physiological pH values and activated to be positively charged at tumor extracellular pH values was internalized efficiently by tumor cells both in vitro and in vivo (see illustration). Intracellular drug release was also enhanced, probably as a result of a decrease in the interaction between the drug and the nanogel in its protonated state.