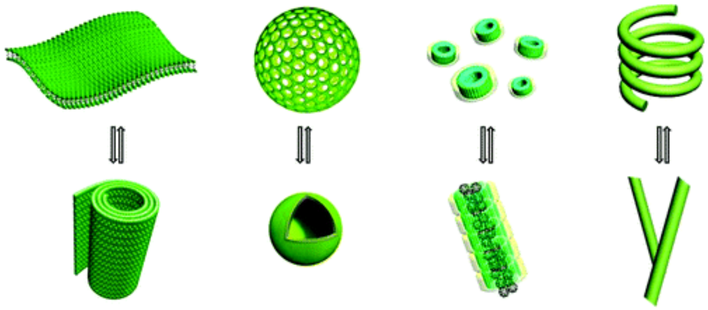
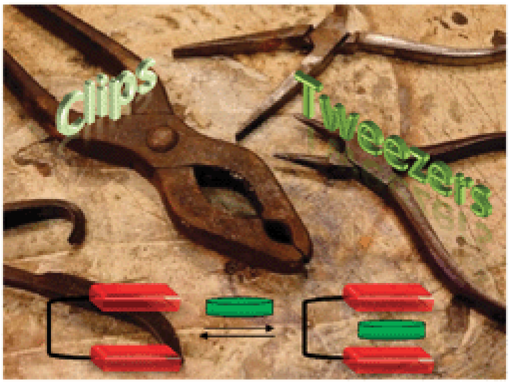
- Responsive Nanostructures from Aqueous Assembly of Rigid−Flexible Block Molecules
  Kim, H.-J.; Kim, T.; Lee, M. *Acc. Chem. Res.* **2011**, *44*, 72–82.
  Abstract:



During the past decade, supramolecular nanostructures produced via self-assembly processes have received considerable attention because these structures can lead to dynamic materials. Among these diverse self-assembly systems, the aqueous assemblies that result from the sophisticated design of molecular building blocks offer many potential applications for producing biocompatible materials that can be used for tissue regeneration, drug delivery, and ion channel regulation. Along this line, researchers have synthesized self-assembling molecules based on ethylene oxide chains and peptide building blocks to exploit water-soluble supramolecular structures. Another important issue in the development of systems that self-assemble is the introduction of stimuli-responsive functions into the nanostructures. Recently, major efforts have been undertaken to develop responsive nanostructures that respond to applied stimuli and dynamically undergo defined changes, thereby producing switchable properties. As a result, this introduction of stimuli-responsive functions into aqueous self-assembly provides an attractive approach for the creation of novel nanomaterials that are capable of responding to environmental changes.

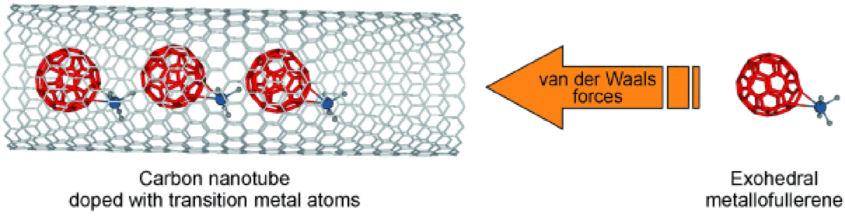
This Account describes recent work in our group to develop responsive nanostructures via the self-assembly of small block molecules based on rigid−flexible building blocks in aqueous solution. Because the rigid−flexible molecules self-assemble into nanoscale aggregates through subtle anisometric interactions, the small variations in local environments trigger rapid transformation of the equilibrium features. First, we briefly describe the general self-assembly of the rod amphiphiles based on a rigid−flexible molecular architecture in aqueous solution. We then highlight the structural changes and the optical/macroscopic switching that occurs in the aqueous assemblies in response to the external signals. For example, the aqueous nanofibers formed through the self-assembly of the rod amphiphiles respond to external triggers by changing their shape into nanostructures such as hollow capsules, planar sheets, helical coils, and 3D networks. When an external trigger is applied, supramolecular rings laterally associate and merge to form 2D networks and porous capsules with gated lateral pores. We expect that the combination of self-assembly principles and responsive properties will lead to a new class of responsive nanomaterials with many applications.

- Molecular clips and tweezers hosting neutral guests
  Hardouin–Lerouge, M.; Hudhomme, P.; Sallé, M. *Chem. Soc. Rev.* **2011**, *40*, 30-43.
  Abstract:



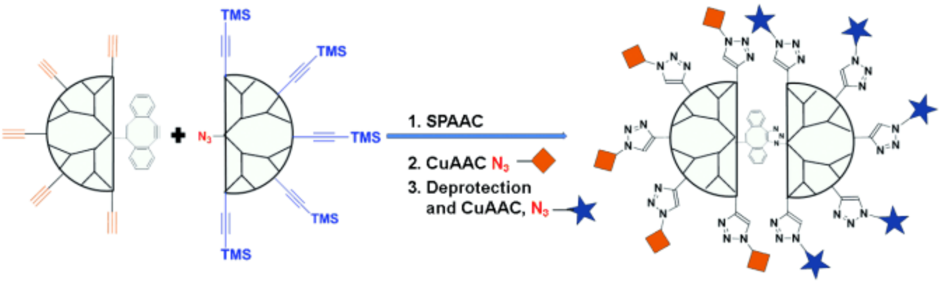
Intense current interest in supramolecular chemistry is devoted to the construction of molecular assemblies displaying controlled molecular motion associated to recognition. On this ground, molecular clips and tweezers have focused an increasing attention. This *tutorial review* points out the recent advances in the construction of always more sophisticated molecular clips and tweezers, illustrating their remarkably broad structural variety and focusing on their binding ability towards neutral guests. A particular attention is brought to recent findings in dynamic molecular tweezers whose recognition ability can be regulated by external stimuli. Porphyrin-based systems will not be covered here as this very active field has been recently reviewed.

- A Piggyback Ride for Transition Metals: Encapsulation of Exohedral Metallofullerenes in Carbon Nanotubes
  Chamberlain, T. W.; Champness, N. R.; Schröder, M.; Khlobystov, A. N. *Chem.-Eur. J.* **2011**, *17*, 668-674.
  Abstract:



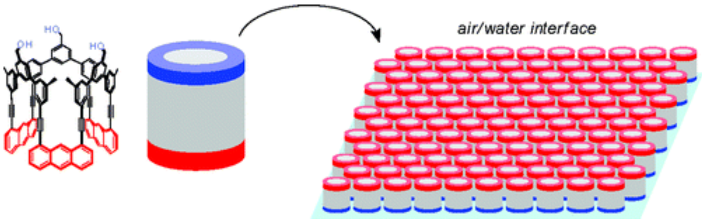
We have developed a method that enables the efficient insertion of transition-metal atoms and their small clusters into carbon nanotubes. As a model system, Os complexes attached to the exterior of fullerene C_{60} (exohedral metallofullerenes) were shown to be dragged into the nanotube spontaneously and irreversibly due to strong van der Waals interactions, specific to fullerenes and carbon nanotubes. The size of the metal-containing groups attached to C_{60} was shown to be critical for successful insertion, as functional groups too bulky to enter the nanotube were stripped off the fullerene during the encapsulation process. Once inside the nanotube, Os atoms catalyse polymerisation and decomposition of fullerene cages, which is related to a much higher catalytic activity of metal atoms situated on the surface of the fullerene cage, as compared to metal atoms in endohedral fullerenes, such as $M@C_{82}$. Thus, exohedral metallofullerenes show promise for applications in catalysis in carbon "nano" test tubes.

- Convergent Assembly and Surface Modification of Multifunctional Dendrimers by Three Consecutive Click Reactions
  Ledin, P. A.; Friscourt, F.; Guo, J.; Boons, G.-J. *Chem.-Eur. J.* **2011**, *17*, 839-846.
  Abstract:



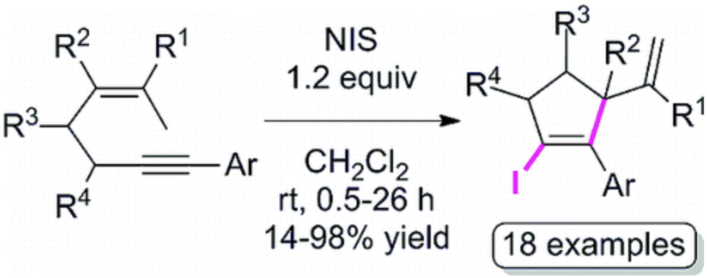
Multifunctional dendrimers bearing two or more surface functionalities have the promise to provide smart drug delivery devices that can for example combine tissue targeting and imaging or be directed more precisely to a specific tissue or cell type. We have developed a concise synthetic methodology for efficient dendrimer assembly and heterobifunctionalization based on three sequential azide–alkyne cycloadditions. The methodology is compatible with biologically important compounds rich in chemical functionalities such as peptides, carbohydrates, and fluorescent tags. In the approach, a strain-promoted azide–alkyne cycloaddition (SPAAC) between polyester dendrons modified at the focal point with an azido and 4-dibenzocyclooctynol (DIBO) moiety provided dendrimers bearing terminal and TMS-protected (TMS=trimethylsilyl) alkynes at the periphery. The terminal alkynes were outfitted with azido-modified polyethylene glycol (PEG) chains or galactosyl residues by using Cu$^{\mathrm{I}}$-catalyzed azide–alkyne cycloadditions (CuAAC). Next, a one-pot TMS deprotection and second click reaction of the resulting terminal alkyne with azido-containing compounds gave multifunctional dendrimers bearing complex biologically active moieties at the periphery.

- Macrocyclic Amphiphiles with 1,8-Anthrylene Fluorophores: Synthesis and Attempts toward Two-Dimensional Organization
  Kissel, P.; van Heijst, J.; Enning, R.; Stemmer, A.; Schlüter, A. D.; Sakamoto, J. *Org. Lett.* **2010**, *12*, 2778-2781.
  Abstract:



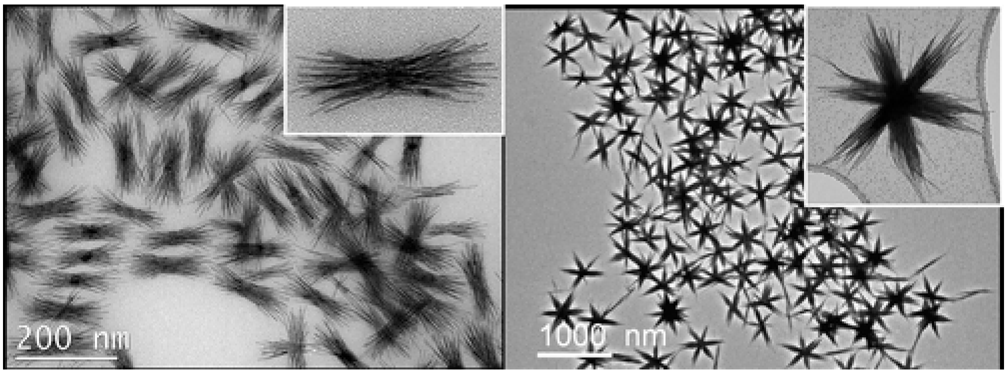
New macrocyclic amphiphiles with two or three integrated 1,8-anthrylenes have been synthesized by an iterative Sonogashira cross-couplingm protocol. The final cyclization has been conducted with 80% yield under cuprous-free dilution conditions. Formation of a monolayer at the air/water interface has also been demonstrated. These results open the intriguing possibility to construct large 2D supramolecular/macromolecular systems for which unique photophysical and -chemical properties are expected.

- Room-Temperature Metal-Free Electrophilic *5-endo*-Selective Iodocarbocyclization of 1,5-Enynes
  Pradal, A.; Nasr, A.; Toullec, P. Y.; Michelet, V. *Org. Lett.* **2010**, *12*, 5222-5225.
  Abstract:



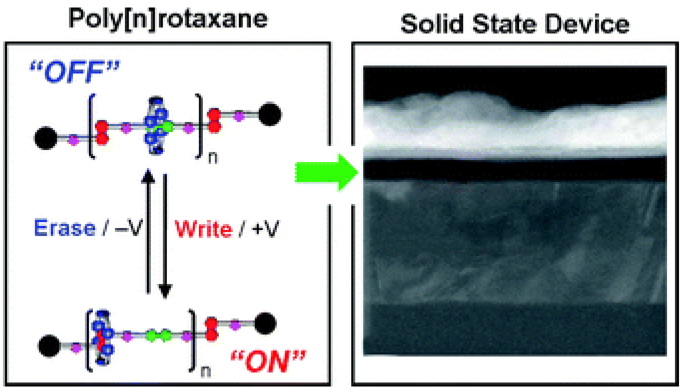
A highly efficient NIS-promoted iodocarbocyclization reaction of various functionalized 1,5-enynes is described via a 5-*endo* diastereoselective process. The cyclizations are conducted in the presence of 1.2 equiv of *N*-iodosuccinimide in dichloromethane at room temperature. The reaction conditions are compatible with several functional groups and lead to original iodo-functionalized carbocycles in good to excellent yields.

- Controlled Synthesis of Uniform Cobalt Phosphide Hyperbranched Nanocrystals Using Tri-*n*-octylphosphine Oxide as a Phosphorus Source
  Zhang, H.; Ha, D.-H.; Hovden, R.; Kourkoutis, L. F.; Robinson, R. D. *Nano Lett.* **2011**, *11*, 188–197.
  Abstract:



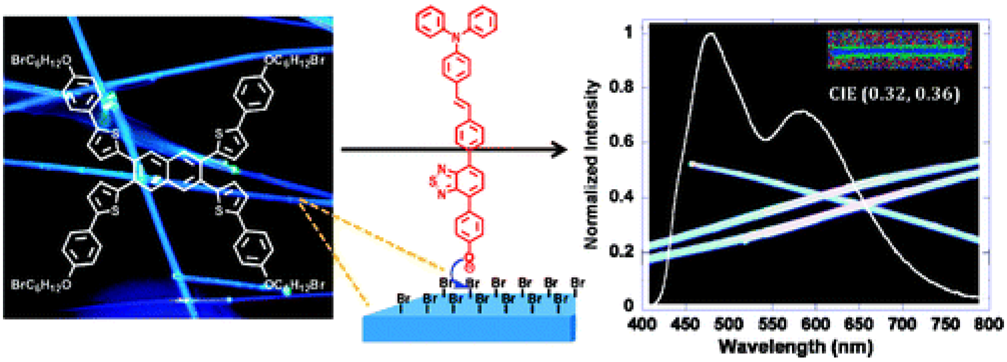
A new method to produce hyperbranched Co_2P nanocrystals that are uniform in size, shape, and symmetry was developed. In this reaction tri-*n*-octylphosphine oxide (TOPO) was used as both a solvent and a phosphorus source. The reaction exhibits a novel monomer-saturation-dependent tunability between Co metal nanoparticle (NP) and Co_2P NP products. The morphology of Co_2P can be controlled from sheaflike structures to hexagonal symmetric structures by varying the concentration of the surfactant. This unique product differs significantly from other reported hyperbranched nanocrystals in that the highly anisotropic shapes can be stabilized as the majority shape (>84%). This is the first known use of TOPO as a reagent as well as a coordinating background solvent in NP synthesis.

- A solid-state switch containing an electrochemically switchable bistable poly[*n*]rotaxane
  Zhang, W.; DeIonno, E.; Dichtel, W. R.; Fang, L.; Trabolsi, A.; Olsen, J.-C.; Benítez, D.; Heath, J. R.; Stoddart, F. J. *J. Mater. Chem.* **2011**, *21*, 1487-1495.
  Abstract:



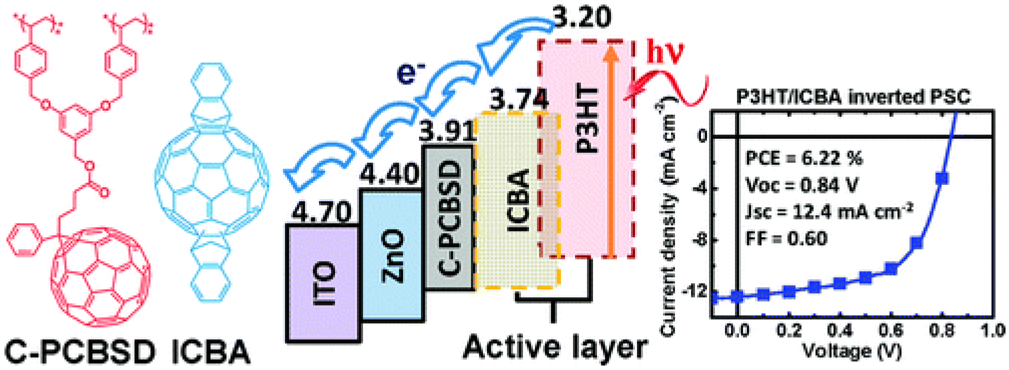
Electrochemically switchable bistable main-chain poly[*n*]rotaxanes have been synthesised using a threading-followed-by-stoppering approach and were incorporated into solid-state, molecular switch tunnel junction devices. In contrast to single-station poly[*n*]rotaxanes of similar structure, the bistable polymers do not fold into compact conformations held together by donor–acceptor interactions between alternating stacked π-electron rich and π-electron deficient aromatic systems. Films of the poly[*n*]rotaxane were incorporated into the devices by spin-coating, and their thickness was easily controlled. The switching functionality was characterised both (1) in solution by cyclic voltammetry and (2) in devices containing either two metal electrodes or one metal and one silicon electrode. Devices with one silicon electrode displayed hysteretic responses with applied voltage, allowing the devices to be switched between two conductance states, whereas devices containing two metal electrodes did not exhibit switching behaviour. The electrochemically switchable bistable poly[*n*]rotaxanes offer significant advantages in synthetic efficiency and ease of device fabrication as compared to bistable small-molecule [2]rotaxanes.

- Surface Modification of Self-Assembled One-Dimensional Organic Structures: White-Light Emission and Beyond
  Wang, X.; Yan, J.; Zhou, Y.; Pei, J. *J. Am. Chem. Soc.* **2010**, *132*, 15872–15874.
  Abstract:



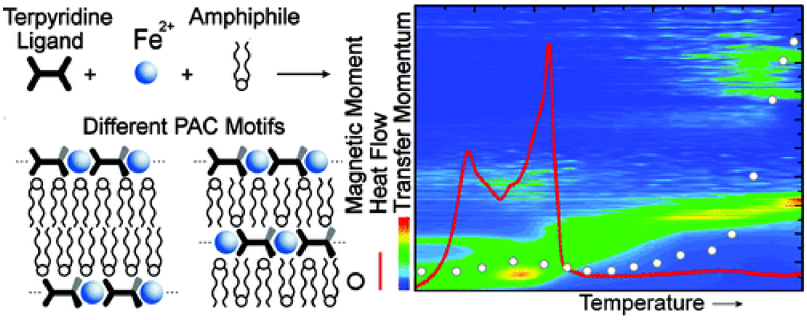
Surface modification is an important method to functionalize micro-/nanostructures, but substrates are mainly confined to robust inorganic compounds. We develop here a facile method to modify the surface of a fragile organic 1D microstructure. The bulk molecules and surface modifier were designed with orthogonal solubility to protect the molecular crystals from destruction under the reaction conditions. As a proof of concept, white-light-emitting 1D microstructures were obtained by grafting red chromophores onto the surface of self-assembled blue-emissive microwires via a heterophase S_N2 reaction. Spatial distribution of the two species is visualized by fluorescent lifetime mapping, which reveals a core−shell structure. The ability to postfunctionalize organic 1D structures enables many applications, where the surface property plays key roles, such as an organic P–N junction and a biosensor.

- Combination of Indene-C_{60} Bis-Adduct and Cross-Linked Fullerene Interlayer Leading to Highly Efficient Inverted Polymer Solar Cells
  Cheng, Y. J.; Hsieh, C.-H.; He, Y.; Hsu, C.-S.; Li, Y. *J. Am. Chem. Soc.* **2010**, *132*, 17381–17383.
  Abstract:



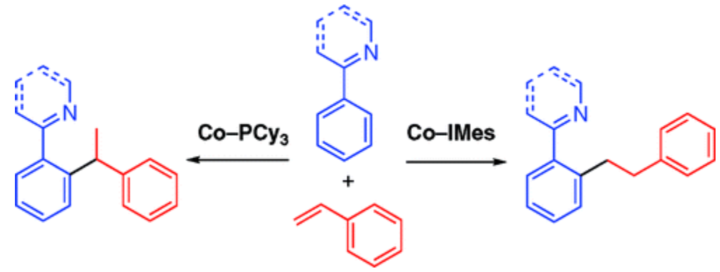
A poly(3-hexylthiophene) (P3HT)-based inverted solar cell using indene-C_{60} bis-adduct (ICBA) as the acceptor achieved a high open-circuit voltage of 0.82 V due to ICBA's higher-lying lowest unoccupied molecular orbital level, leading to an exceptional power-conversion efficiency (PCE) of 4.8%. By incorporating a cross-linked fullerene interlayer, C-PCBSD, to further modulate the interface characteristics, the ICBA:P3HT-based inverted device exhibited an improved short-circuit current and fill factor, yielding a record high PCE of 6.2%.

- Tuning the Structure and the Magnetic Properties of Metallo-supramolecular Polyelectrolyte–Amphiphile Complexes
  Schwarz, G.; Bodenthin, Y.; Tomkowicz, Z.; Haase, W.; Geue, T.; Kohlbrecher, J.; Pietsch, U.; Kurth, D. G. *J. Am. Chem. Soc.* **2011**, *133*, 547–558.
  Abstract:



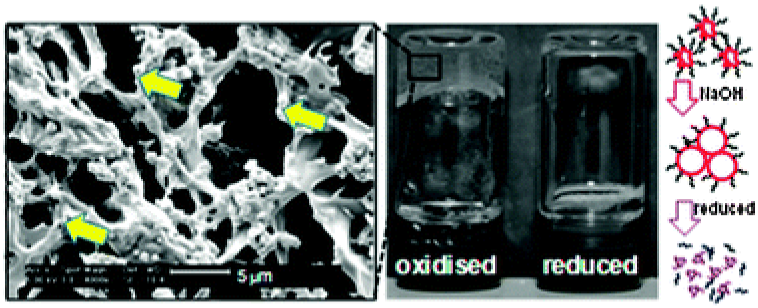
Self-assembly of Fe2+ ions and the rigid ditopic ligand 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene results in metallo-supramolecular coordination polyelectrolytes (MEPE). Sequential self-assembly of MEPE and dialkyl phosphoric acid esters of varying chain length via electrostatic interactions leads to the corresponding polyelectrolyte–amphiphile complexes (PAC), which have liquid–crystalline properties. The PACs have a stratified architecture where the MEPE is embedded in between the amphiphile layers. Upon heating above room temperature, the PACs show either a reversible or an irreversible spin-crossover (SCO) in a temperature range from 360 to 460 K depending on the architecture of the amphiphilic matrix. As the number of amphiphiles per metal ion is increased in the sequence 1:2, 1:4, and 1:6, the temperature of the SCO is shifted to higher values whereas the amphiphile chain length does not have a significant impact on the SCO temperature. In summary, we describe in this article how the structure and the magnetic response function of PACs can be tailored through the design of the ligand and the composition. To investigate the structure and the magnetic behavior, we use X-ray scattering, X-ray absorption spectroscopy, differential scanning calorimetry, faraday-balance, and superconducting quantum interference measurements in combination with molecular modeling.

- Regioselectivity-Switchable Hydroarylation of Styrenes
  Gao, K.; Yoshikai, N. *J. Am. Chem. Soc.* **2011**, *133*, 400–402.
  Abstract:



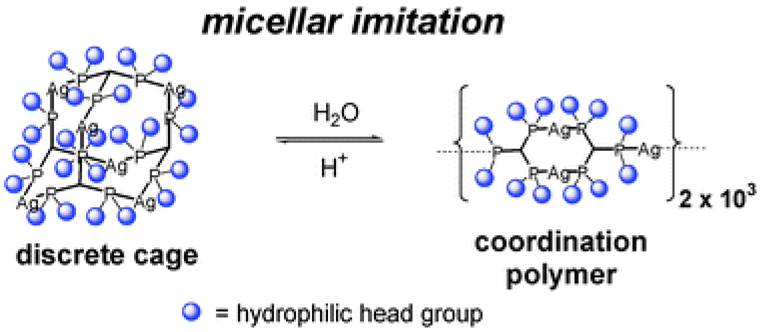
Cobalt−phosphine and cobalt−carbene catalysts have been developed for the hydroarylation of styrenes via chelation-assisted C−H bond activation, to afford branched and linear addition products, respectively, in a highly regioselective fashion. Deuterium-labeling experiments suggested a mechanism involving reversible C−H bond cleavage and olefin insertion steps and reductive elimination as the rate- and regioselectivity-determining step.

- Hollow polymer particles that are pH-responsive and redox sensitive: two simple steps to triggered particle swelling, gelation and disassembly
  Bird, R.; Freemont, T. J.; Saunders, B. R. *Chem. Commun.* **2011**, *47*, 1443-1445.
  Abstract:



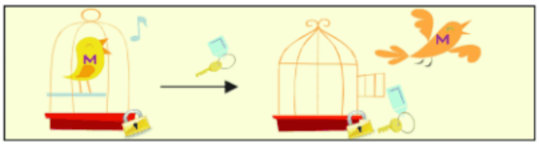
A new, simple, two-step method is introduced for preparing hollow particles that are both pH-responsive and redox sensitive. Hollow poly(methyl methacrylate-*co*-methacrylic acid) particles swell at moderate pH values, form gels in concentrated dispersions and can be disassembled by adding reducing agents.

- Imitating micelles as a way to control coordination self-assembly: cage-polymer switching directed rationally by solvent polarity or pH
  Giri, N.; James, S. L. *Chem. Commun.* **2011**, *47*, 1458-1460.
  Abstract:



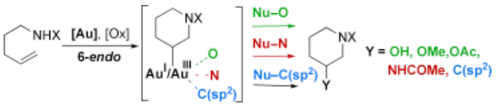
Disguising a metal complex as a micelle by using amphiphilic phosphine ligands enables it to switch between a coordination polymer and a discrete cage in response to solvent polarity or pH; this medium-dependent behaviour of the complex is rational because it parallels that of true micelles.

- Keys for Unlocking Photolabile Metal-Containing Cages
  Ciesienski, K. L.; Franz, K. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 814-824.
  Abstract:



Photolabile metal-containing cages are metal complexes that undergo a change in coordination environment upon exposure to light of an appropriate wavelength. The light-responsive functionality can either be a component of the encapsulating ligand or a property of the metal complex itself. The altered coordination properties of light-responsive complexes can result in release of the coordinated metal ion into its surroundings, a differential reactivity of the metal center, or the liberation of a reactive molecule that had been passivated by binding to the metal center. These triggerable agents can be useful tools for manipulating the bioavailability of metals or their coordinating ligands in order to study biological pathways or for potential therapeutic purposes.

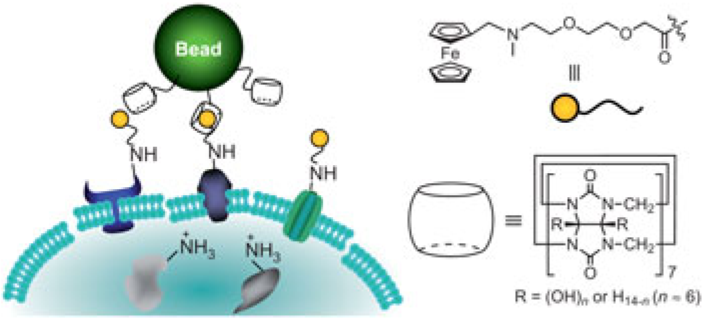
- Flexible Gold-Catalyzed Regioselective Oxidative Difunctionalization of Unactivated Alkenes
  Haro, T.; Nevado, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 906-910.
  Abstract:



AuI/AuIIIcatalytic cycles can trigger three highly regioselective alkene difunctionalization processes that involve the formation of C(sp^3)O, C(sp^3)N, and C(sp^3)C(sp^2) bonds. The reaction can proceed by reductive elimination on the oxidized gold center with complete retention of the configuration or through two subsequent nucleophilic substitution reactions via an aziridine intermediate.

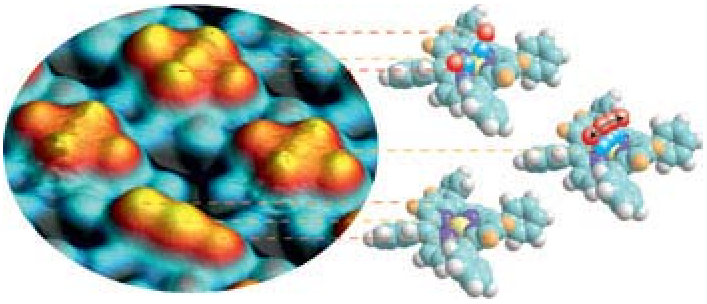
- Supramolecular fishing for plasma membrane proteins using an ultrastable synthetic host–guest binding pair

Lee, D.-W.; Park, K. M.; Banerjee, M.; Ha, S. H.; Lee, T.; Suh, K.; Paul, S.; Jung, H.; Kim, J.; Selvapalam, N.; Ryu, S. H.; Kim, K. *Nature Chem.* **2010**, *3*, 154–159.
Abstract:



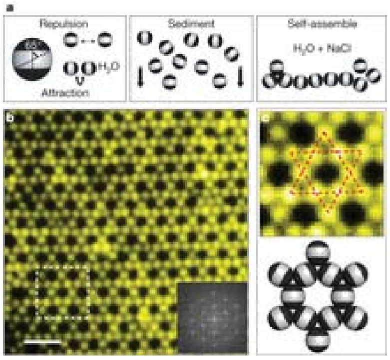
Membrane proteomics, the large-scale global analysis of membrane proteins, is often constrained by the efficiency of separating and extracting membrane proteins. Recent approaches involve conjugating membrane proteins with the small molecule biotin and using the receptor streptavidin to extract the labelled proteins. Despite the many advantages of this method, several shortcomings remain, including potential contamination by endogenously biotinylated molecules and interference by streptavidin during analytical stages. Here, we report a supramolecular fishing method for membrane proteins using the synthetic receptor–ligand pair cucurbit[7]uril–1-trimethylammoniomethylferrocene (CB[7]–AFc). CB[7]-conjugated beads selectively capture AFc-labelled proteins from heterogeneous protein mixtures, and AFc-labelling of cells results in the efficient capture of membrane proteins by these beads. The captured proteins can be recovered easily at room temperature by treatment with a strong competitor such as 1,1′-*bis*(trimethylammoniomethyl)ferrocene. This synthetic but biocompatible host–guest system may be a useful alternative to streptavidin–biotin for membrane proteomics as well as other biological and biotechnological applications.

- Cis-dicarbonyl binding at cobalt and iron porphyrins with saddle-shape conformation
  Seufert, K.; Bocquet, M.-L.; Auwärter, W.; Weber-Bargioni, A.; Reichert, J.; Lorente, N.; Barth, J. V. *Nature Chem.* **2010**, *3*, 114–119.
  Abstract:



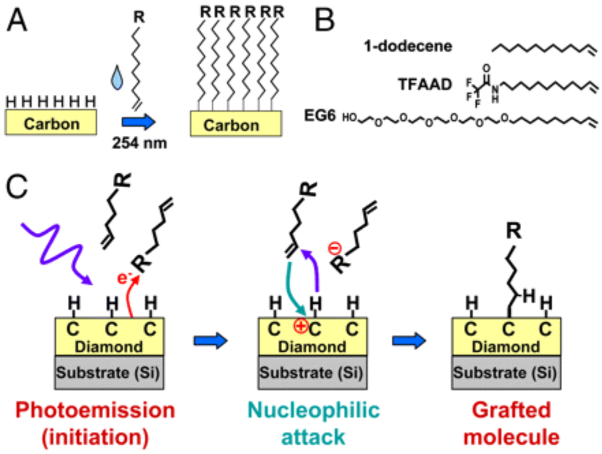
Diatomic molecules attached to complexed iron or cobalt centres are important in many biological processes. In natural systems, metallotetrapyrrole units carry respiratory gases or provide sensing and catalytic functions. Conceiving synthetic model systems strongly helps to determine the pertinent chemical foundations for such processes, with recent work highlighting the importance of the prosthetic groups' conformational flexibility as an intricate variable affecting their functional properties. Here, we present simple model systems to investigate, at the single molecule level, the interaction of carbon monoxide with saddle-shaped iron– and cobalt–porphyrin conformers, which have been stabilized as two-dimensional arrays on well-defined surfaces. Using scanning tunnelling microscopy we identified a novel bonding scheme expressed in tilted monocarbonyl and *cis*-dicarbonyl configurations at the functional metal-macrocycle unit. Modelling with density functional theory revealed that the weakly bonded diatomic carbonyl adduct can effectively bridge specific pyrrole groups with the metal atom as a result of the pronounced saddle-shape conformation of the porphyrin cage.

- Directed self-assembly of a colloidal kagome lattice
  Chen, Q.; Bae, S. C.; Granick, S. *Nature Chem.* **2010**, *469*, 381–384.
  <u>Abstract:</u>



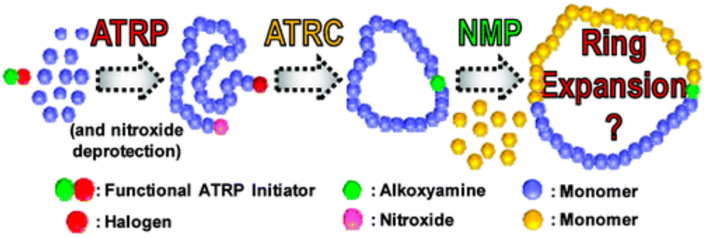
A challenging goal in materials chemistry and physics is spontaneously to form intended superstructures from designed building blocks. In fields such as crystal engineering and the design of porous materials, this typically involves building blocks of organic molecules, sometimes operating together with metallic ions or clusters. The translation of such ideas to nanoparticles and colloidal-sized building blocks would potentially open doors to new materials and new properties, but the pathways to achieve this goal are still undetermined. Here we show how colloidal spheres can be induced to self-assemble into a complex predetermined colloidal crystal—in this case a colloidal kagome lattice—through decoration of their surfaces with a simple pattern of hydrophobic domains. The building blocks are simple micrometre-sized spheres with interactions (electrostatic repulsion in the middle, hydrophobic attraction at the poles, which we call ‘triblock Janus’) that are also simple, but the self-assembly of the spheres into an open kagome structure contrasts with previously known close-packed periodic arrangements of spheres. This open network is of interest for several theoretical reasons. With a view to possible enhanced functionality, the resulting lattice structure possesses two families of pores, one that is hydrophobic on the rims of the pores and another that is hydrophilic. This strategy of ‘convergent’ self-assembly from easily fabricated colloidal building blocks encodes the target supracolloidal architecture, not in localized attractive spots but instead in large redundantly attractive regions, and can be extended to form other supracolloidal networks.

- Surface Chemistry Special Feature: Surface functionalization of thin-film diamond for highly stable and selective biological interfaces
  Stavis, C.; Lasseter Clare, T.; Butler, J. E.; Radadia, A. D.; Carr, R.; Zeng, H.; King, W. P.; Carlisle, J. A.; Aksimentiev, A.; Bashir, R.; Hamers, R. J. *Proc. Nat. Acad. Sci.* **2011**, *108*, 983-988.
  <u>Abstract:</u>



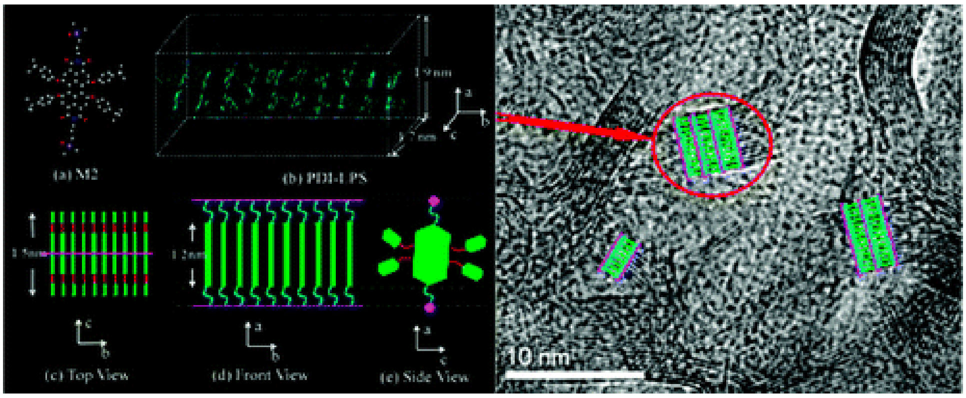
Carbon is an extremely versatile family of materials with a wide range of mechanical, optical, and mechanical properties, but many similarities in surface chemistry. As one of the most chemically stable materials known, carbon provides an outstanding platform for the development of highly tunable molecular and biomolecular interfaces. Photochemical grafting of alkenes has emerged as an attractive method for functionalizing surfaces of diamond, but many aspects of the surface chemistry and impact on biological recognition processes remain unexplored. Here we report investigations of the interaction of functionalized diamond surfaces with proteins and biological cells using X-ray photoelectron spectroscopy (XPS), atomic force microscopy, and fluorescence methods. XPS data show that functionalization of diamond with short ethylene glycol oligomers reduces the nonspecific binding of fibrinogen below the detection limit of XPS, estimated as > 97% reduction over H-terminated diamond. Measurements of different forms of diamond with different roughness are used to explore the influence of roughness on nonspecific binding onto H-terminated and ethylene glycol (EG)-terminated surfaces. Finally, we use XPS to characterize the chemical stability of *Escherichia coli* K12 antibodies on the surfaces of diamond and amine-functionalized glass. Our results show that antibody-modified diamond surfaces exhibit increased stability in XPS and that this is accompanied by retention of biological activity in cell-capture measurements. Our results demonstrate that surface chemistry on diamond and other carbon-based materials provides an excellent platform for biomolecular interfaces with high stability and high selectivity.

- Synthesis of Cyclic (Co)polymers by Atom Transfer Radical Cross-Coupling and Ring Expansion by Nitroxide-Mediated Polymerization
  Nicola, R; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 240–247.
  Abstract:



A novel approach to prepare cyclic polymers via a combination of atom transfer radical polymerization (ATRP) and atom transfer radical cross-coupling (ATRC) is presented. A functional ATRP initiator possessing an alkoxyamine group was synthesized and used to prepare well-defined linear telechelic α-nitroxy,ω-bromo homo- and block copolymers via ATRP and subsequent thermal deprotection of the α-terminal nitroxide function. Cyclization reactions were achieved by intramolecular ATRC under high dilution. Ring expansion of a cyclic polystyrene alkoxyamine prepared by ATRC was conducted via nitroxide-mediated polymerization (NMP) of styrene and yielded a mixture of linear and cyclic polycondensates. This result is discussed in detail and explained by the persistent radical effect (PRE), thermal initiation, and the occurrence of radical crossover reactions during chain extension via NMP.

- Synthesis of a Polymeric Electron Acceptor Based on Perylenediimide-Bridged Ladder Polysiloxane
  Fu, W.; He, C.; Jiang, S.; Chen, Z.; Zhang, J.; Li, Z.; Yan, S.; Zhang, R. *Macromolecules* **2011**, *44*, 203–207.
  Abstract:



A soluble perylenediimide (PDI) bridged ladder polysiloxane (PDI-LPS) was prepared using ladder superstructure (LS) directed dehydration polycondensation. LS was first assembled via synergistic interactions of hydrogen-bonding and π–π stacking of tetrasilanol monomers (M2s) as verified from XRD, 29Si NMR, and VPO characterizations. The ladder regularity of PDI-LPS was confirmed by a narrow half-peak width (Δ) of <1 ppm for SiO2/2 unit in the 29Si NMR spectra. The alignment of ladder chains was also demonstrated from high-resolution transmission electronic microscopy (HR-TEM) observations. We successfully used ladderlike structure to chemically confine PDI cores within one-dimensional polymeric semiconductor. The resulting PDI-LPS not only retained PDI's optoelectronic properties but also gained enhanced solubility in common organic solvents and improved thermal stability.