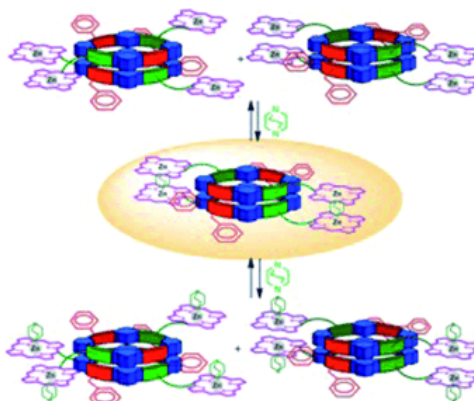


- Regioisomeric Control Induced by DABCO Coordination to Rotatable Self-Assembled Bis- and Tetraporphyrin α,γ -Cyclic Octapeptide Dimers
Hernández-Eguía, L. P.; Brea, R. J.; Castedo, L.; Ballester, P.; Granja, J. R. *Chem.-Eur. J.* **2011**, *17*, 1220-1229.

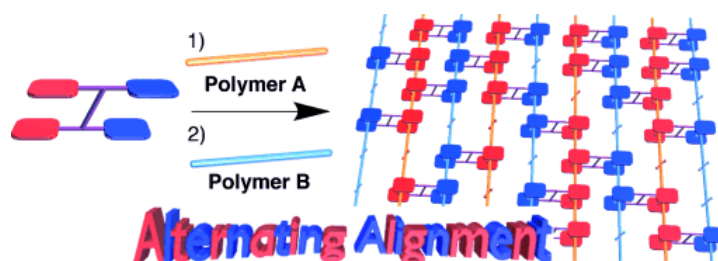
Abstract:



The design and synthesis of two α,γ -cyclic octapeptides decorated with one and two Zn-porphyrin units in their periphery is described. In nonpolar organic solvents the α,γ -cyclic octapeptides quantitatively self-assemble into Zn-bis- or -tetraporphyrin architectures that could act as molecular tweezers. The self-assembly process, however, is not regioselective and affords a mixture of different regioisomers that are involved in chemical exchange processes. The regioisomers with the Zn-porphyrin units positioned in register with respect to each other are proposed to be the less abundant species in the solution mixture. It has been demonstrated that the coordination of 1,4-diazabicyclo[2.2.2]octane (DABCO) to the supramolecular bis- or tetraporphyrin tweezers is an effective way to achieve regioisomeric control of the self-assembled mixture of dimers. Thus, DABCO functions as an external molecular trigger and, when used under strict stoichiometric control with respect to the Zn-porphyrin units, provokes the exclusive formation of self-assembled dimers with a cofacial arrangement of Zn-porphyrin units through the formation of sandwich-type complexes. The use of excess DABCO fragments the sandwich complexes and affords open dimers of high stoichiometry with DABCO molecules axially monocoordinated to the Zn-porphyrin units, probably as a regioisomeric mixture. In the case of Zn-tetraporphyrin tweezers, the ditopic coordination of DABCO at the two binding sites shows a moderate positive cooperativity factor, $\alpha P=5$. These assemblies have potential applications as light-induced energy and electron-transfer switches regulated by DABCO coordination; such applications would require the introduction of additional chromophores in the cyclic peptide scaffold.

- Alternating Arrays of Different Conjugated Polymers Utilizing a Synthetic Cross-Linker
Kaseyama, T.; Wakabayashi, R.; Shinkai, S.; Kaneko, K.; Takeuchi, M. *Chem.-Eur. J.* **2011**, *17*, 1793-1797.

Abstract:

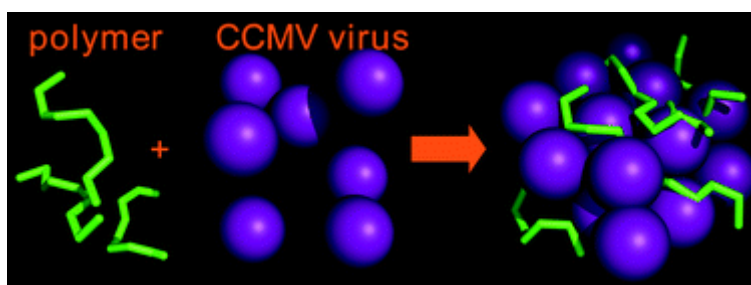


The ordered structures of two different kinds of polymers were efficiently formed through a supramolecular bundling approach by using an aligner molecule with two heterogeneous binding sites, zinc porphyrin and a palladium complex, to interact with poly(p-phenylene ethynylene)s and polyanilines (see scheme).

- Electrostatic self-assembly of virus–polymer complexes

Kostiainen, A. M. ; Hiekkataipale, P. ; De la Torre, J. A.; Nolte, R. J. M. ; Cornelissen, J. J. M. L. *J. Mater. Chem.* **2011**, *21*, 2112-2117.

Abstract:

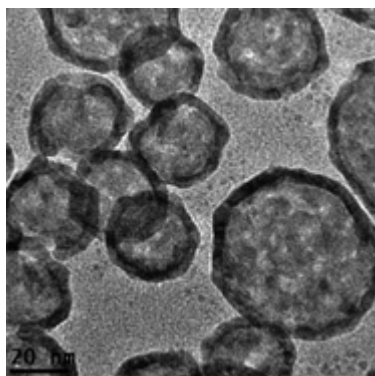


Amine functionalised and consequently cationic linear polymers, Newkome-type dendrons and PAMAM dendrimers can efficiently form electrostatic complexes with negatively charged cowpea chlorotic mottle viruses (CCMV). The complexes have been characterised by dynamic light scattering (DLS), gel electrophoresis, transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS), which describe in detail how the size and structure topology of the polyamine controls the complex formation with the virus. DLS results show that the complexes are approximately 1–2 μm in diameter, and their size can be tuned with the charge valency of the polymer and the ionic concentration of the media. TEM images and SAXS measurements demonstrate that individual virus particles can adopt hexagonal close packing within the complex and the observed distance between lattice points (27.9 nm) corresponds to the diameter of the native virus, which is 28 nm. Also the empty viral capsids and capsids loaded with Prussian blue nanoparticles can be assembled, which suggests that by controlling the assembly of the virus, it is possible to control the assembly of any material that is held inside the virus.

- Highly reproducible synthesis of hollow gold nanospheres with near infrared surface plasmon absorption using PVP as stabilizing agent

Preciado-Flores, S.; Wang, D.; Wheeler, D. A.; Newhouse, R.; Hensel, J. K.; Schwartzberg, A.; Wang, L.; Zhu, J.; Barboza-Flores, M.; Zhang, J. Z. *J. Mater. Chem.* **2011**, *21*, 2344-2350.

Abstract:

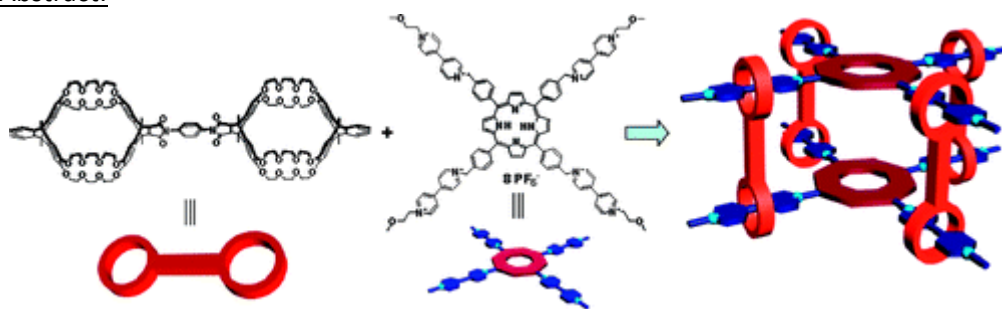


An improved synthetic method has been designed and demonstrated to reproducibly generate hollow gold nanospheres (HGNs) with strong surface plasmon resonance (SPR) absorption in the near infrared (NIR). The HGNs have been synthesized *via* galvanic replacement of cobalt with gold while utilizing different amounts of poly(vinylpyrrolidone) (PVP) as a template stabilizing agent. Ninety percent of syntheses performed by this modified method resulted in HGNs with an SPR near 800 nm, which is highly desirable for biomedical applications such as photothermal ablation (PTA) therapy, while other polymers (PAA and PEG) did not. Based on absorption and TEM measurements, PVP stabilizes the cobalt template particles *via* carbonyl-induced stabilization that slows nucleation and growth of the gold shell allowing for the generation of a reproducibly thin shell, thereby inducing a significant red shift of the SPR to 800 nm. The results are significant to various potential applications of HGNs, *e.g.* cancer therapy and sensing.

- Self-Assembled Interwoven Cages from Triptycene-Derived Bis-Macrotricyclic Polyether and Multiple Branched Paraquat-Derived Subunits

Guo, J.-B.; Jiang, Y.; Chen, C.-F. *Org. Lett.* **2010**, *12*, 5764-5767.

Abstract:

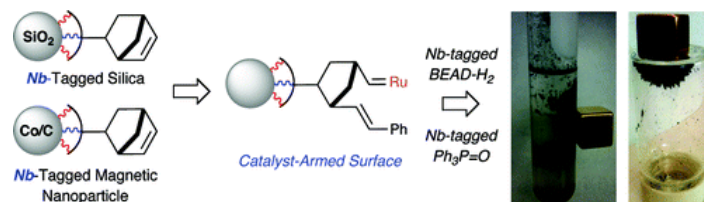


On the basis of formation of a 1:2 complex between the triptycene-derived bis-macrotricyclic polyether and the paraquat derivative, two novel well-defined interwoven supramolecular cages were constructed by the [3 + 2] and [4 + 2] self-assembly of the polyether and trifurcated and cross paraquat-derived subunits under millimolar concentrations, respectively.

- Monomer-on-Monomer (MoM) Mitsunobu Reaction: Facile Purification Utilizing Surface-Initiated Sequestration

Maity, P. K.; Rolfe, A.; Samarakoon, T. B.; Faisal, S.; Kurtz, R. D.; Long, T. R.; Schätz, A.; Flynn, D. L.; Grass, R. N.; Stark, W. J.; Reiser, O.; Hanson, P. R. *Org. Lett.* **2011**, *13*, 90-93.

Abstract:

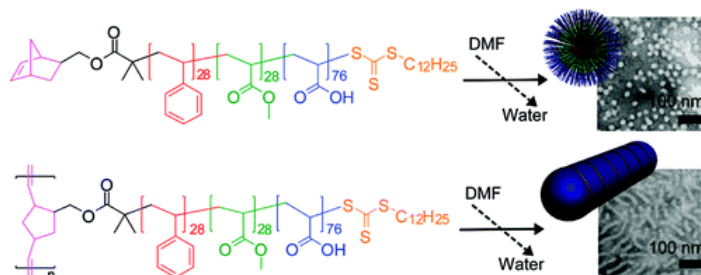


A monomer-on-monomer (MoM) Mitsunobu reaction utilizing norbornenyl-tagged (Nb-tagged) reagents is reported, whereby purification was rapidly achieved by employing ring-opening metathesis polymerization, which was initiated by any of three methods utilizing Grubbs catalyst: (i) free catalyst in solution, (ii) surface-initiated catalyst-armed silica, or (iii) surface-initiated catalyst-armed Co/C magnetic nanoparticles.

- Dynamic Cylindrical Assembly of Triblock Copolymers by a Hierarchical Process of Covalent and Supramolecular Interactions

Li, Z.; Ma, J.; Lee, N. S.; Wooley, K. L. *J. Am. Chem. Soc.* **2011**, *133*, 1228–1231.

Abstract:

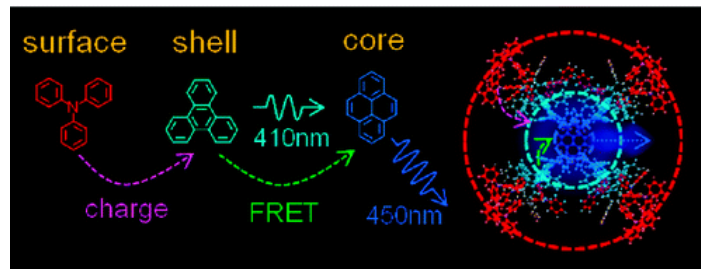


We have developed a hierarchical process that combines linear triblock copolymers into concentric globular subunits through strong chemical bonds and is followed by their supramolecular assembly *via* weak noncovalent interactions to afford one-dimensionally assembled, dynamic cylindrical nanostructures. The molecular brush architecture forces triblock copolymers to adopt intramolecular interactions within confined frameworks and then drives their intermolecular interactions in the mixtures of organic solvent and water. In contrast, the triblock copolymers, when not preconnected into the molecular brush architectures, organize only into globular assemblies.

- Core, Shell, and Surface-Optimized Dendrimers for Blue Light-Emitting Diodes

Qin, T.; Wiedemair, W.; Nau, S.; Trattnig, R.; Sax, S.; Winkler, S.; Vollmer, A.; Koch, N.; Baumgarten, M.; List, E. J. W.; Müllen, K. *J. Am. Chem. Soc.* **2011**, *133*, 1301–1303.

Abstract:

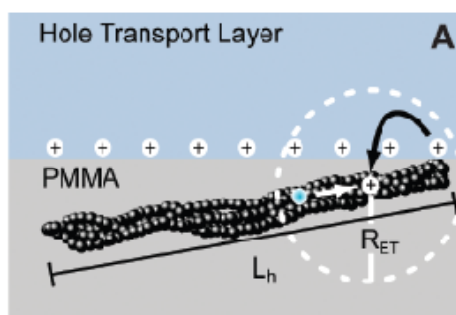


We present a novel core–shell–surface multifunctional structure for dendrimers using a blue fluorescent pyrene core with triphenylene dendrons and triphenylamine surface groups. We find efficient excitation energy transfer from the triphenylene shell to the pyrene core, substantially enhancing the quantum yield in solution and the solid state (4-fold) compared to dendrimers without a core emitter, while TPA groups facilitate the hole capturing and injection ability in the device applications. With a luminance of up to 1400 cd/m², a saturated blue emission CIE_{xy} = (0.15, 0.17) and high operational stability, these dendrimers belong to the best reported fluorescence-based blue-emitting organic molecules.

- Ultralong-Range Polaron-Induced Quenching of Excitons in Isolated Conjugated Polymers

Bolinger, J. C.; Traub, M. C.; Adachi, T.; Barbara, P. F. *Science* **2011**, *331*, 565–567.

Abstract:

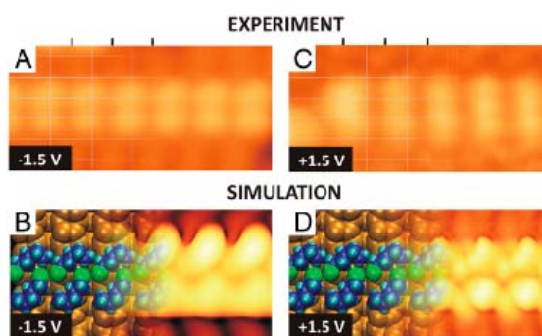


In conjugated polymers, radiative recombination of excitons (electron-hole pairs) competes with nonradiative thermal relaxation pathways. We visualized exciton quenching induced by hole polarons in single-polymer chains in a device geometry. The distance-scale for quenching was measured by means of a new subdiffraction, single-molecule technique—bias-modulated intensity centroid spectroscopy—which allowed the extraction of a mean centroid shift of 14 nanometers for highly ordered, single-polymer nanodomains. This shift requires energy transfer over distances an order of magnitude greater than previously reported for bulk conjugated polymers and far greater than predicted by the standard mechanism for exciton quenching, the unbiased diffusion of free excitons to quenching sites. Instead, multistep “energy funneling” to trapped, localized polarons is the probable mechanism for polaron-induced exciton quenching.

- Imprinting self-assembled patterns of lines at a semiconductor surface, using heat, light, or electrons

Harikumar, K. R.; McNab, I. R.; Polanyi, J. C.; Zabet-Khosousi, A.; Hofer, W. A. *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 950-955.

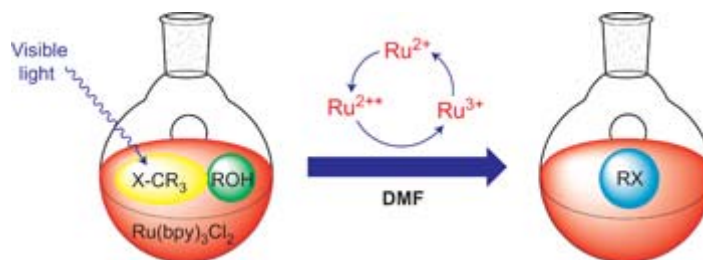
Abstract:



The fabrication of nano devices at surfaces makes conflicting demands of mobility for self-assembly (SA) and immobility for permanence. The solution proposed in earlier work from this laboratory involved pattern formation in physisorbed molecules by SA, followed by localized reaction to chemically imprint the pattern substantially unchanged, a procedure we termed molecular-scale imprinting (MSI). Here, as proof of generality we extended this procedure, previously applied to imprinting circles on Si(111)-7 × 7, to SA lines of 1-chloropentane (CP) on Si(100)-2 × 1. The physisorbed lines consisted of pairs of CP that grew perpendicular to the Si dimer rows, as shown by scanning tunneling microscopy and ab initio theory. Chemical reaction of these lines with the surface was triggered in separate experiments by three different modes of energization: heat, electrons, or light. In all cases the CP molecules underwent MSI with a Si atom beneath so that the physisorbed lines of CP pairs were imprinted as chemisorbed lines of Cl pairs.

- Visible-light-mediated conversion of alcohols to halides
Dai, C.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nature Chemistry* **2011**, 3, 140–145.

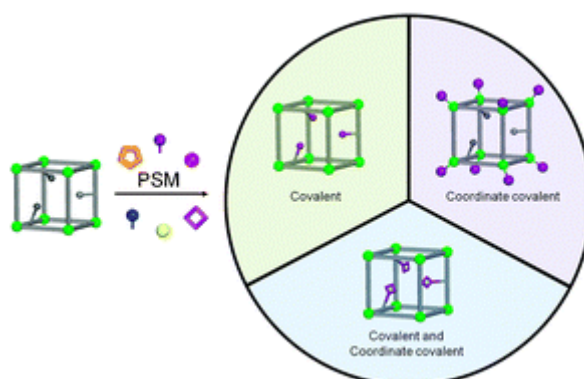
Abstract:



The development of new means of activating molecules and bonds for chemical reactions is a fundamental objective for chemists. In this regard, visible-light photoredox catalysis has emerged as a powerful technique for chemoselective activation of chemical bonds under mild reaction conditions. Here, we report a visible-light-mediated photocatalytic alcohol activation, which we use to convert alcohols to the corresponding bromides and iodides in good yields, with exceptional functional group tolerance. In this fundamentally useful reaction, the design and operation of the process is simple, the reaction is highly efficient, and the formation of stoichiometric waste products is minimized.

- Postsynthetic modification of metal–organic frameworks—a progress report
Tanabe, K. K.; Cohen, S. M. *Chem. Soc. Rev.* **2011**, 40, 498-519.

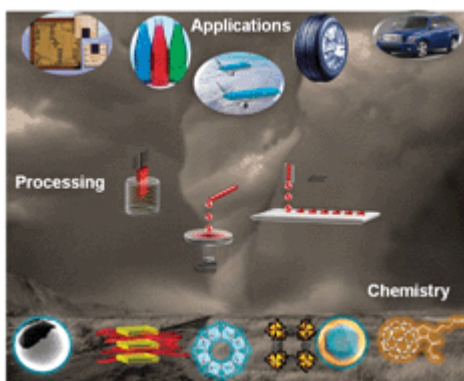
Abstract:



Metal–organic frameworks (MOFs) are an important class of hybrid inorganic–organic materials. In this *tutorial review*, a progress report on the postsynthetic modification (PSM) of MOFs is provided. PSM refers to the chemical modification of the MOF lattice in a heterogeneous fashion. This powerful synthetic approach has grown in popularity and resulted in a number of advances in the functionalization and application of MOFs. The use of PSM to develop MOFs with improved gas sorption, catalytic activity, bioactivity, and more robust physical properties is discussed. The results reported to date clearly show that PSM is an important approach for the development and advancement of these hybrid solids.

- Applications of advanced hybrid organic–inorganic nanomaterials: from laboratory to market
Sanchez, C.; Belleville, P.; Popall, M.; Nicole, L. *Chem. Soc. Rev.* **2011**, 40, 696-753.

Abstract:



Today cross-cutting approaches, where molecular engineering and clever processing are synergistically coupled, allow the chemist to tailor complex hybrid systems of various shapes with perfect mastery at different size scales, composition, functionality, and morphology. Hybrid materials with organic–inorganic or bio–inorganic character represent not only a new field of basic research but also, *via* their remarkable new properties and multifunctional nature, hybrids offer prospects for many new applications in extremely diverse fields. The description and discussion of the major applications of hybrid inorganic–organic (or biologic) materials are the major topic of this *critical review*. Indeed, today the very large set of accessible hybrid materials span a wide spectrum of properties which yield the emergence of innovative industrial applications in various domains such as optics, micro-electronics, transportation, health, energy, housing, and the environment among others (526 references).