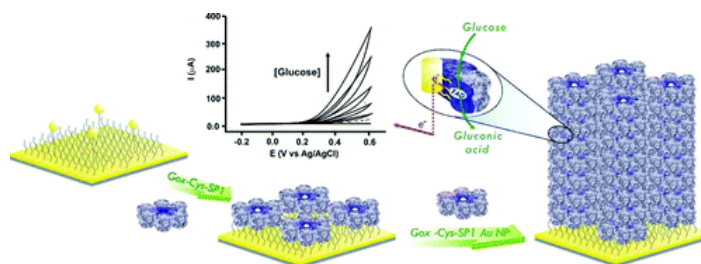


- Wiring of Redox Enzymes on Three Dimensional Self-Assembled Molecular Scaffold
Frasconi, M.; Heyman, A.; Medalsy, I.; Porath, D.; Mazzei, F.; Shoseyov, O. *Langmuir* **2011**, *27*, 12606-12613.

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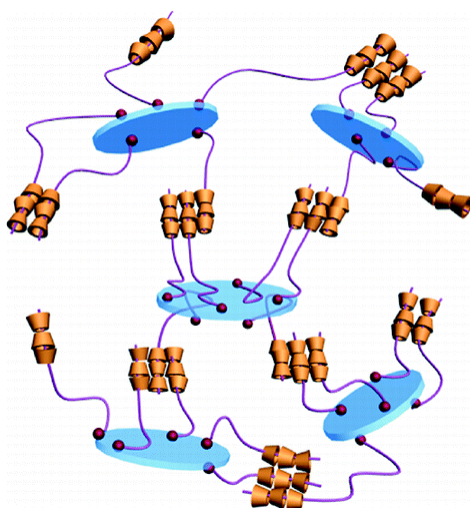
Abstract:



The integration of biological molecules and nanoscale components provides a fertile basis for the construction of hybrid materials of synergic properties and functions. Stable protein 1 (SP1), a highly stable ring shaped protein, was recently used to display different functional domains, to bind nanoparticles (NPs), and to spontaneously form two and three-dimensional structures. Here we show an approach to wire redox enzymes on this self-assembled protein–nanoparticle hybrid. Those hybrids are genetically engineered SP1s, displaying glucose oxidase (GOx) enzymes tethered to the protein inner pore. Moreover, the Au-NP–protein hybrids self-assembled to multiple enzymatic layers on the surface. By wiring the redox enzymes to the electrode, we present an active structure for the bioelectrocatalytic oxidation of glucose. This system demonstrates for the first time a three-dimensional assembly of multiple catalytic modules on a protein scaffold with an efficient electrical wiring of the enzyme units on an electrode surface, thus implementing a hybrid electrically active unit for nanobioelectronic applications.

- Pseudopolyrotaxanes on Inorganic Nanoplatelets and their Supramolecular Hydrogels
Liao, X.; Chen, G.; Jiang, M. *Langmuir* **2011**, *27*, 12650-12656.

Abstract:



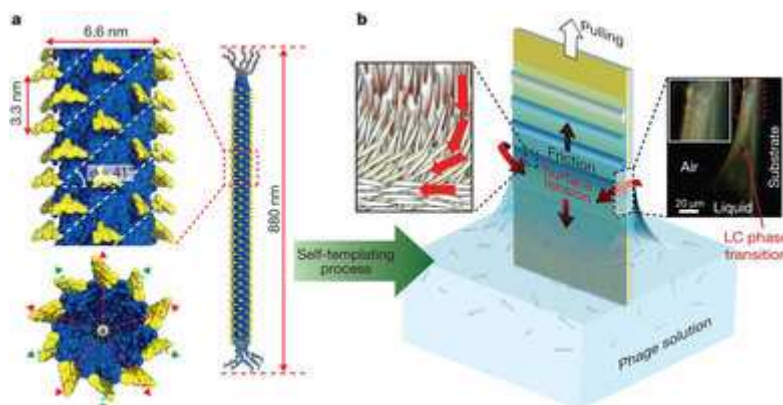
In this paper, we demonstrate the first hybrid suprastructure of pseudopolyrotaxanes (PPRs) on clay nanoplatelets. Simple end-modification of poly(ethylene glycol) with pyridinium (PEG- N^+) enabled the chains to form brushlike conformation on clay surfaces. Thus, the PEG chains were able to thread into the cavities of α -cyclodextrins (α -CDs), leading to hybrid PPR hydrogels. This was very different from the unmodified PEG chains, which were absorbed onto the clay surface and thus made the PPR formation impossible. The hydrogels made of this PPR-on-clay structure displayed a dynamic

modulus 1 order of magnitude higher than those of the native PPR hydrogels. Furthermore, based on the competitive host–guest interactions, such hybrid hydrogels showed fully photoreversible sol–gel transition after a competitive guest containing azobenzene moiety was introduced.

- Biomimetic self-templating supramolecular structures

Chung, W.-J.; Oh, J.-W.; Kwak, K.; Lee, B. Y.; Meyer, J.; Wang, E.; Hexemer, A.; Lee, S.-W. *Nature* **2011**, *478*, 364–368.

Abstract:

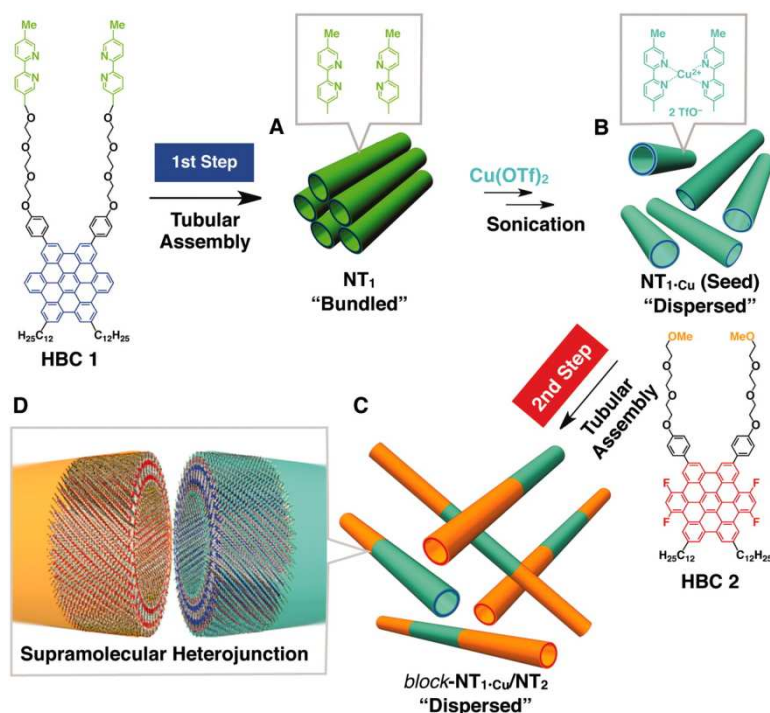


In nature, helical macromolecules such as collagen, chitin and cellulose are critical to the morphogenesis and functionality of various hierarchically structured materials. During tissue formation, these chiral macromolecules are secreted and undergo self-templating assembly, a process whereby multiple kinetic factors influence the assembly of the incoming building blocks to produce non-equilibrium structures. A single macromolecule can form diverse functional structures when self-templated under different conditions. Collagen type I, for instance, forms transparent corneal tissues from orthogonally aligned nematic fibres, distinctively coloured skin tissues from cholesteric phase fibre bundles, and mineralized tissues from hierarchically organized fibres. Nature's self-templated materials surpass the functional and structural complexity achievable by current top-down and bottom-up fabrication methods. However, self-templating has not been thoroughly explored for engineering synthetic materials. Here we demonstrate the biomimetic, self-templating assembly of chiral colloidal particles (M13 phage) into functional materials. A single-step process produces long-range-ordered, supramolecular films showing multiple levels of hierarchical organization and helical twist. Three distinct supramolecular structures are created by this approach: nematic orthogonal twists, cholesteric helical ribbons and smectic helicoidal nanofilaments. Both chiral liquid crystalline phase transitions and competing interfacial forces at the interface are found to be critical factors in determining the morphology of the templated structures during assembly. The resulting materials show distinctive optical and photonic properties, functioning as chiral reflector/filters and structural colour matrices. In addition, M13 phages with genetically incorporated bioactive peptide ligands direct both soft and hard tissue growth in a hierarchically organized manner. Our assembly approach provides insight into the complexities of hierarchical assembly in nature and could be expanded to other chiral molecules to engineer sophisticated functional helical-twisted structures.

- Supramolecular Linear Heterojunction Composed of Graphite-Like Semiconducting Nanotubular Segments

Zhang, W.; Jin, W.; Fukushima, T.; Saeki, A.; Seki, S.; Aida, T. *Science* **2011**, *334*, 340-343.

Abstract:

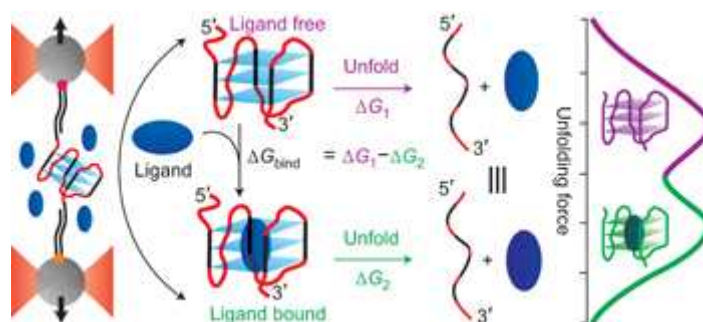


One-dimensionally connected organic nanostructures with dissimilar semiconducting properties are expected to provide a reliable platform in understanding the behaviors of photocarriers, which are important for the development of efficient photon-to-electrical energy conversion systems. Although bottom-up supramolecular approaches are considered promising for the realization of such nanoscale heterojunctions, the dynamic nature of molecular assembly is problematic. We report a semiconducting nanoscale organic heterojunction, demonstrated by stepwise nanotubular coassembly of two strategically designed molecular graphenes. The dissimilar nanotubular segments, thus connected noncovalently, were electronically communicable with one another over the heterojunction interface and displayed characteristic excitation energy transfer and charge transport properties not present in a mixture of the corresponding homotropically assembled nanotubes.

- A single-molecule platform for investigation of interactions between G-quadruplexes and small-molecule ligands

Koirala, D.; Dhakal, S.; Ashbridge, B.; Sannohe, Y.; Rodriguez, R.; Sugiyama, H.; Balasubramanian, S.; Mao, H. *Nature Chem.* **2011**, *3*, 782-787.

Abstract:



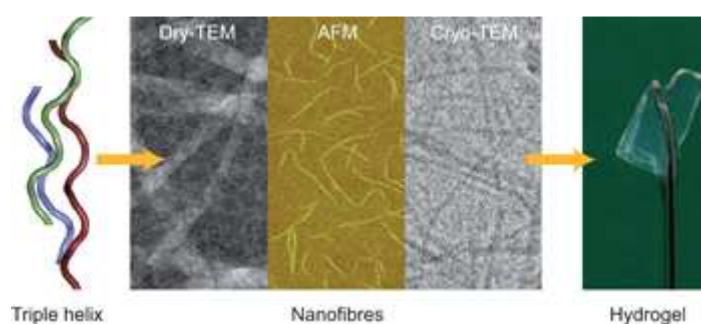
Ligands that stabilize the formation of telomeric DNA G-quadruplexes have potential as cancer treatments, because the G-quadruplex structure cannot be extended by telomerase, an enzyme over-expressed in many cancer cells. Understanding the kinetic, thermodynamic and mechanical

properties of small-molecule binding to these structures is therefore important, but classical ensemble assays are unable to measure these simultaneously. Here, we have used a laser tweezers method to investigate such interactions. With a force jump approach, we observe that pyridostatin promotes the folding of telomeric G-quadruplexes. The increased mechanical stability of pyridostatin-bound G-quadruplex permits the determination of a dissociation constant K_d of 490 ± 80 nM. The free-energy change of binding obtained from a Hess-like process provides an identical K_d for pyridostatin and a K_d of 42 ± 3 mM for a weaker ligand RR110. We anticipate that this single-molecule platform can provide detailed insights into the mechanical, kinetic and thermodynamic properties of liganded bio-macromolecules, which have biological relevance.

- Multi-hierarchical self-assembly of a collagen mimetic peptide from triple helix to nanofibre and hydrogel

O'Leary, L. E. R.; Fallas, J. A.; Bakota, E. L.; Kang, M. K.; Hartgerink, J. D. *Nature Chem.* **2011**, *3*, 821-828.

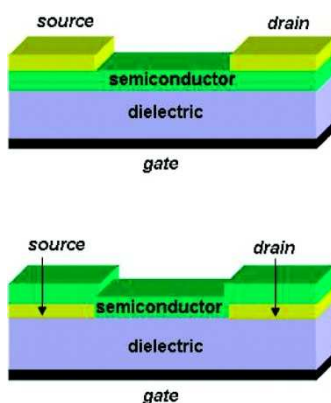
Abstract:



Replicating the multi-hierarchical self-assembly of collagen has long-attracted scientists, from both the perspective of the fundamental science of supramolecular chemistry and that of potential biomedical applications in tissue engineering. Many approaches to drive the self-assembly of synthetic systems through the same steps as those of natural collagen (peptide chain to triple helix to nanofibres and, finally, to a hydrogel) are partially successful, but none simultaneously demonstrate all the levels of structural assembly. Here we describe a peptide that replicates the self-assembly of collagen through each of these steps. The peptide features collagen's characteristic proline–hydroxyproline–glycine repeating unit, complemented by designed salt-bridged hydrogen bonds between lysine and aspartate to stabilize the triple helix in a sticky-ended assembly. This assembly is propagated into nanofibres with characteristic triple helical packing and lengths with a lower bound of several hundred nanometres. These nanofibres form a hydrogel that is degraded by collagenase at a similar rate to that of natural collagen.

- Role of Molecular Order and Solid-State Structure in Organic Field-Effect Transistors
Mas-Torrent, M.; Rovira, C. *Chem. Rev.*, **2011**, *111*, 4833–4856.

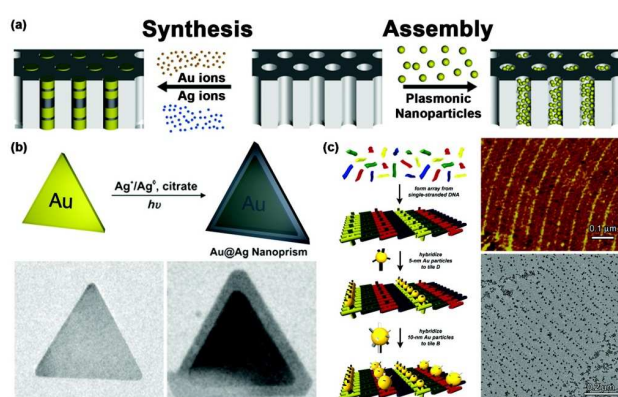
Abstract:



The invention of the transistor in 1947 by John Bardeen, William Shockley, and Walter Brattain is regarded as one of the greatest discoveries of the 20th century since it is the basic component in modern electronics. Since the first Ge-based device a few centimeters in size, the microelectronics industry has developed rapidly, and microprocessors with hundreds of millions of transistors are currently fabricated. However, due to the fact that inorganic electronics have some technological limitations associated with them, organic-based devices have recently emerged in the market, beginning to replace amorphous silicon in some applications, and also have great possibility to find their place in a wide range of new applications. One of their main advantages is solution-processability, and thus, organic materials offer the possibility to fabricate low-cost and flexible devices and are also suitable for large area applications. This has been the motivation for why this field has been labeled “organic and large area electronics (OLAE)”. In addition, the versatility of organic synthesis allows for the preparation of materials “à la carte”. That is, since by chemically modifying their molecular structure and functionality the solid-state structure and the resulting macroscopic properties are altered, it is feasible to synthesize tailored materials for specific uses.

- Templated Techniques for the Synthesis and Assembly of Plasmonic Nanostructures
Jones, M. R.; Osberg, K. D.; Macfarlane, R. J.; Langille, M. R.; Mirkin, C. A. *Chem. Rev.*, **2011**, *111*, 3736–3827.

Abstract:



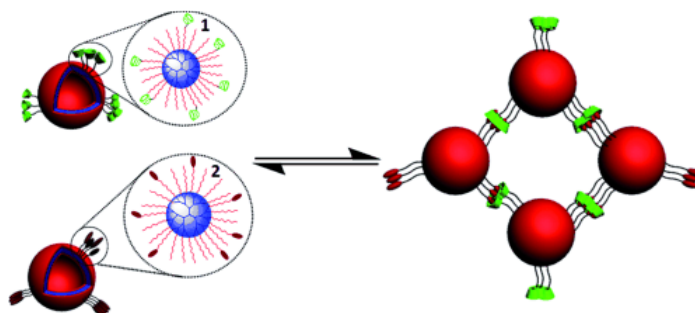
The field of plasmonics has become one of the most interesting and active research areas in nanotechnology, enabling numerous fundamental studies and applications in a variety of scientific disciplines. A plasmon oscillation can be described as the collective motion of conduction band electrons relative to fixed positive ions (i.e., atoms) in a metal that is driven by the electric field component of incident light. When excited in subwavelength structures, these oscillations allow for extraordinary confinement and manipulation of light at nanometer length scales. In addition, coupling between neighboring nanostructures, particularly when arranged in a periodic lattice, can

lead to unique emergent properties that have motivated an understanding of the assembly of these materials. Such phenomena have already led to applications as diverse as ultrasensitive detection schemes and waveguides and lenses, as well as advances in the fields of light harvesting and metamaterials. While relatively simple, generally isotropic, and homogeneous nanostructures have demonstrated some of these effects and have been crucial for understanding the fundamental phenomena underlying this field, building structures with increased complexity and hierarchy will be necessary to realize the most useful and scientifically fruitful nanoscale architectures. Many recent advances by chemists and materials scientists to overcome the barriers for achieving these requisite levels of intricacy can be traced to a simple and generalizable synthetic strategy—the use of a nanoscale template that serves to influence the growth or assembly of nanostructures with rationally designed dimensions, morphologies, phases, and/or supercrystal symmetries.

- Reversible and Large-Scale Cytomimetic Vesicle Aggregation: Light-Responsive Host–Guest Interactions

Jin, H.; Zheng, Y.; Liu, Y.; Cheng, H.; Zhou, Y.; Yan, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 10352–10356.

Abstract:

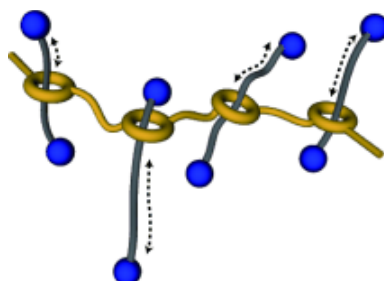


Sleeping giants: As a mimic of cell agglomeration to form tissues, a novel vesicle aggregation process with the characteristic advantages of being highly efficient, light-responsive, reversible, large-scale, and stable is reported. Giant hyperbranched polymer vesicles (5–10 μm) are used as the building blocks (see scheme), and the vesicle aggregates can assemble and disassemble with alternating UV and Vis irradiation.

- Graft Polyrotaxanes: A New Class of Graft Copolymers with Mobile Graft Chains

Kohsaka, Y.; Koyama, Y.; Takata, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 10417–10420.

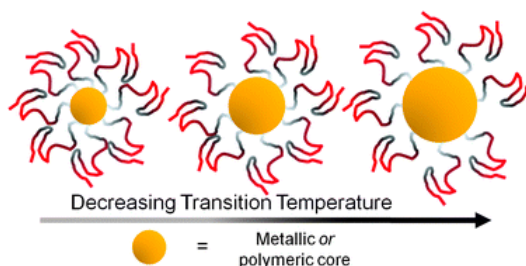
Abstract:



The synthesis and structure of graft polyrotaxane, a novel class of graft copolymer possessing mobile graft chains, is described. Poly(tetrahydrofuran) was bound to the axle components of pseudo[2]rotaxane as the graft chain by a grafting-onto method to afford the corresponding graft polyrotaxane (see picture). *N*-Acetylation of the ammonium moieties lead to an increase in the dynamic radius of the graft polyrotaxane.

- The critical importance of size on thermoresponsive nanoparticle transition temperatures: gold and micelle-based polymer nanoparticles
leong, N. S.; Brebis, K.; Daniel, L. E.; O'Reilly, R. K.; Gibson, M. I. *Chem. Commun.* **2011**, 47, 11627-11629.

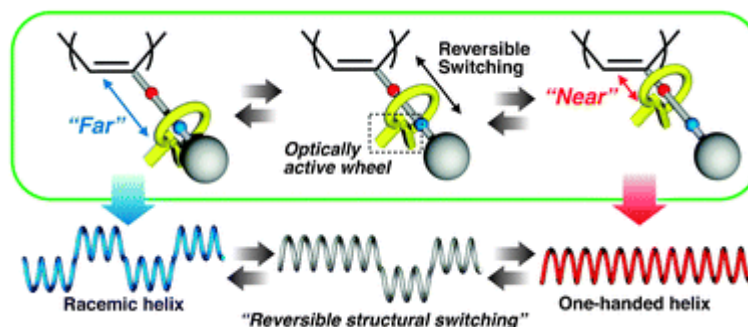
Abstract:



The synthesis and application of thermally-responsive macromolecules and nanoparticles relies on the underpinning control of their transition temperatures. The present study shows that two structurally diverse classes of nanoparticle have very strong diameter-dependent responses to temperature-stimuli, demonstrating that the exact size of the nanostructure can significantly impact its performance.

- Rational control of a polyacetylene helix by a pendant rotaxane switch
Ishiwari, F.; Nakazono, K.; Koyama, Y.; Takata, T. *Chem. Commun.* **2011**, 47, 11739-11741.

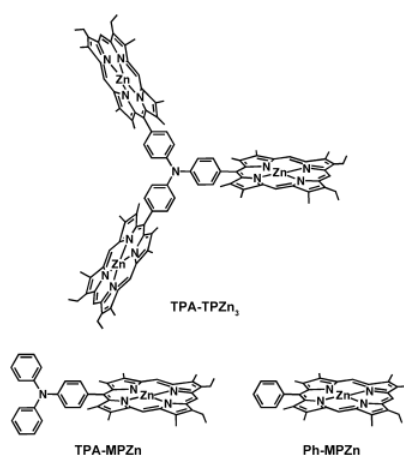
Abstract:



Polyacetylene bearing a pendant rotaxane moiety with an optically active wheel component was synthesized to realize reversible structural control of its helical structure by position control of the wheel component. Polyacetylene formed a one-handed helical structure only when the optically active wheel component moved close to the main chain.

- Greatly Enhanced Intermolecular π -Dimer Formation of a Porphyrin Trimer Radical Trications through Multiple π Bonds
Takai, A.; Gros, C. P.; Barbe, J.-M.; Fukuzumi, S. *Chem. Eur. J.* **2011**, 17, 3420-3428.

Abstract:

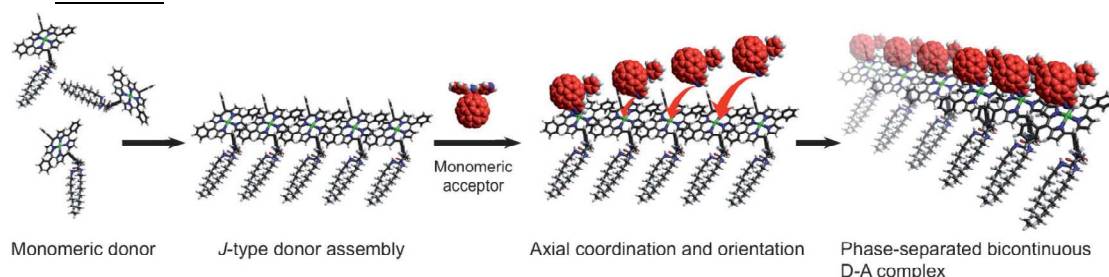


A trefoil-like porphyrin trimer linked by triphenylamine (TPA-TPZn₃) was synthesized. A three-electron oxidation of TPA-TPZn₃ forms a radical trication (TPA-TPZn₃³⁺), in which each porphyrin ring undergoes a one-electron oxidation. The radical trication TPA-TPZn₃³⁺ spontaneously dimerizes to afford (TPA-TPZn₃)₂⁶⁺ in CH₂Cl₂. The characteristic charge-resonance band due to the charge delocalization over the π system of (TPA-TPZn₃)₂⁶⁺ was observed in the NIR region. The initial oxidation potential of TPA-TPZn₃ is negatively shifted relative to that of the corresponding monomer porphyrin, which results from the stabilization of the oxidized state of TPA-TPZn₃ associated with the dimerization. The thermodynamic parameters (i.e., ΔH , ΔS , and ΔG) for the formation of (TPA-TPZn₃)₂⁶⁺ were determined by measuring Vis/NIR spectra at various temperatures. The formation constant of (TPA-TPZn₃)₂⁶⁺ is significantly larger than that of the radical cation dimer of the corresponding monomer porphyrin (e.g., over 2000-fold at 233 K). The electronic states were investigated using EPR spectroscopic analysis. The greatly enhanced dimerization of TPA-TPZn₃³⁺ results from multiple π -bond formation between the porphyrin radical cations.

- Noncovalent One-to-One Donor–Acceptor Assembled Systems Based on Porphyrin Molecular Gels for Unusually High Electron-Transfer Efficiency

Jintoku, H.; Sagawa, T.; Takafuji, M.; Ihara, H. *Chem. Eur. J* **2011**, *17*, 11628–11636.

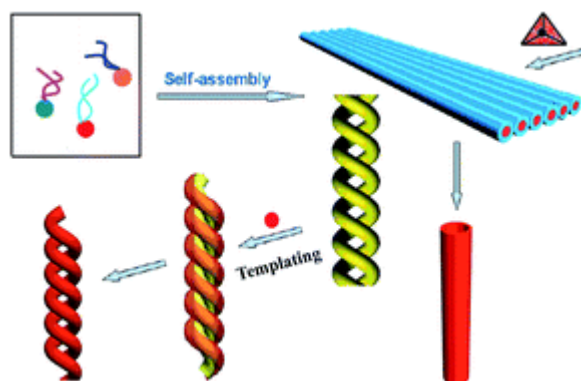
Abstract:



A new approach for fabricating donor–acceptor assembled systems is demonstrated, based on J-type ordered aggregation of a low-molecular zinc porphyrin derivative and subsequent integration of a pyridylated fullerene derivative with coordination and orientation onto the porphyrin aggregates. This system achieves unusually high efficiencies in fluorescence quenching during one-to-one mixing of the donor and acceptor. Moreover, the Stern–Volmer constant (KSV) and association constant (K) of this system are 2520 and 56 times higher, respectively, than those of the corresponding nonassembled system. The quenching efficiency is thermotropically switchable, since ordered-to-disordered transitions are essential characteristics of noncovalent low molecular assemblies.

- Construction and application of tunable one-dimensional soft supramolecular assemblies
Yan, Y.; Lin, Y.; Qiao, Y.; Huang, J. *Soft Matter* **2011**, *7*, 6385-6398.

Abstract:



Self-assembly of small molecules into one-dimensional soft nanostructures offers many advantages in understanding biological process and fabrication of electronically active materials. In recent decades, various one-dimensional soft nanostructures have been fabricated. The present review focuses on the following content: (1) frequently occurring forces in one-dimensional molecular self-assembly; (2) how these forces are used to construct this type of nanostructures; (3) fine-tuning one-dimensional self-assemblies by employing tools such as photo, pH, temperature, additives, and concentration; (4) some examples of the applications of one-dimensional self-assemblies in fabrication of one-dimensional hard materials are described.

- Spectral insights into gelation microdynamics of *N*-octyl-D-gluconamide in water
Sun, S.; Wu, P. *Soft Matter* **2011**, *7*, 6451-6456.

Abstract:



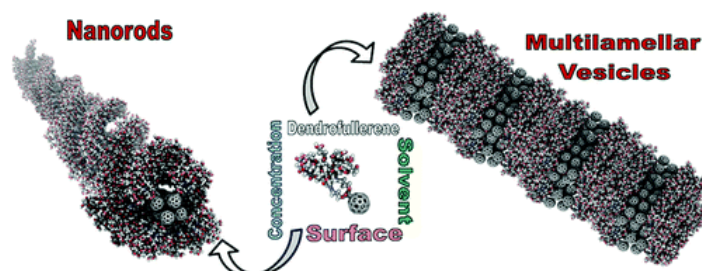
Near infrared spectroscopy in combination with two-dimensional correlation spectroscopy (2DCos) and perturbation correlation moving window (PCMW) technique is employed to illustrate the gelation microdynamic mechanism of hydrogelator *N*-octyl-D-gluconamide (8-GA), which can rapidly self-agglomerate into helical bilayer micellar fibers upon cooling from spherical micelles. Boltzmann fitting and PCMW easily determined the gelation temperature to be *ca.* 72 °C and the transition temperature range to be 70–75 °C. Moreover, band shifting and splitting phenomena can be observed for CH-related overtones, indicating the formation of much ordered and tight hydrophobic core from octyl tails. On the other hand, 2DCos was used to discern the sequential orders during the gelation process and concluded that all the group motions have a continuous transfer from the octyl tail to the chiral carbohydrate head followed by the final immobilization of the solvent, which meanwhile, is actually a continuous dehydration process from the hydrophobic core to the outer hydrophilic chiral head. The driving force of the gelation process in microdynamics can only be the dehydration process of hydrophobic octyl chains, but with final helical superstructures being stabilized by amide-associated hydrogen bonding and the “chiral bilayer effect” of carbohydrate heads.

- Nanorods versus Nanovesicles from Amphiphilic Dendrofullerenes

Muñoz, A.; Illescas, B. M.; Sánchez-Navarro, M.; Rojo, J.; Martín, N. *J. Am. Chem. Soc.* **2011**, *133*, 16758–16761.

10

Abstract:

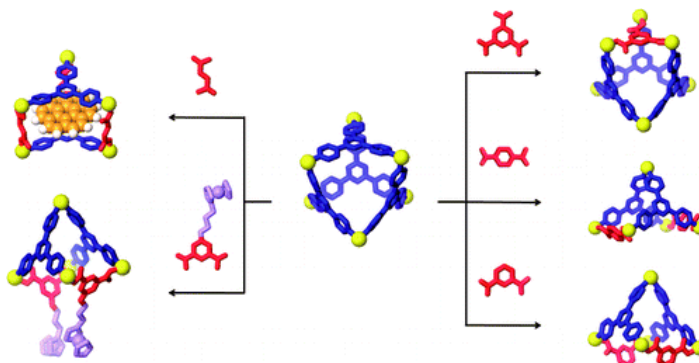


Three new amphiphilic dendrofullerenes endowed with 4, 8, and 16 carboxylic groups have been efficiently prepared by using a click chemistry methodology. These amphiphilic fullerene derivatives aggregate forming micelles, nanorods, or hollow vesicles depending on the concentration and on the solid substrate.

- Designed Post-Self-Assembly Structural and Functional Modifications of a Truncated Tetrahedron

Zheng, Y.-R.; Lan, W.-J.; Wang, M.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 17045–17055.

Abstract:

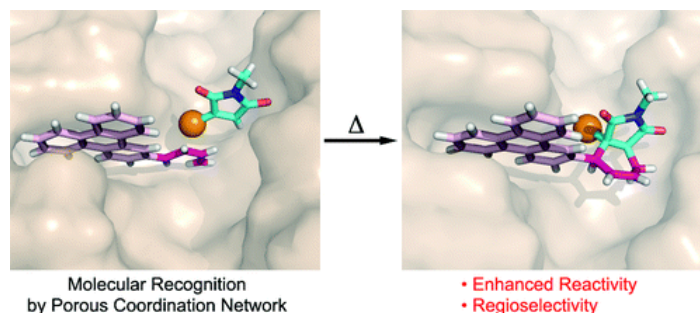


Post-self-assembly modifications of a discrete metal–organic supramolecular structure have been developed. Such modifications allow the properties of the self-assembled supramolecular species to be changed in a simple and efficient manner (>90% yield). Initiated by the application of chemical stimuli, the post-self-assembly modifications described herein result in three distinct changes to the supramolecular system: an individual building-block component change, an overall structural modification, and a functional evolution of a [6+4] metal–organic supramolecular structure. The three modifications have been carefully examined by a range of characterization methods, including NMR and UV–vis spectroscopy, electrospray ionization mass spectrometry, pulsed field gradient spin echo NMR measurements, electrochemical analysis, and computational simulations.

- Diels–Alder via Molecular Recognition in a Crystalline Molecular Flask

Ikemoto, K.; Inokuma, Y.; Fujita, M. *J. Am. Chem. Soc.* **2011**, *133*, 16806–16808.

Abstract:

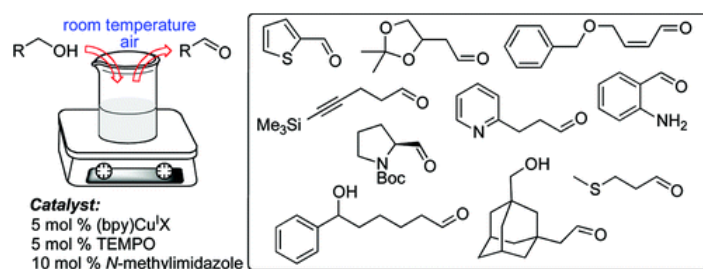


In the pore of a porous coordination network, Diels–Alder reactants, a diene and a dienophile, are recognized by donor–acceptor and multiple H-bond interactions, respectively, and fixed at ideal positions for the reaction. Heating the crystals promoted the Diels–Alder reactions with enhanced reactivity and controlled regioselectivity as clearly monitored by in situ X-ray crystallography.

- Highly Practical Copper(I)/TEMPO Catalyst System for Chemoselective Aerobic Oxidation of Primary Alcohols

Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 16901-16910.

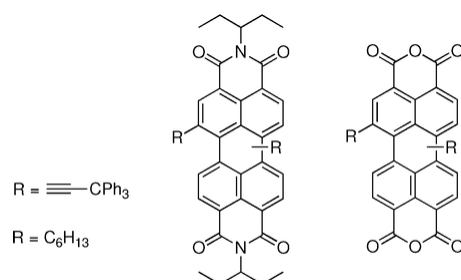
Abstract:



Aerobic oxidation reactions have been the focus of considerable attention, but their use in mainstream organic chemistry has been constrained by limitations in their synthetic scope and by practical factors, such as the use of pure O₂ as the oxidant or complex catalyst synthesis. Here, we report a new (bpy)Cu^I/TEMPO catalyst system that enables efficient and selective aerobic oxidation of a broad range of primary alcohols, including allylic, benzylic, and aliphatic derivatives, to the corresponding aldehydes using readily available reagents, at room temperature with ambient air as the oxidant. The catalyst system is compatible with a wide range of functional groups and the high selectivity for 1° alcohols enables selective oxidation of diols that lack protecting groups.

- Syntheses and Properties of 1,6 and 1,7 Perylene Diimides and Tetracarboxylic Dianhydrides

Abstract:



Chromatographically separable 1,6 and 1,7 regioisomers

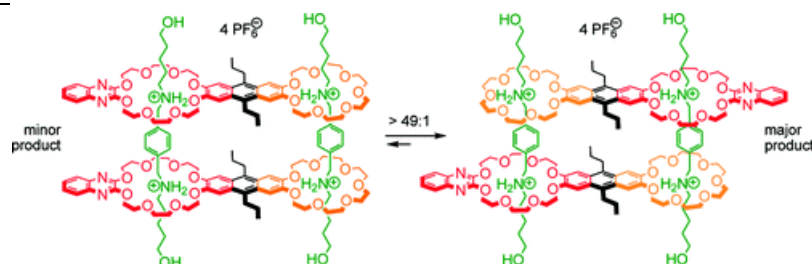
Via Sonogashira cross-coupling with different alkynes, 1,6 and 1,7 perylene diimides (PDIs) and perylene tetracarboxylic dianhydrides (PTCDs) were synthesized from the corresponding

regioisomeric mixture of 1,6/1,7-dibromo precursors. Both bulky triphenyl propyne (TPP) groups and nonbulky hexyl groups allow for facile chromatographic separation. The optical properties of these compounds are discussed. Neutral bay substituents hypsochromically shift both the absorption and emission through deformation from planarity of the perylene core.

- [4]Pseudorotaxanes with Remarkable Self-Sorting Selectivities

Jiang, W.; Sattler, D.; Rissanen, K.; Schalley, C. A. *Org. Lett.* **2011**, *13*, 4502–4505.

Abstract:

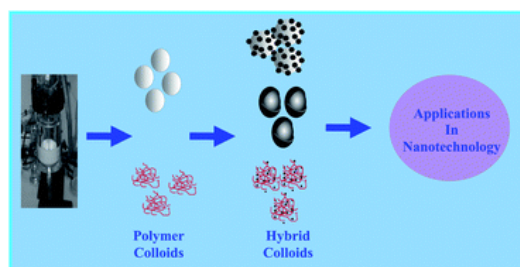


The synthesis and characterization of several self-assembled [4]pseudorotaxanes is reported, some of which form in a programmed way based on two similar yet orthogonal crown ether/secondary ammonium ion binding motifs. A preference for the formation of a [4]pseudorotaxane with an antiparallel rather than parallel alignment of crown ether building blocks is observed even in the absence of such orthogonal binding sites, when a homodivalent axle is used.

- Recent developments in fabrication and applications of colloid based composite particles

Agrawal, M.; Gupta, S.; Stamm, M. *J. Mater. Chem.* **2011**, *21*, 615-627.

Abstract:

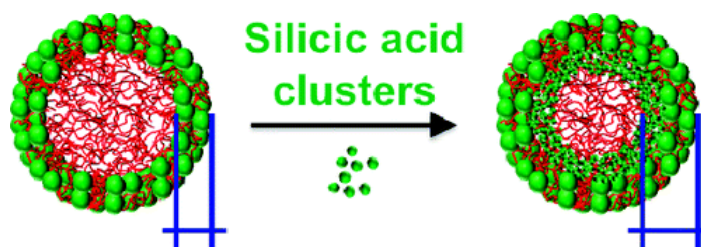


In recent years, a variety of nano-(micro) scale organic–inorganic composite particles with well defined chemical composition, size and morphology have been fabricated and their applications in wide spectrum of cutting-edge technological areas have been explored. This review is focused on recent developments towards various fabrication methodologies and applications of such colloid based composite particles. Strategies for preparation of nano and micro scale composite materials are presented by choosing as examples hard core based composite particles having core–shell and raspberry-like morphologies and soft core based composite microgels. Applications of these materials in wide range of potential areas are discussed including the fabrication of colloidal crystal arrays, hollow spheres, superhydrophobic surfaces, filler carriers and smart nanomaterials.

- Shell Thickness Control of Nanoparticle/Polymer Assembled Microcapsules

Bagaria, H. G.; Kadali, S. B.; Wong, M. S. *Chem. Mater.* **2011**, *23*, 301–308.

Abstract:

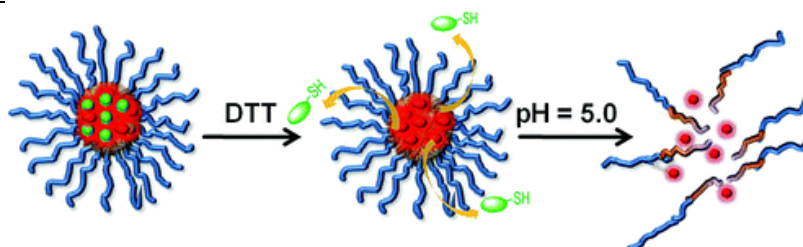


Organic/inorganic composite microcapsules can be produced in water through a two-step charge-driven assembly of polyallylamine, citrate anions, and 13 nm silica nanoparticles. The shell is composed of nanoparticles intermixed with polymer, and is thick enough (100s of nm) to provide structural stability before or after drying. Controlling shell thickness, however, is currently difficult to perform. Presented here is a new method in which the shell wall can be thickened by contacting the as-synthesized capsules with silicic acid. This shell thickening was observed and quantified for a moderately broad, unimodal size distribution of capsular particles, through a combination of transmission electron and confocal fluorescence microscopies. Thermogravimetric analysis confirmed the deposition of additional silica, and Coulter counter measurements showed the mean capsule diameter of $\sim 4.5 \pm 2.2 \mu\text{m}$ changed negligibly with silicic acid treatment. The shell-thickening process occurred in an inward direction, in which the nanosized silicic acid oligomers most likely diffused through the permeable capsule wall and deposited within the wall and on the inner shell wall surface. Adjustable shell wall thicknesses in hybrid microcapsules provide enhanced capability for chemical encapsulation, storage, and release applications.

- Acid Degradable and Biocompatible Polymeric Nanoparticles for the Potential Codelivery of Therapeutic Agents

Duong, H. T. T.; Marquis, C. P.; Whittaker, M.; Davis, T. P.; Boyer, C. *Macromolecules* **2011**, *44*, 8008–8019

Abstract:



DTT: reducing agent

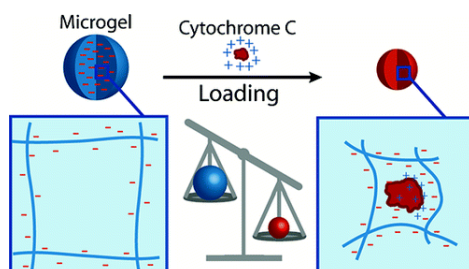
The synthesis of well-defined functional nanoparticles for the encapsulation of hydrophobic and hydrophilic drugs is described. Nanoparticles were built from amphiphilic copolymers consisting of P(OEG-A) homopolymers chain extended with vinyl benzyl chloride (VBC) and pentafluorophenyl acrylate (PFP-A) comonomers. Subsequently, the pendant chlorine atoms, introduced into the chains by VBC units, were substituted using sodium methanethiosulfonate, yielding copolymer chains with methanethiosulfonate (MTS) pendant functionality. The thiol/MTS exchange chemistry afforded by the MTS groups was then used to introduce different functional groups by reacting with a range of thiols. These copolymers were self-assembled in water yielding nanoparticles with sizes of 20 nm. The activated esters in the copolymer were used to cross-link the nanoparticles with difunctional amino compounds (cross-linkers). A cross-linker bearing an acid cleavable bond (ketal) was used to generate pH-sensitive core-shell nanoparticles. Drug encapsulation and release was modeled using hydrophobic (Nile Red) and hydrophilic (thiol-modified fluorescein isothiocyanate, FITC) dye

molecules. The release of each dye was monitored using UV–vis spectroscopy, demonstrating the possibility of selective release of single dye or the simultaneous release of both dyes depending on the experimental stimuli. An *in vitro* study confirmed that the nanoparticles were nontoxic to the NIH-3T3 cell line. Cell uptake analysis by flow cytometry and fluorescence microscopy indicated a higher uptake for cross-linked nanoparticles than for non-cross-linked nanoparticles.

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- Tunable Encapsulation of Proteins within Charged Microgels
Smith, M. H.; Lyon, L. A. *Macromolecules* **2011**, *44*, 8154–8160.

Abstract:



The binding of cytochrome c to pH and thermoresponsive colloidal hydrogels was investigated using multiangle light scattering, measuring loading through changes in particle molar mass and root-mean-square radius. Loosely cross-linked microgels [composed of a random copolymer of N-isopropylacrylamide (NIPAm) and acrylic acid (AAc)] demonstrated a high loading capacity for protein. Encapsulation was dependent on both the charge characteristics of the network and the salinity of the medium. Under favorable binding conditions (neutral pH, low ionic strength), microgels containing the highest studied charge density (30 mol % AAc) were capable of encapsulating greater than 9.7×10^5 cytochrome c molecules per particle. Binding resulted in the formation of a polymer–protein complex and condensation of the polymer. Anionic microgels demonstrated a change in density 20-fold in the presence of oppositely charged proteins. These studies of cytochrome c encapsulation represent a significant step toward direct measurement of encapsulation efficiency in complex media as we pursue responsive nanogels and microgels for the delivery of macromolecular therapeutic agents.