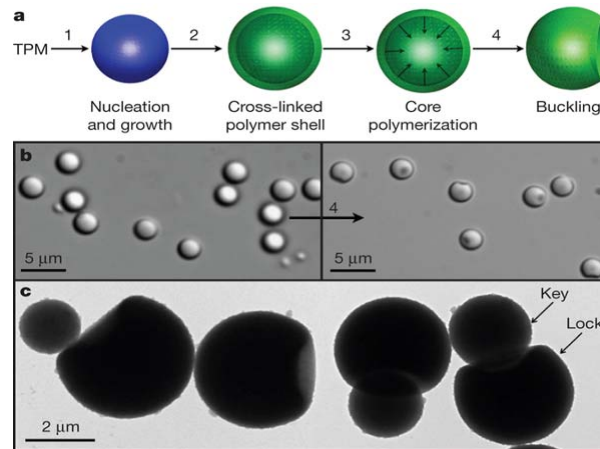


- Lock and Key Colloids

Sacanna, S.; Irvine, W. T. M.; Chaikin, P. M.; Pine, D. J. *Nature*, **2010**, *464*, 575-578.

Abstract:

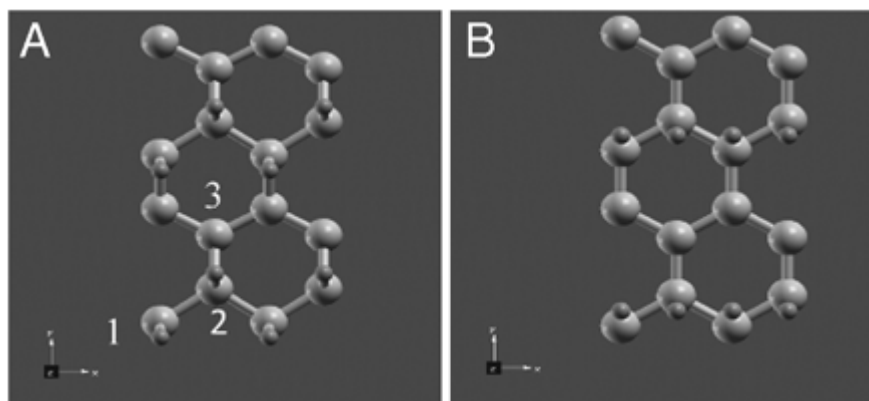


New functional materials can in principle be created using colloids that self-assemble into a desired structure by means of a programmable recognition and binding scheme. This idea has been explored by attaching 'programmed' DNA strands to nanometer- and micrometer-sized particles and then using DNA hybridization to direct the placement of the particles in the final assembly. Here we demonstrate an alternative recognition mechanism for directing the assembly of composite structures, based on particles with complementary shapes. Our system, which uses Fischer's lock-and-key principle, employs colloidal spheres as keys and monodisperse colloidal particles with a spherical cavity as locks that bind spontaneously and reversibly via the depletion interaction. The lock- and key binding is specific because it is controlled by how closely the size of a spherical colloidal key particle matches the radius of the spherical cavity of the lock particle. The strength of the binding can be further tuned by adjusting the solution composition or temperature. The composite assemblies have the unique feature of having flexible bonds, allowing us to produce flexible dimeric, trimeric and tetrameric colloidal molecules as well as more complex colloidal polymers. We expect that this lock-and-key recognition mechanism will find wider use as a means of programming and directing colloidal self-assembly.

- Chemical storage of hydrogen in few-layer grapheme

Subrahmanyama, K. S.; Kumara, P.; Maitraa, U.; Govindaraja, A.; Hembramb, K. P. S. S.; Waghmareb, U. V.; Rao, C. N. R. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 2674-2677.

Abstract:

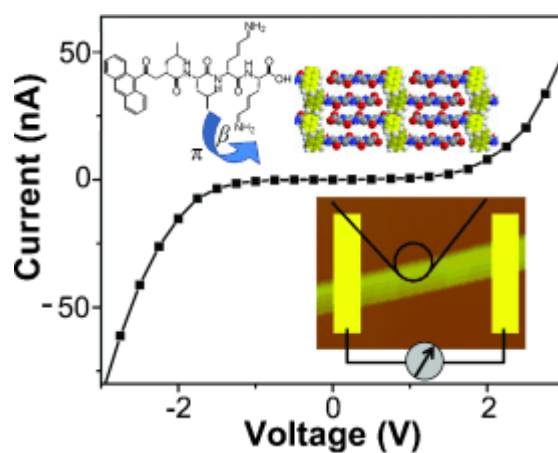


Birch reduction of few-layer graphene samples gives rise to hydrogenated samples containing up to 5 wt % of hydrogen. Spectroscopic studies reveal the presence of sp³ C-H bonds in the hydrogenated graphenes. They, however, decompose readily on heating to 500°C or on irradiation with UV or laser radiation releasing all the hydrogen, thereby demonstrating the possible use of few-layer graphene for chemical storage of hydrogen. First-principles calculations throw light on the mechanism of dehydrogenation that appears to involve a significant reconstruction and relaxation of the lattice.

- Semiconductive, One-Dimensional, Self-Assembled Nanostructures Based on Oligopeptides with π -Conjugated Segments

Sun, Y.; Jiang, L.; Schuermann, K. C.; Adriaens, W.; Zhang, L.; Boey, F. Y. C.; De Cola, L.; Brunsveld, L.; Chen, X. *Chem. Eur. J.* **2011**, *17*, 4746–4749.

Abstract:



π Stacking between the β sheets: A newly designed π -conjugated peptide can be assembled into a one-dimensional nanostructure with strong π - π intermolecular electronic communication. A nanoelectronic device based on the achieved individual nanostructure was used to measure conductivity (see graphic).

- Dendron-Functionalized Bis(terpyridine)–Iron(II) or –Cadmium(II) Metallomacrocycles: Synthesis, Traveling-Wave Ion-Mobility Mass Spectrometry, and Photophysical Properties
Wang, J. L.; Li, X.; Lu, X.; Chan, Y. T.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem. Eur. J.* **2011**, *17*, 4830 – 4838.

Abstract:

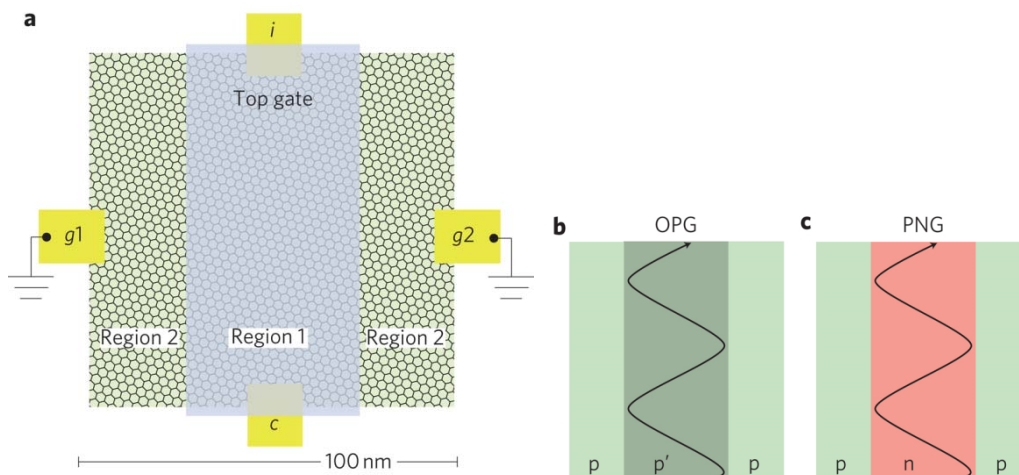


Abstract: Fives, sixes, and sevens: A series of metallomacrocycles (an example is shown here), utilizing $\langle \text{tpy-M-tpy} \rangle$ connectivity (M=FeII or CdII) and possessing the first- or second-generation dendrons with 1→3 C-branching, has been prepared by a one-pot self-assembly procedure, purified, and characterized. Collision cross sections were obtained by traveling-wave ion-mobility mass spectrometry providing detailed images of their sizes and architectures.

- Gate-controlled guiding of electrons in graphene

Williams, J. R.; Low, T.; Lundstrom, M. S.; Marcus, C. M. *Nature Nanotech.* **2011**, *6*, 166–169.

Abstract:

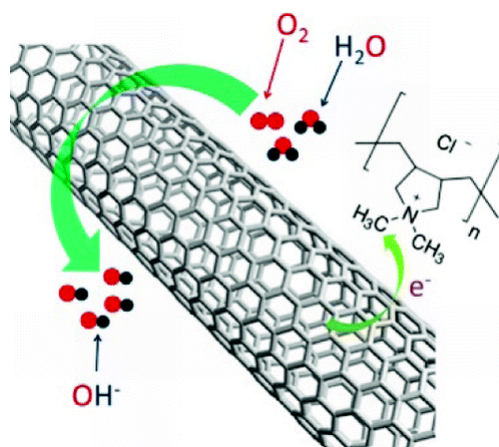


Ballistic semiconductor structures have allowed the realization of optics-like phenomena in electronic systems, including the magnetic focusing and electrostatic lensing of electrons. An extension that appears unique to graphene is to use both n and p carrier types to create electronic analogues of optical devices with both positive and negative indices of refraction. Here, we use the gate-controlled density of both p and n carrier types in graphene to demonstrate the electronic analogue of fibre-optic guiding. Two basic effects are investigated: bipolar p–n junction guiding, based on the principle of angle-selective transmission through the interface between the graphene and the p–n junction; and unipolar fibre-optic guiding, using total internal reflection controlled by carrier density. We also demonstrate modulation of the guiding efficiency through gating, and comparison of these data with numerical simulations indicates that guiding performance is limited by the roughness of the interface. The development of p–n and fibre-optic guiding in graphene may lead to electrically reconfigurable wiring in high-mobility devices.

- Polyelectrolyte Functionalized Carbon Nanotubes as Efficient Metal-free Electrocatalysts for Oxygen Reduction

Wang, S.; Yu, D.; Dai, L. *J. Am. Chem. Soc.* **2011**, *133*, 5182–5185.

Abstract:

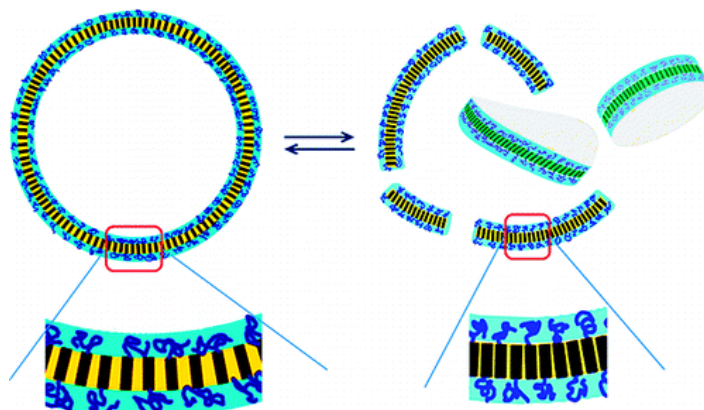


Having a strong electron-withdrawing ability, poly(diallyldimethylammonium chloride) (PDDA) was used to create net positive charge for carbon atoms in the nanotube carbon plane via intermolecular charge transfer. The resultant PDDA functionalized/adsorbed carbon nanotubes (CNTs), either in an aligned or nonaligned form, were demonstrated to act as metal-free catalysts for oxygen reduction reaction (ORR) in fuel cells with similar performance as Pt catalysts. The adsorption-induced intermolecular charge-transfer should provide a general approach to various carbon-based efficient metal-free ORR catalysts for oxygen reduction in fuel cells, and even new catalytic materials for applications beyond fuel cells.

- Electrical Switching between Vesicles and Micelles via Redox-Responsive Self-Assembly of Amphiphilic Rod-Coils

Kim, H.; Jeong, S.-M.; Park, J.-W. *J. Am. Chem. Soc.* **2011**, *133*, 5206–5209.

Abstract:

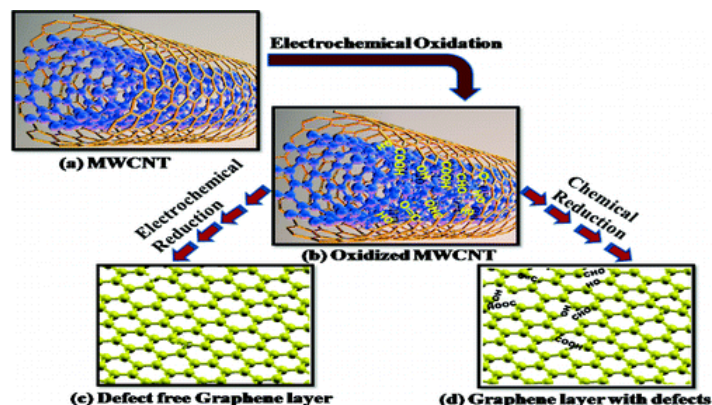


An aqueous vesicular system that is switchable by electric potential without addition of any chemical redox agents into the solution is demonstrated using redox-responsive self-assembly of an amphiphilic rod-coil molecule consisting of a tetraaniline and a poly(ethylene glycol) block. The vesicle membrane is split by an oxidizing voltage into smaller pucklike micelles that can reassemble to form vesicles upon exposure to a reducing voltage. The switching mechanism is explained by the packing behavior of the tetraaniline units constituting the membrane core, which depends on their oxidation states.

- Electrochemical Unzipping of Multi-walled Carbon Nanotubes for Facile Synthesis of High-Quality Graphene Nanoribbons

Shinde, D. B.; Debgupta, J.; Kushwaha, A.; Aslam, M.; Pillai, V. K. *J. Am. Chem. Soc.* **2011**, *133*, 4168-4171.

Abstract:

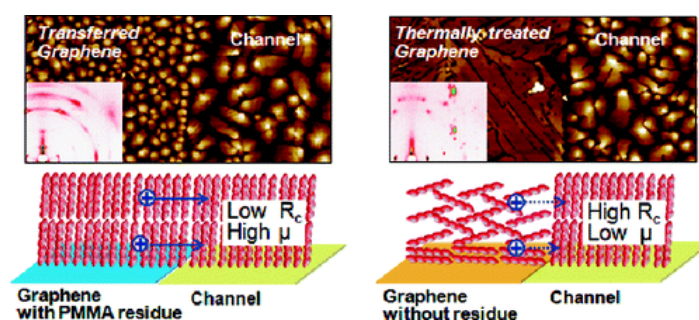


Here we report a remarkable transformation of carbon nanotubes (CNTs) to nanoribbons composed of a few layers of graphene by a two-step electrochemical approach. This consists of the oxidation of CNTs at controlled potential, followed by reduction to form grapheme nanoribbons (GNRs) having smooth edges and fewer defects, as evidenced by multiple characterization techniques, including Raman spectroscopy, atomic force microscopy, and transmission electron microscopy. This type of “unzipping” of CNTs (single-walled, multi-walled) in the presence of an interfacial electric field provides unique advantages with respect to the orientation of CNTs, which might make possible the production of GNRs with controlled widths and fewer defects.

- Surface-Directed Molecular Assembly of Pentacene on Monolayer Graphene for High-Performance Organic Transistors

Lee, W. H.; Park, J.; Sim, S. H.; Lim, S.; Kim, K. S.; Hong, B. H.; Cho, K. *J. Am. Chem. Soc.* **2011**, *133*, 4447-4454.

Abstract:



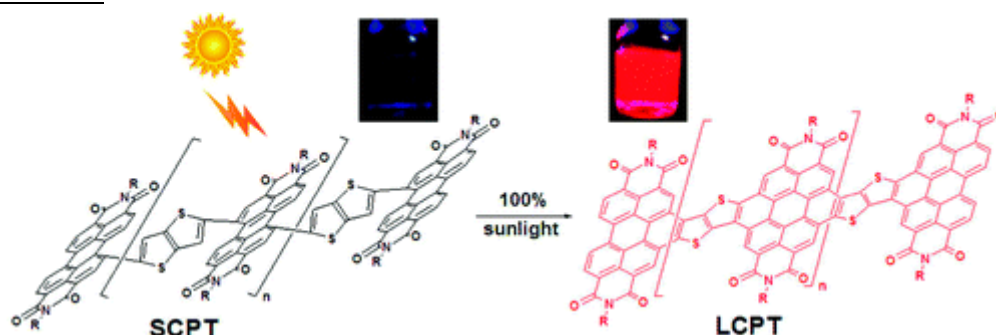
Organic electronic devices that use graphene electrodes have received considerable attention because graphene is regarded as an ideal candidate electrode material. Transfer and lithographic processes during fabrication of patterned graphene electrodes typically leave polymer residues on the graphene surfaces. However, the impact of these residues on the organic semiconductor growth mechanism on graphene surface has not been reported yet. Here, we demonstrate that polymer residues remaining on graphene surfaces induce a stand-up orientation of pentacene, thereby controlling pentacene growth such that the molecular assembly is optimal for charge transport. Thus, pentacene field-effect transistors (FETs) using source/drain monolayer graphene electrodes with polymer residues show a high field-effect mobility of 1.2 cm²/V s. In contrast, epitaxial growth of pentacene having molecular assembly of lying-down structure is facilitated by π - π interaction between pentacene and the clean graphene electrode without polymer residues, which adversely

affects lateral charge transport at the interface between electrode and channel. Our studies provide that the obtained high field-effect mobility in pentacene FETs using monolayer graphene electrodes arises from the extrinsic effects of polymer residues as well as the intrinsic characteristics of the highly conductive, ultrathin two-dimensional monolayer graphene electrodes.

6

- Soluble Ladder Conjugated Polymer Composed of Perylenediimides and Thieno[3,2-*b*]thiophene (LCPT): A Highly Efficient Synthesis via Photocyclization with the Sunlight
Yuan, Z.; Xiao, Y.; Yang, Y.; Xiong, T. *Macromolecules* **2011**, *44*, 1788–1791.

Abstract:

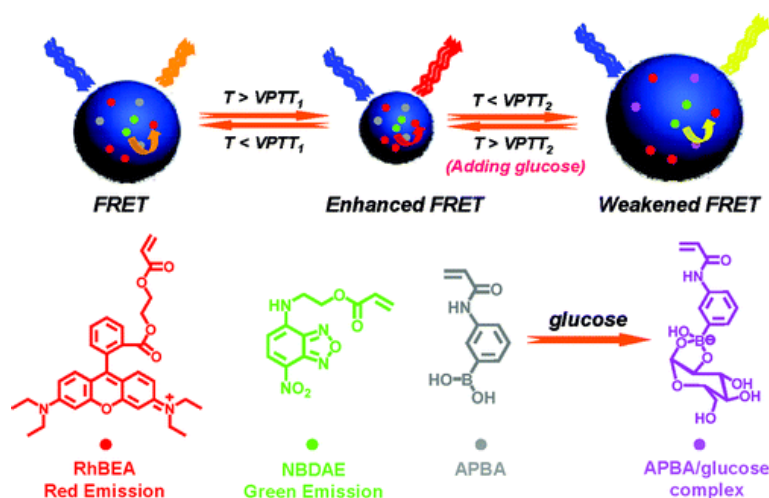


Organic semiconductors are an important class of electronic materials that offer intriguing prospects for high throughput, low-cost electronic circuitry on flexible substrates. Design and synthesis of novel organic semiconductors is essential work. Ladder conjugated polymers have rigid and planar frameworks, which enhance electron delocalization, conductivity, and thermal stability, and some of them have proved to be excellent organic semiconductors. For example, BBL with ladder planar conjugated system shows high performance in air-stable organic field-effect transistors and solar cells, and LPPP and its derivatives with ladder conjugated systems have been utilized in efficient solution processable blue-light-emitting diodes. At present, limited ladder conjugated polymers were reported, and some of them such as BBL, polyquinoxalines, and their derivatives were insoluble in organic solvent, which cause processing difficulties. Only limited methods are feasible to obtain soluble ladder conjugated polymers due to challenges such as synthetic inaccessibility, poor solubility, and chemical instability, and thus the soluble ladder conjugated polymers are scarce. Considering their intriguing photoelectric properties and promising applications, intensive efforts should be directed toward novel design and highly efficient synthesis of those polymers.

- Stimuli-Responsive Fluorescent Poly(*N*-isopropylacrylamide) Microgels Labeled with Phenylboronic Acid Moieties as Multifunctional Ratiometric Probes for Glucose and Temperatures

Wang, D.; Liu, T.; Yin, J.; Liu, S. *Macromolecules* **2011**, *44*, 2282–2290.

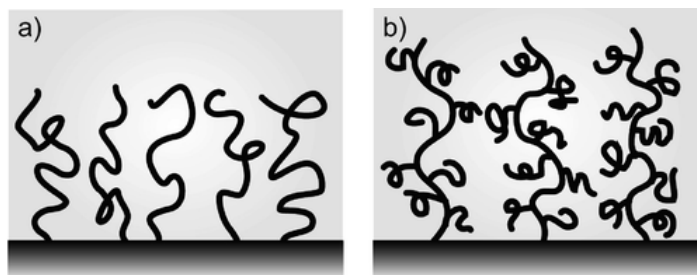
Abstract:



We report on the fabrication of multifunctional ratiometric probes for glucose and temperatures based on thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) microgels covalently incorporated with glucose-recognizing moieties, *N*-acryloyl-3-aminophenylboronic acid (APBA), fluorescence resonance energy transfer (FRET) donor dyes, 4-(2-acryloyloxyethylamino)-7-nitro-2,1,3-benzoxadiazole (NBDAE), and rhodamine B-based FRET acceptors (RhBEA). P(NIPAM-APBA-NBDAE-RhBEA) microgels containing FRET pairs and APBA were synthesized via free radical emulsion copolymerization. The spatial proximity of FRET donors and acceptors within microgels can be tuned via thermo-induced microgel collapse or glucose-induced microgel swelling at appropriate pH and temperatures, leading to the facile modulation of FRET efficiencies. APBA moieties within P(NIPAM-APBA-NBDAE-RhBEA) microgels can bind with glucose at appropriate pH to form cyclic boronate moieties, which can decrease the pK_a of APBA residues and increase the volume phase transition (VPT) temperature of microgels. The gradual addition of glucose into fluorescent microgel dispersions at intermediate temperatures, i.e., between microgel VPT temperatures in the absence and presence of glucose, respectively, can lead to the reswelling of initially collapsed microgels. Thus, P(NIPAM-APBA-NBDAE-RhBEA) microgels can serve as dual ratiometric fluorescent probes for glucose and temperatures by monitoring the changes in fluorescence emission intensity ratios. Moreover, P(NIPAM-APBA-NBDAE-RhBEA) microgels at pH 8 and 37 °C can serve as a ratiometric fluorescent glucose sensor with improved detection sensitivity as compared to that at 25 °C. MTT assays further revealed that thermoresponsive microgels are almost noncytotoxic up to a concentration of 1.6 g/L. These results augur well for the application of P(NIPAM-APBA-NBDAE-RhBEA) microgels for multifunctional purposes such as sensing, imaging, and triggered-release nanocarriers under in vivo conditions.

- Modeling the Structure and Antifouling Properties of a Polymer Brush of Grafted Comb-Polymers
de Vos, W. M.; Leermakers, F. A. M.; Lindhoud, S.; Prescott, S. W. *Macromolecules* **2011**, *44*, 2334–2342.

Abstract:

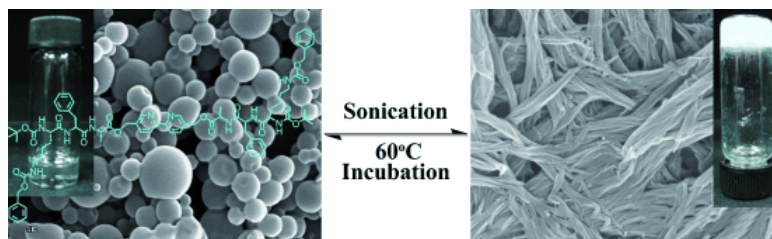


Numerical self-consistent field theory is used to study the structural characteristics of a polymer brush consisting of end-grafted comb-polymers. A comb-polymer brush is shown to retain the parabolic density profile characteristic of the unbranched brush. Increasing either the number of branches or the length of the side-chains leads to an increase in the height (H) of the brush. This is partly because of the branched structure: it is more favorable to stretch the polymer backbone, while leaving the side-chains almost unstretched. The other reason for the increased stretching is simply because of the extra polymer in the brush due to the branches. We find that it does not matter how the side-chains are distributed along the backbone for the predicted density profile; it is only the total amount of polymer in the side-chains that is important. The effect of branching on the brush height can be captured in a simple scaling law: $H \sim N_b(N_T/N_b)^{2/3}$, where N_b is the chain length of the polymer backbone, N_T is the total chain length, thus including the side-chains, and their ratio N_T/N_b is a measure for the amount of branching. The structure of the branched brush is less suitable for keeping away small particles from the grafted interface. It is, however, a good way of increasing the polymer density, and thus its antifouling properties, when the grafting density of the brush is limited.

- Morphological Transformation between Nanofibers and Vesicles in a Controllable Bipyridine–Tripeptide Self-Assembly

Ke, D.; Zhan, C.; Li, A. D. Q.; Yao, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 3715–3719.

Abstract:

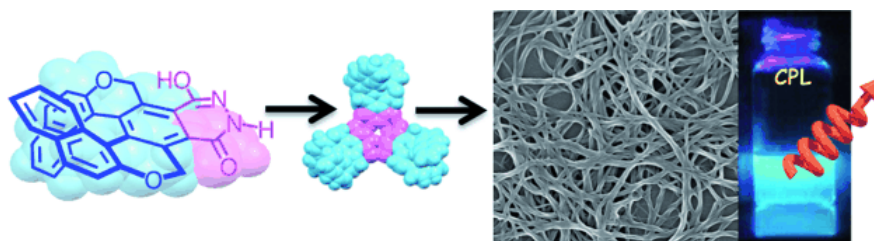


Tuning structures: Stimulus-responsive peptide self-assembly requires a balance of conformational change and structural continuity of stable β sheets. In an amphiphilic bipyridine–tripeptide model, temperature, and ultrasound switch a reversible morphological transformation between vesicles and nanofibers (see picture) through the synergistic effects of terminal β -sheet-forming peptides, flexible linkers, and rotatable bipyridine groups.

- Hierarchical Assembly of a Phthalhydrazide-Functionalized Helicene

Kaseyama, T.; Furumi, S.; Zhang, X.; Tanaka, K.; Takeuchi, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 3684–3687.

Abstract:

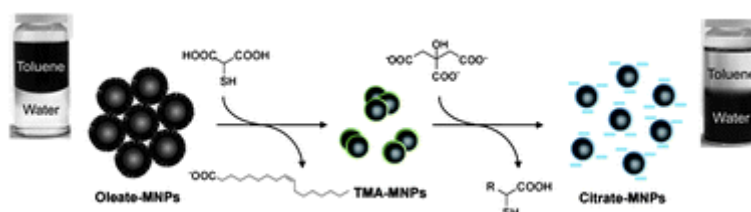


High in fiber: 1D fibrous superstructures are formed by an enantiopure phthalhydrazide-functionalized helicene in nonpolar solvents. Trimeric disks are formed by hydrogen-bonding interactions of phthalhydrazide units that are longitudinally interlocked for optimal packing (see picture). The resulting supramolecular assemblies exhibited large circularly polarized luminescence in solution.

- A two-step ligand exchange reaction generates highly water-dispersed magnetic nanoparticles for biomedical applications

Hatakeyama, M.; Kishi, H.; Kita, Y.; Imai, K.; Nishio, K.; Karasawa, S.; Masaike, Y.; Sakamoto, S.; Sandhu, A.; Tanimoto, A.; Gomi, T.; Kohda, E.; Abe, M.; Handa, H. *J. Mater. Chem.* **2011**, *21*, 5959-5966.

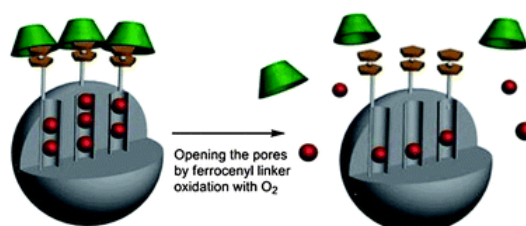
Abstract:



The high-temperature thermolysis of fatty acid-iron complexes generates magnetic nanoparticles (MNPs) of a precisely controlled size coated with fatty acids and dispersed in oil. Because they are water-immiscible, MNPs are unsuitable for water-based biomedical applications. Ligand exchange reactions that transform oil- into water-dispersed MNPs have attracted considerable attention, but are difficult to perform. In this paper, we report the successful preparation of size-controlled and highly water-dispersed MNPs, which have 4, 8 and 20 nm diameter by a unique two-step ligand exchange reaction. As temporary ligands, we selected thiomalic acid (TMA), which possesses moderate affinity toward MNPs and is soluble in both oil and water to remove fatty acids by XANES analyses. Next we selected the citric acids as secondary ligands for TMA-exchanged MNPs to be highly dispersed in water to remove TMA from the surface of MNPs. And the resulting highly water-dispersed MNPs are expected to be available as MRI contrast agents and hyperthermia carriers.

- Nanoreservoir operated by ferrocenyl linker oxidation with molecular oxygen
- Silveira, G. Q.; Vargas, M. D.; Ronconi, C. M. *J. Mater. Chem.* **2011**, *21*, 6034-6039.

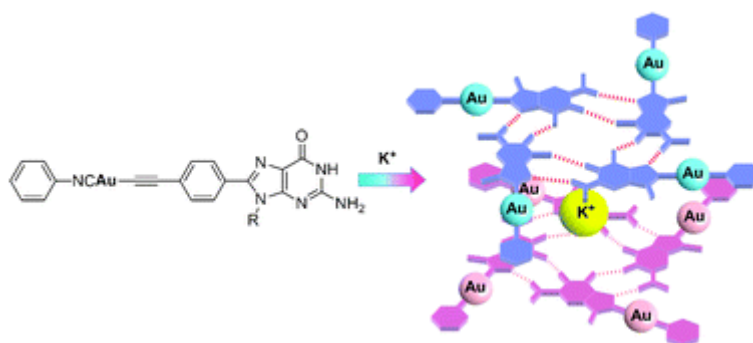
Abstract:



The fabrication and efficient operation of a redox-driven hybrid nanoreservoir that contains the host-guest pair β -cyclodextrin (β -CD) and a ferrocenyl (-Fc) group attached to MCM-41 nanoparticles loaded with rhodamine B are reported. The operation process is based on the effects of pH that is related to the acid catalyzed oxidation of the ferrocenyl group by molecular oxygen (O_2). By a thorough set of experiments, the combined effects of pH and oxygen are exploited to control the releasing process. Such experiments characterize the nanoreservoir at various points along the pathway, and show the level of control achieved over the release of rhodamine B. The results show that the same system can operate under different conditions, *i.e.*, at high O_2 levels and pH close to the physiological one, where the drug-like molecules could be rapidly released, or at low O_2 levels and slightly acidic conditions (pH 5.5 and 6.5), where the drug will be slowly released. In essence, the work presented herein is a step forward in terms of redox-triggered release drug-like molecules from MCM-41.

- A G-octamer scaffold *via* self-assembly of a guanosine-based Au(I) isonitrile complex for Au(I)-Au(I) interaction
Meng, X.; Moriuchi, T.; Kawahata, M.; Yamaguchi, K.; Hirao, T. *Chem. Commun.* **2011**, 47, 4682-4684.

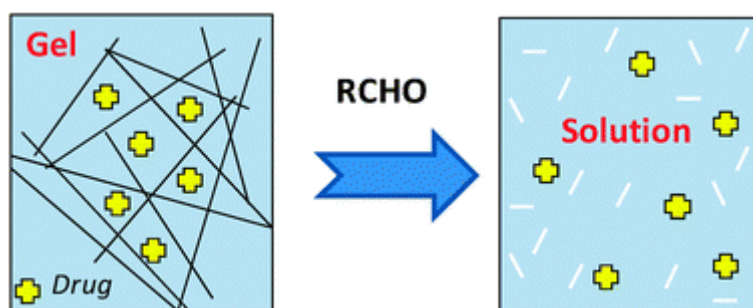
Abstract:



A guanosine-based Au(I) isonitrile complex was demonstrated to serve as the reliable scaffold *via* self-assembly, wherein the quartet and octamer were formed in the absence and presence of a potassium ion, respectively, exhibiting a switchable emission based on Au(I)-Au(I) interaction.

- Aldehyde responsive supramolecular hydrogels: towards biomarker-specific delivery systems
Rodríguez-Llansola, F.; Miravet, J. F.; Escuder, B. *Chem. Commun.* **2011**, 47, 4706-4708.

Abstract:

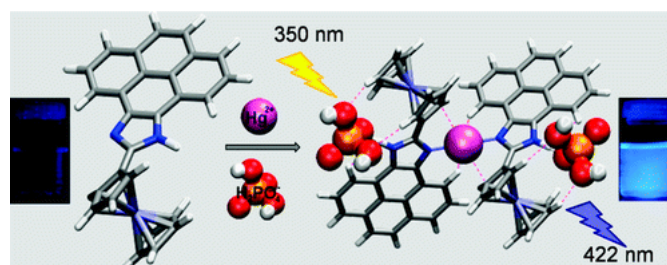


A reactive supramolecular hydrogel reacts with hydrophobic aldehydes causing disassembly of the fibrillar network and release of molecules entrapped within.

- A Simple but Effective Dual Redox and Fluorescent Ion Pair Receptor Based on a Ferrocene–Imidazopyrene Dyad

Alfonso, M.; Espinosa, A.; Trraga, A.; Molina, P. *Org. Lett.* **2011**, *13*, 2078–2081.

Abstract:



The ferrocene–imidazopyrene dyad, bearing the imidazole ring as the only receptor site, acts as a redox and optical molecular sensor for ion pairs, exhibiting an easily detectable signal change in the redox potential of the ferrocene/ferrocenium redox couple and in the emission spectrum. Perturbation of the emission spectrum follows the order $\text{Pb}^{2+} > \text{Hg}^{2+} > \text{Zn}^{2+}$ for cations and $\text{H}_2\text{PO}_4^- > \text{AcO}^-$ for anions.

- Sequence Stereoisomerism in Calixarene-Based Pseudo[3]rotaxanes

Talotta, C.; Gaeta, C.; Pierro, T.; Neri, P. *Org. Lett.* **2011**, *13*, 2098–2101.

Abstract:

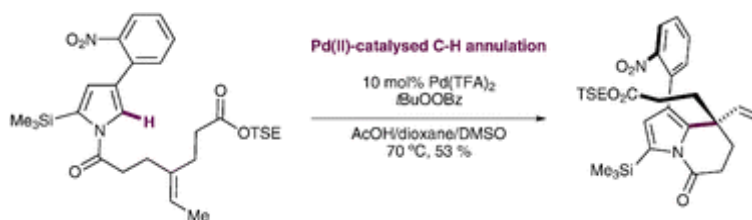


Two calix[6]arene directional wheels can be ordered in the right stereosequence by their *through-the-annulus* threading with a rationally designed bis(benzylalkylammonium) axle. These stereoisomeric pseudo[3]rotaxanes can be considered as a minimal “informational system” because the “written information” on the thread is transferred to a specific sequence stereoisomer.

- Recent developments in natural product synthesis using metal-catalysed C–H bond functionalisation

McMurray, L.; O’Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885–1898.

Abstract:



Metal-catalysed C–H bond functionalisation has had a significant impact on how chemists make molecules. Translating the methodological developments to their use in the assembly of complex natural products is an important challenge for the continued advancement of chemical synthesis. In this *tutorial review*, we describe selected recent examples of how the metal-catalysed C–H bond functionalisation has been able to positively affect the synthesis of natural products.