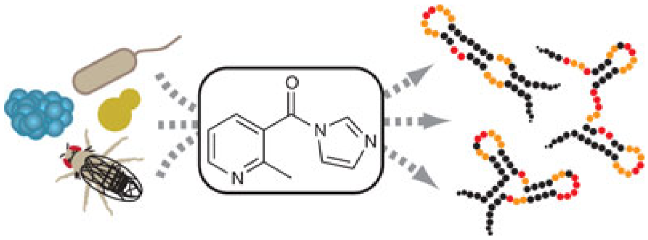
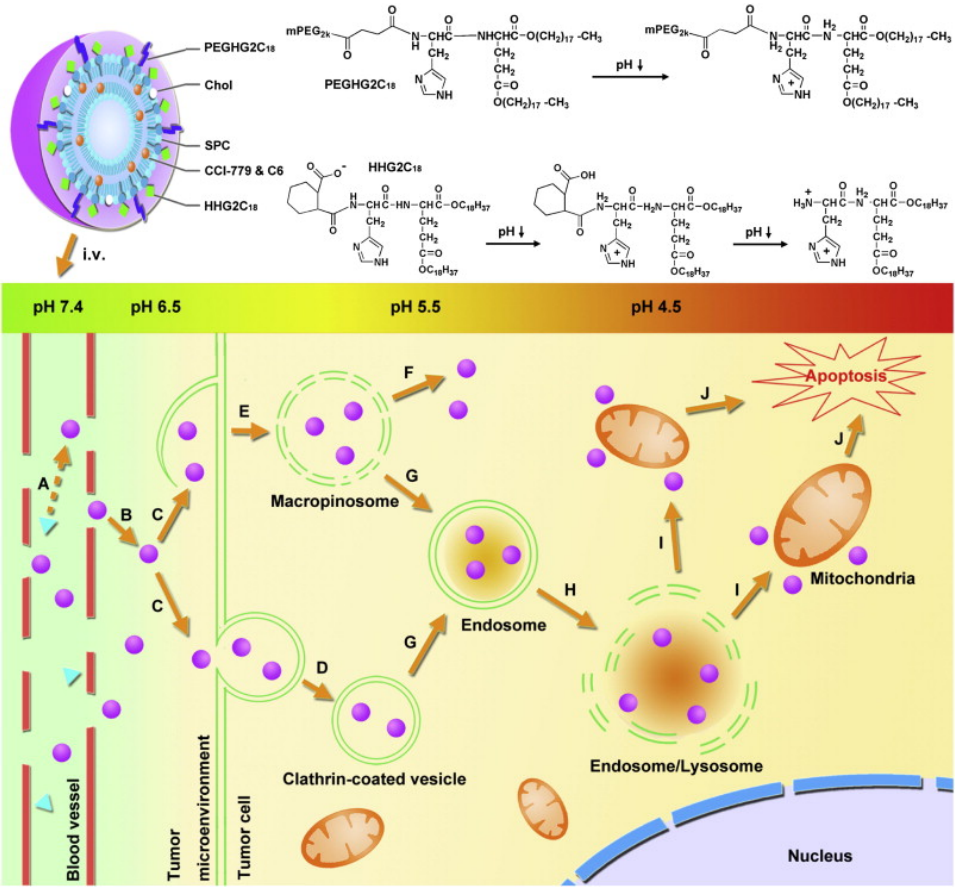
- RNA SHAPE analysis in living cells
  Spitale, R. C.; Crisalli, P.; Flynn, R. A.; Torre, E. A.; Kool, E. T.; Chang, H. Y. *Nature Chem. Biol.* **2013**, *9*, 18–20.
  Abstract:



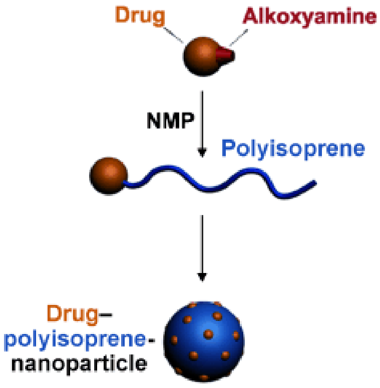
RNA structure has important roles in practically every facet of gene regulation, but the paucity of *in vivo* structural probes limits current understanding. Here we design, synthesize and demonstrate two new chemical probes that enable selective 2′-hydroxyl acylation analyzed by primer extension (SHAPE) in living cells. RNA structures in human, mouse, fly, yeast and bacterial cells are read out at single-nucleotide resolution, revealing tertiary contacts and RNA-protein interactions.

- Intracellular delivery and antitumor effects of pH-sensitive liposomes based on zwitterionic oligopeptide lipids
  Mo, R.; Sun, Q.; Li, N.; Zhang, C. *Biomaterials* **2011,** 34, 2773-2786.
  Abstract:



pH-sensitive liposomes (HHG2C$_{18}$-L and PEGHG2C$_{18}$-L) based on zwitterionic oligopeptide lipids as anticancer drug carriers were developed and evaluated for effective intracellular delivery and enhanced antitumor activity. The amino acid-based lipids, 1,5-dioctadecyl-l-glutamyl 2-histidyl-hexahydrobenzoic acid (HHG2C$_{18}$) and 1,5-distearyl *N*-(*N*-α-(4-mPEG2000) butanedione)-histidyl-lglutamate ($PEGHG2C_{18}$), were synthesized, which have the multistage pH-response to tumor microenvironmental pH (pH_e, pH 6.0–7.0) and endosomal/lysosomal pH (pH_i, pH 4.0–6.0) successively. $HHG2C_{18}$-L contains $HHG2C_{18}$, while $PEGHG2C_{18}$-L includes $HHG2C_{18}$ and $PEGHG2C_{18}$. Both of them displayed the capability of charge conversion to the surrounding pH. The zeta potentials of $HHG2C_{18}$-L and $PEGHG2C_{18}$-L were negative at pH 7.4, whereas positive at pH 6.5 and more positive at lower pH. Coumarin 6-loaded $HHG2C_{18}$-L (C6/$HHG2C_{18}$-L) and $PEGHG2C_{18}$-L (C6/$PEGHG2C_{18}$-L) showed higher tumor cellular uptake due to electrostatic absorptive endocytosis at pH_e (pH 6.5), produced proton sponge effect for endo-lysosomal escape, and accumulated to the mitochondria based on stronger positive charge by the hydrolysis of a pH-sensitive linker at pH_i (pH 5.5 and pH 4.5). Furthermore, temsirolimus (CCI-779)-loaded $HHG2C_{18}$-L (CCI-779/$HHG2C_{18}$-L) and $PEGHG2C_{18}$-L (CCI-779/$PEGHG2C_{18}$-L) had significantly higher antiproliferative and apoptosis inducing effects toward the human renal carcinoma (A498) cells at pH 6.5 relative to that at pH 7.4. The half maximal inhibitory concentration (IC50) of CCI-779/$HHG2C_{18}$-L and CCI-779/$PEGHG2C_{18}$-L were about 3 μg/mL and 5 μg/mL at pH 6.5, 1.67-fold and 1.60-fold improved relative to that at pH 7.4, respectively. The total apoptotic ratio of CCI-779/$HHG2C_{18}$-L and CCI-779/$PEGHG2C_{18}$-L increased from 9.90% and 7.78% at pH 7.4 to 19.53% and 12.10% at pH 6.5, respectively. *In vivo*, CCI-779/$PEGHG2C_{18}$-L after intravenous administration presented remarkably higher bioavailability and blood persistence compared with unPEGylated CCI-779/$HHG2C_{18}$-L, and had the strongest antitumor efficacy against xenograft renal cancer (Renca) tumor models. Accordingly, the results provide the feasibility of using pH-sensitive zwitterionic oligopeptide lipids to extend the applications of liposomes to efficient anticancer drug delivery in cancer therapy.

- Nanoparticles with In Vivo Anticancer Activity from Polymer Prodrug Amphiphiles Prepared by Living Radical Polymerization
  Harrisson, S.; Nicolas, J.; Maksimenko, A.; Bui, D. T.; Mougin, J.; Couvreur, P. *Angew. Chem. Int. Ed.* **2013**, *52*, 1678–1682.
  Abstract:

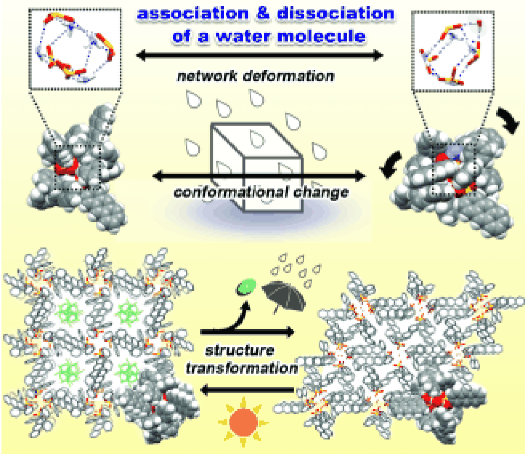


Magic rubber bullets: Novel anticancer nanoparticles made of well-defined polymer–drug conjugate amphiphiles are prepared by the controlled growth of a hydrophobic polyisoprene chain from a drug macroinitiator by using nitroxide-mediated polymerization (NMP; see picture). The resulting conjugates self-assembled into nanoparticles exhibiting high drug payloads and significant anticancer activities both in vitro and in vivo.

- Dynamically Deformable Cube-like Hydrogen-Bonding Networks in Water-Responsive Diamondoid Porous Organic Salts

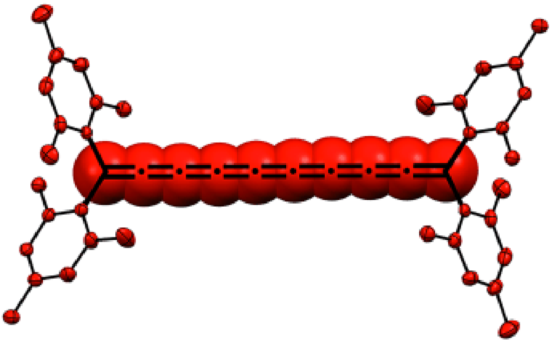
Yamamoto, A.; Hamada, T.; Hisaki, I.; Miyata, M.; Tohnai, N. *Angew. Chem. Int. Ed.* **2013**, *52*, 1709–1712.

Abstract:



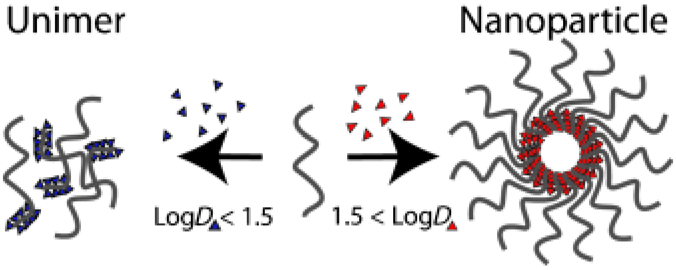
Just add water: A cube-like hydrogen-bonding network in a fluorescent supramolecular cluster dynamically deforms upon the specific addition of a water molecule. The deformation is amplified through the conformational change of the cluster to result in the transformation of host frameworks. This transformation provides water-responsive guest-exclusion and fluorescent-modulation behaviors.

- Synthesis and Structure of Tetraarylcumulenes: Characterization of Bond-Length Alternation versus Molecule Length
  Januszewski, J. A. ; Wendinger, D.; Methfessel, C. D.; Hampel, F.; Tykwinski, R. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 1817-1821.
  Abstract:



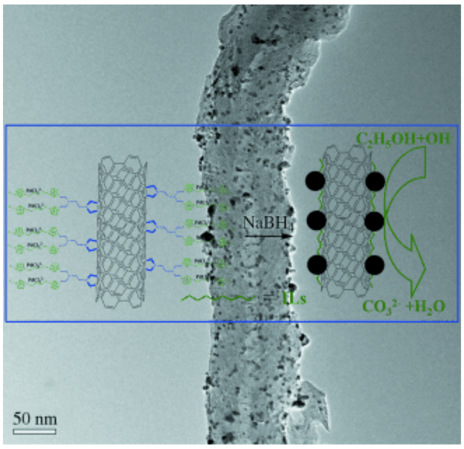
BLA=0? Not so fast! A series of tetraarylcumulenes up to the length of a [9]cumulene has been synthesized and analyzed by X-ray crystallography. The structural data show a distinct reduction in bond-length alternation (BLA) as a function of molecule length, but this trend appears to reach a limit before a cumulenic structure with BLA=0 is achieved.

- Self-Assembly of Thermally Responsive Nanoparticles of a Genetically Encoded Peptide Polymer by Drug Conjugation
  McDaniel, J. R. Bhattacharyya, J.; Vargo, K. B.; Hassouneh, W.; Hammer, D. A.; Chilkoti, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 1683-1687.
  Abstract:



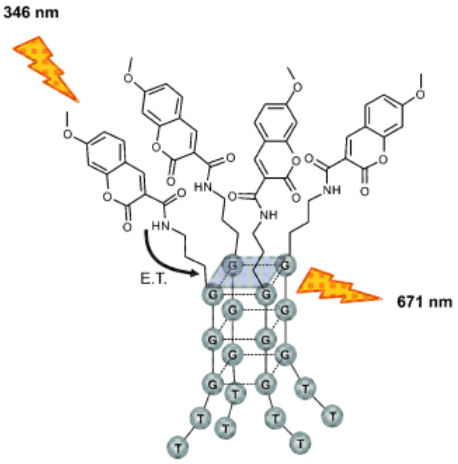
Nanoparticles on demand: Upon the site-specific covalent attachment of hydrophobic molecules to one end of the biopolymer backbone, chimeric polypeptides (derived from elastin-like polypeptides) can self-assemble to form thermoresponsive nanoparticles suitable for drug delivery. Molecules with a distribution coefficient greater than 1.5 imparted sufficient amphiphilicity to drive self-assembly into sub-100 nm nanoparticles (see picture).

- Microenvironment Effects in Electrocatalysis: Ionic-Liquid-Like Coating on Carbon Nanotubes Enhances the Pd-Electrocatalytic Alcohol Oxidation
  Li, S.; Dong, Z.; Yang, H.; Guo, S.; Gou, G.; Ren, R.; Zhu, Z.; Jin, J.; Ma, J. *Chem. Eur. J.* **2013**, *19*, 2384–2391.
  Abstract:



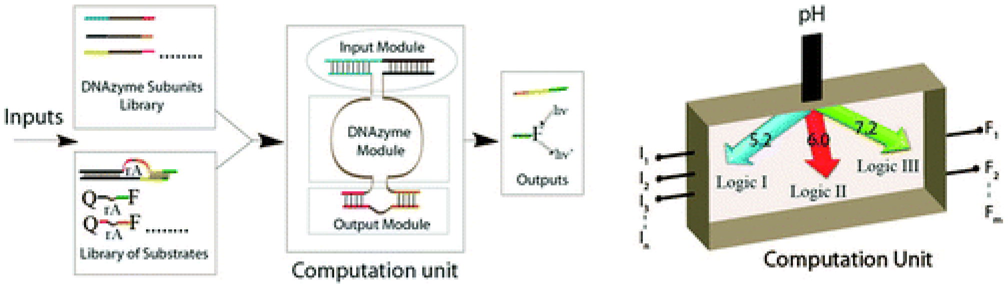
A new catalyst consisting of ionic liquid (IL)-functionalized carbon nanotubes (CNTs) obtained through 1,3-dipolar cycloaddition support-enhanced electrocatalytic Pd nanoparticles (Pd@IL(Cl^-)-CNTs) was successfully fabricated and applied in direct ethanol alkaline fuel cells. The morphology, structure, component and stability of Pd@IL(Cl^-)-CNTs were systematic characterized by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Raman spectra, thermogravimetric analysis (TGA) and X-ray diffraction (XRD). The new catalyst exhibited higher electrocatalytic activity, better tolerance and electrochemical stability than the Pd nanoparticles (NPs) immobilized on CNTs (Pd@CNTs), which was ascribed to the effects of the IL, larger electrochemically active surface area (ECSA), and greater processing performance. Cyclic voltammograms (CVs) at various scan rates illustrated that the oxidation behaviors of ethanol at all electrodes were controlled by diffusion processes. The investigation of the different counteranions demonstrated that the performance of the IL-CNTs hybrid material was profoundly influenced by the subtly varied structures of the IL moiety. All the results indicated that the Pd@IL(Cl^-)-CNTs catalyst is an efficient anode catalyst, which has potential applications in direct ethanol fuel cells and the strategy of IL functionalization of CNTs could be available to prepare other carbonaceous carrier supports to enhance the dispersivity, stability, and catalytic performance of metal NPs as well.

- Hierarchical Self-Assembly of a Biomimetic Light-Harvesting Antenna Based on DNA G-Quadruplexes
  Sancho Oltra, N.; Browne, W. R.; Roelfes, G. *Chem. Eur. J.* **2013**, *19*, 2457–2461.
  <u>Abstract:</u>



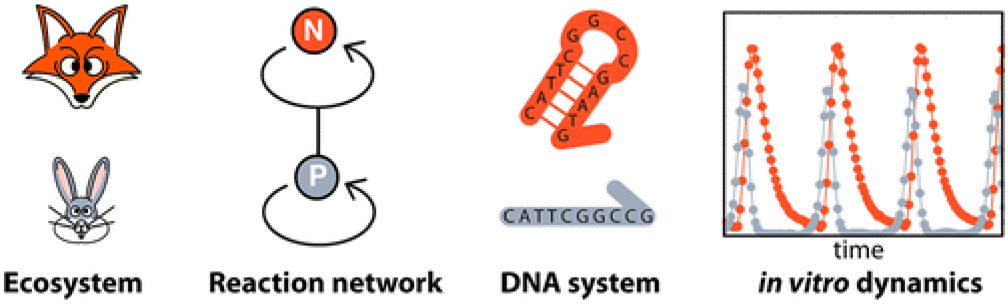
A new modular approach to an artificial light-harvesting antenna system is presented. The approach involves the hierarchical self-assembly of porphyrin acceptor molecules to G-quadruplexes tethered to coumarin donor moieties.

- pH-Programmable DNA Logic Arrays Powered by Modular DNAzyme Libraries
  Elbaz, J.; Wang, F.; Remacle, F.; Willner, I. *Nano Lett.* **2012**, *12*, 6049-6054.
  <u>Abstract:</u>



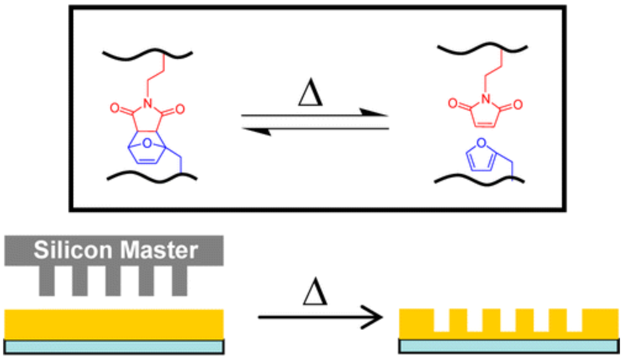
Nature performs complex information processing circuits, such the programmed transformations of versatile stem cells into targeted functional cells. Man-made molecular circuits are, however, unable to mimic such sophisticated biomachineries. To reach these goals, it is essential to construct programmable modular components that can be triggered by environmental stimuli to perform different logic circuits. We report on the unprecedented design of artificial pH-programmable DNA logic arrays, constructed by modular libraries of Mg2+- and UO22+-dependent DNAzyme subunits and their substrates. By the appropriate modular design of the DNA computation units, pH-programmable logic arrays of various complexities are realized, and the arrays can be erased, reused, and/or reprogrammed. Such systems may be implemented in the near future for nanomedical applications by pH-controlled regulation of cellular functions or may be used to control biotransformations stimulated by bacteria.

- Predator–Prey Molecular Ecosystems
  Fujii, T.; Rondelez, Y. *ACS Nano* **2013**, *7*, 27-34
  <u>Abstract:</u>



Biological organisms use intricate networks of chemical reactions to control molecular processes and spatiotemporal organization. In turn, these living systems are embedded in self-organized structures of larger scales, for example, ecosystems. Synthetic in vitro efforts have reproduced the architectures and behaviors of simple cellular circuits. However, because all these systems share the same dynamic foundations, a generalized molecular programming strategy should also support complex collective behaviors, as seen, for example, in animal populations. We report here the bottom-up assembly of chemical systems that reproduce in vitro the specific dynamics of ecological communities. We experimentally observed unprecedented molecular behaviors, including predator–prey oscillations, competition-induced chaos, and symbiotic synchronization. These synthetic systems are tailored through a novel, compact, and versatile design strategy, leveraging the programmability of DNA interactions under the precise control of enzymatic catalysis. Such self-organizing assemblies will foster a better appreciation of the molecular origins of biological complexity and may also serve to orchestrate complex collective operations of molecular agents in technological applications.

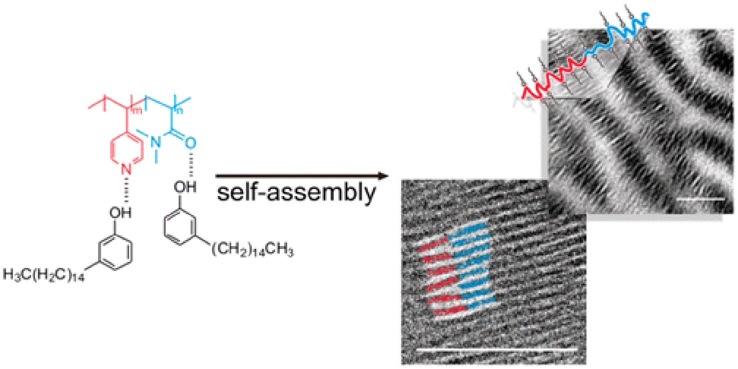
- Thermally Induced Nanoimprinting of Biodegradable Polycarbonates Using Dynamic Covalent Cross-Links
  Thongsomboon, W.; Sherwood, M.; Arellano, N.; Nelson, A. *ACS Macro Lett.* **2013**, *2*, 19-22.
  Abstract:



The introduction of reversible covalent bonds into polymeric systems afford robust, yet dynamic, materials that can respond to external stimuli. A series of aliphatic polycarbonate polymers were synthesized via ring-opening polymerization of furanyl and maleimido-bearing cyclic carbonate monomers. These side chains undergo thermally induced Diels–Alder reactions to afford cross-linked films. Because both the diene and dienophile were incorporated into the same polymer backbone, a protected maleimido group, in the form of the furan adduct, was used. Both the forward and reverse Diels–Alder reaction are triggered thermally, which allows the deprotection of the maleimido group and the subsequent reaction with the furanyl side chains to form cross-links. Random copolymers and poly(ethylene glycol) containing block copolymers were formed using diazabicyclo[5.4.0]undec-7-ene as the catalyst and a thiourea cocatalyst. The polymers form uniform films that can be cross-linked in the bulk state. To further illustrate the dynamic nature of the covalent bonds within the cross-linked

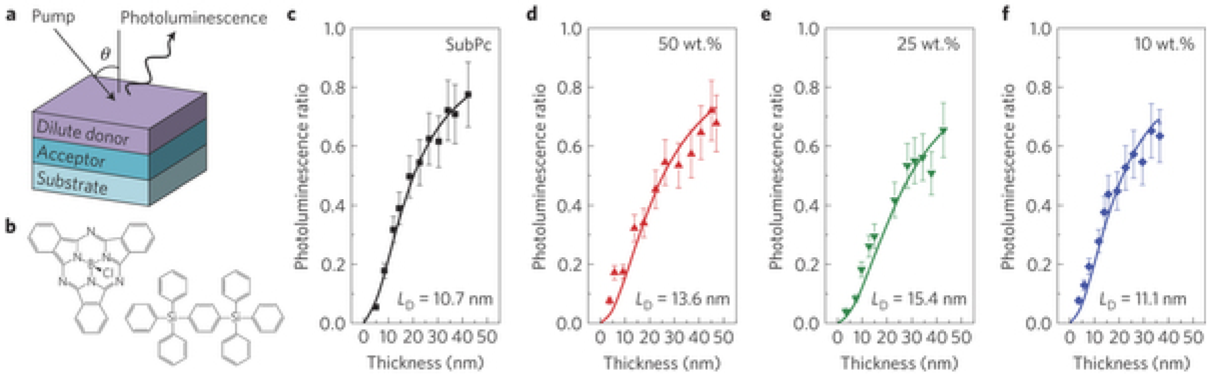
films, a patterned silicon mold was used to transfer a series of nanoscale patterns using a thermal nanoimprint process.

- Hierarchical Self-Assembly in Supramolecular Double-Comb Diblock Copolymer Complexes
  Faber, M.; Hofman, A. H.; Polushkin, E.; van Ekenstein, G. A.; Seitsonen, J.; Ruokolainen, J.; Loos, K.; ten Brinke, G. *Macromolecules* **2013**, *46*, 500-517.
  Abstract:



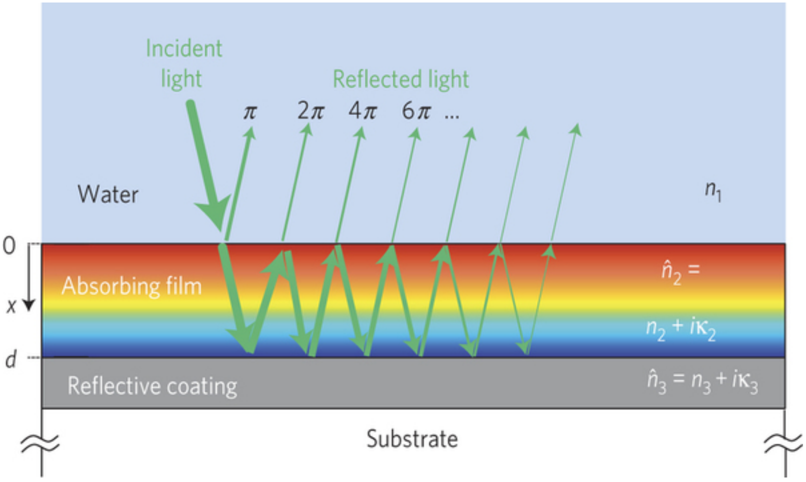
Hierarchical self-assembly of supramolecular double-comb diblock copolymer complexes, based on a diblock copolymer in which both blocks can participate in the hydrogen bonding with short amphiphiles, is discussed. A symmetric poly(4-vinylpyridine)-b-poly(N,N-dimethylacrylamide) (P4VP-b-PDMA) diblock copolymer was synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerization. Supramolecular double-comb complexes were prepared by hydrogen bonding of 3-pentadecylphenol (PDP) to both blocks, as confirmed by infrared spectroscopy. The self-assembled structures were studied using small-angle X-ray scattering (SAXS), wide-angle X-ray scattering, and transmission electron microscopy (TEM). Self-assembly of the supramolecular complex containing a stoichiometric amount of PDP resulted in a lamellar-in-lamellar structure in which the large length scale is formed by the phase separation between the supramolecular blocks of the supramolecular complex. Both domains contain a smaller lamellar morphology of a different short length scale periodicity, orientated perpendicular with respect to the large length scale lamellar structure. Because of the difference in periodicity, the two short length scales can be distinguished clearly in SAXS and TEM.

- Tailored exciton diffusion in organic photovoltaic cells for enhanced power conversion efficiency
  Menke, S. M.; Luhman, W. A.; Holmes, R. J. *Nature Materials* **2013**, *12*, 152–157.
  Abstract:



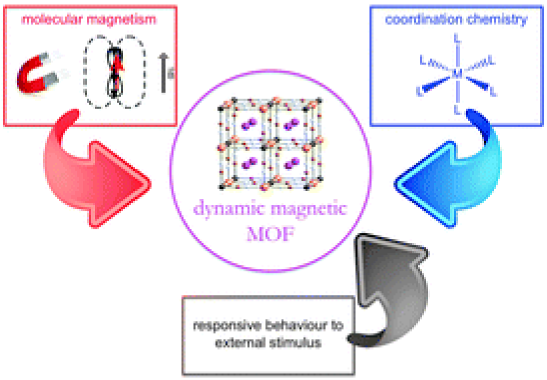
Photoconversion in planar-heterojunction organic photovoltaic cells (OPVs) is limited by a short exciton diffusion length (L_D) that restricts migration to the dissociating electron donor/acceptor interface. Consequently, bulk heterojunctions are often used to realize high efficiency as these structures reduce the distance an exciton must travel to be dissociated. Here, we present an alternative approach that seeks to directly engineer L_D by optimizing the intermolecular separation and consequently, the photophysical parameters responsible for excitonic energy transfer. By diluting the electron donor boron subphthalocyanine chloride into a wide-energy-gap host material, we optimize the degree of interaction between donor molecules and observe a ~50% increase inL_D. Using this approach, we construct planar-heterojunction OPVs with a power conversion efficiency of (4.4 ± 0.3)%, > 30% larger than the case of optimized devices containing an undiluted donor layer. The underlying correlation between L_D and the degree of molecular interaction has wide implications for the design of both OPV active materials and device architectures.

- Resonant light trapping in ultrathin films for water splitting
  Dotan, H.; Kfir, O.; Sharlin, E.; Blank, O.; Gross, M.; Dumchin, I.; Ankonina, G.; Rothschild, A.
  Nature Materials **2013**, *12*, 158–164.
  Abstract:



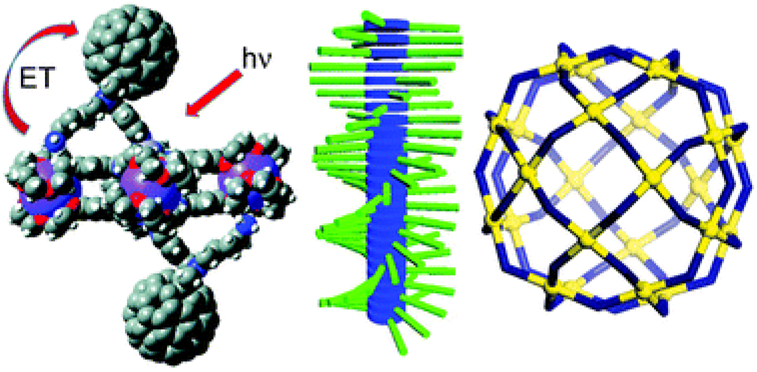
Semiconductor photoelectrodes for solar hydrogen production by water photoelectrolysis must employ stable, non-toxic, abundant and inexpensive visible-light absorbers. Iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) is one of few materials meeting these requirements, but its poor transport properties present challenges for efficient charge-carrier generation, separation, collection and injection. Here we show that these challenges can be addressed by means of resonant light trapping in ultrathin films designed as optical cavities. Interference between forward- and backward-propagating waves enhances the light absorption in quarter-wave or, in some cases, deeper subwavelength films, amplifying the intensity close to the surface wherein photogenerated minority charge carriers (holes) can reach the surface and oxidize water before recombination takes place. Combining this effect with photon retrapping schemes, such as using V-shaped cells, provides efficient light harvesting in ultrathin films of high internal quantum efficiency, overcoming the trade-off between light absorption and charge collection. A water photo-oxidation current density of 4 mA.cm^{-2} was achieved using a V-shaped cell comprising ~ 26-nm-thick Ti-doped $\alpha\text{-Fe}_2\text{O}_3$ films on back-reflector substrates coated with silver–gold alloy.

- Dynamic magnetic MOFs
  Coronado, E.; Mínguez Espallargas, G. *Chem. Soc. Rev.* **2013**, *42*, 1525-1539.
  Abstract:



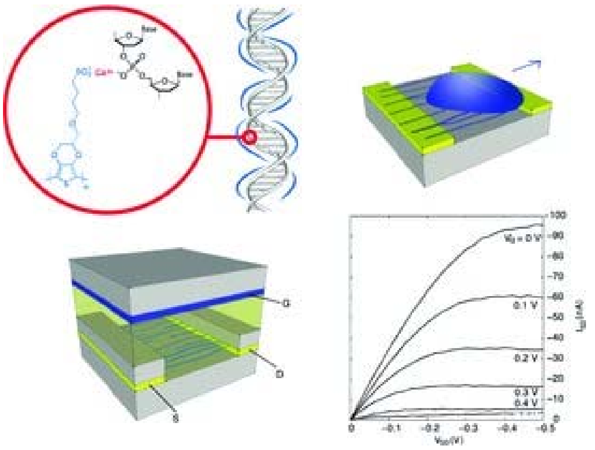
In this review we combine the use of coordination chemistry with the concepts of molecular magnetism to design magnetic Metal–Organic Frameworks (MOFs) in which the crystalline network undergoes a dynamic change upon application of an external stimulus. The various approaches so far developed to prepare these kinds of chemically or physically responsive MOFs with tunable magnetic properties are presented.

- Functional behaviour from controlled self-assembly: challenges and prospects
  Ward, M. D.; Raithby, P. R. *Chem. Soc. Rev.* **2013**, *42*, 1619-1636.
  Abstract:



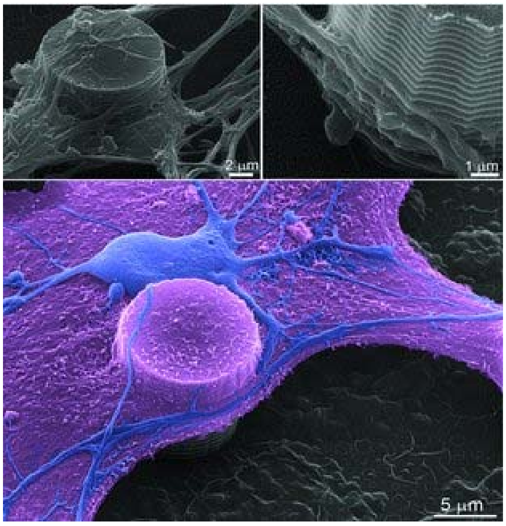
Many naturally occurring systems show us how multi-component supramolecular assemblies can generate useful functional behaviour. In this article the problems and limitations associated with achieving such behaviour in artificial multi-component assemblies is discussed, together with two examples of functions in artificial supramolecular assemblies based on (i) host–guest chemistry in cavities of cages, and (ii) light-harvesting in multi-chromophore arrays. Important challenges for the future are summarised.

- Electronic Polymers and DNA Self-Assembled in Nanowire Transistors
  Hamedi, M.; Elfwing, A.; Gabrielsson, R.; Inganäs, O. *Small* **2013**, *9*, 363–368.
  Abstract:



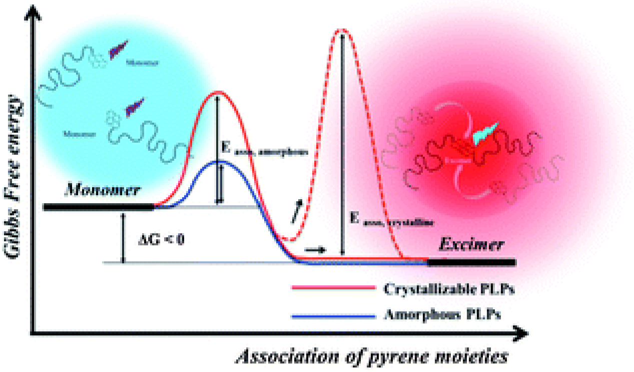
Aqueous self-assembly of DNA and molecular electronic materials can lead to the creation of innumerable copies of identical devices, and inherently programmed complex nanocircuits. Here self-assembly of a water soluble and highly conducting polymer PEDOT-S with DNA in aqueous conditions is shown. Orientation and assembly of the conducting DNA/PEDOT-S complex into electrochemical DNA nanowire transistors is demonstrated.

- Nanostructured Superhydrophobic Substrates Trigger the Development of 3D Neuronal Networks
  Limongi, T.; Cesca, F.; Gentile, F.; Marotta, R.; Ruffilli, R.; Barberis, A.; Dal Maschio, M.; Petrini, E. M.; Santoriello, S.; Benfenati, F.; Di Fabrizio, E. *Small* **2013**, *9*, 402–412.
  Abstract:



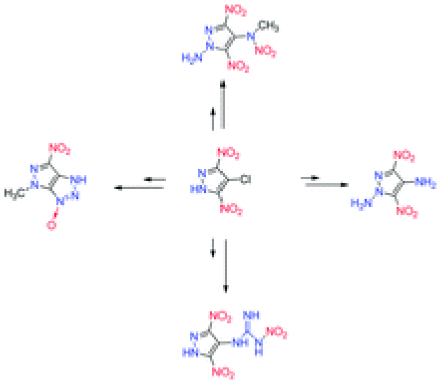
The generation of 3D networks of primary neurons is a big challenge in neuroscience. Here, a novel method is presented for a 3D neuronal culture on superhydrophobic (SH) substrates. How nano-patterned SH devices stimulate neurons to build 3D networks is investigated. Scanning electron microscopy and confocal imaging show that soon after plating neurites adhere to the nanopatterned pillar sidewalls and they are subsequently pulled between pillars in a suspended position. These neurons display an enhanced survival rate compared to standard cultures and develop mature networks with physiological excitability. These findings underline the importance of using nanostructured SH surfaces for directing 3D neuronal growth, as well as for the design of biomaterials for neuronal regeneration.

- Photo-induced pyrene association in pyrene-labeled polymers for optical recording
  Li, M.-C.; Ho, R.-M.; Lee, Y.-D. *J. Mater. Chem. C* **2013**, *1*, 1601-1606.
  Abstract:



Here, we aim to systematically examine the mechanism of photo-induced pyrene association in pyrene-labeled polymers (PLPs) for optical recording. By taking advantage of polymer glass transition, the associated pyrene moieties can be frozen in the glassy matrix of the PLP to give the emission contrast for optical recording, as evidenced by the phenomenon of room-temperature phosphorescence. *In situ* time profiles of the fluorescence emission during recording reflect that the association of pyrene moieties in PLPs is a diffusion-controlled process, and it is highly dependent on the mobility of the polymer chain. For crystallizable PLPs, the polymer chain can also be frozen in the crystalline state that inhibits the association of pyrene moieties in PLPs. As a result, T_g and T_m of the PLPs can be exploited as energy barriers for the induction of the association of pyrene moieties in PLPs and the recording capabilities of the PLPs will be dependent upon the thermal properties of the PLPs.

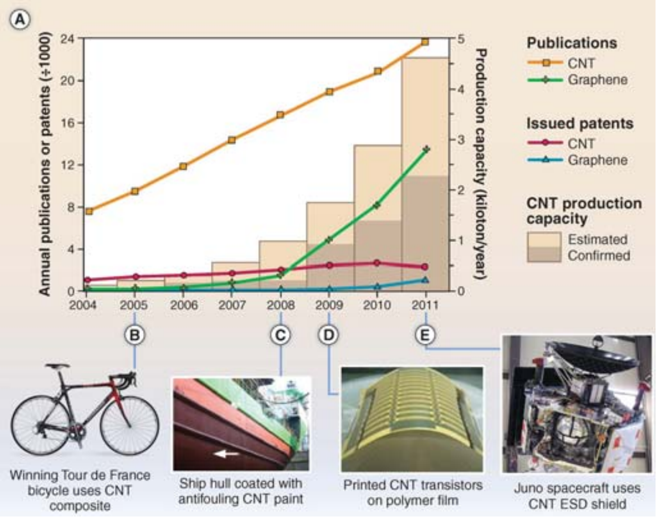
- 4-Chloro-3,5-dinitropyrazole: a precursor for promising insensitive energetic compounds
  He, C.; Zhang, J.; Parrish, D. A.; Shreeve, J. M. *J. Mater. Chem. A*, **2013**, *1*, 2863-2868.
  Abstract:



A series of 3,5-dinitropyrazole derivatives was prepared from 4-chloro-3,5-dinitropyrazole in good yields and characterized by IR, ^{1}H, and ^{13}C NMR (some cases ^{15}N NMR) spectroscopy, elemental analysis, and DSC. The structures of **7** and **13** were confirmed by single crystal X-ray diffraction. The impact sensitivity was determined using a standard BAM method, and detonation properties were obtained using experimental densities and calculated heats of formation.

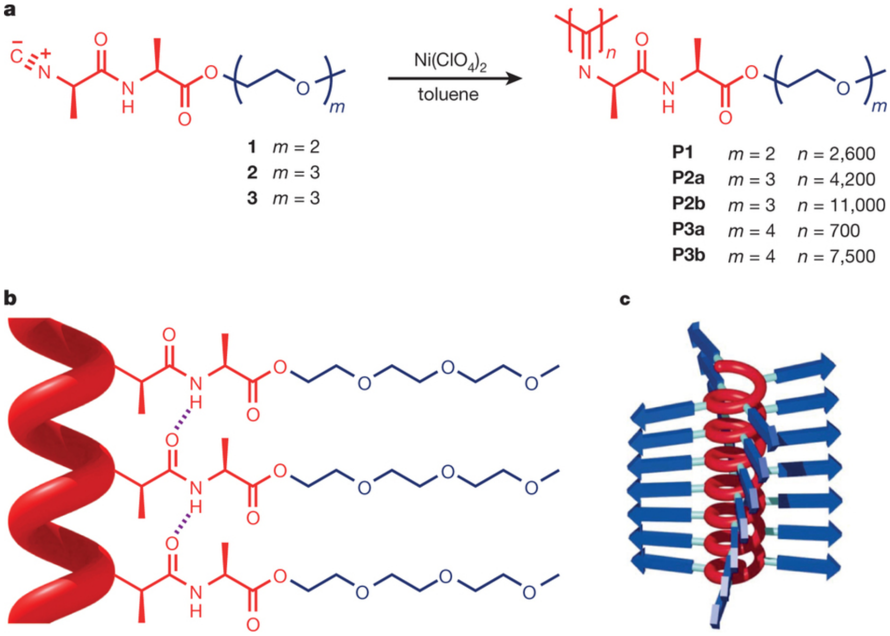
- Carbon nanotubes: present and future commercial applications
  De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. *Science* **2013**, *339*, 535-539.

Abstract:



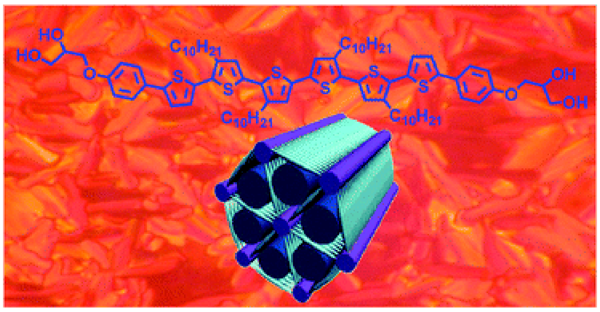
Worldwide commercial interest in carbon nanotubes (CNTs) is reflected in a production capacity that presently exceeds several thousand tons per year. Currently, bulk CNT powders are incorporated in diverse commercial products ranging from rechargeable batteries, automotive parts, and sporting goods to boat hulls and water filters. Advances in CNT synthesis, purification, and chemical modification are enabling integration of CNTs in thin-film electronics and large-area coatings. Although not yet providing compelling mechanical strength or electrical or thermal conductivities for many applications, CNT yarns and sheets already have promising performance for applications including supercapacitors, actuators, and lightweight electromagnetic shields.

- Responsive biomimetic networks from polyisocyanopeptide hydrogels
  Kouwer, P. H. J.; Koepf, M.; Le Sage, V. A. A.; Jaspers, M.; van Buul, A. M.; Eksteen-Akeroyd, Z. H.; Woltinge, T.; Schwartz, E.; Kitto, H. J.; Hoogenboom, R.; Picken, S. J.; Nolte, R. J. M.; Mendes, E.; Rowan, A. E. *Nature* **2013**, *493*, 651–655.
  Abstract:



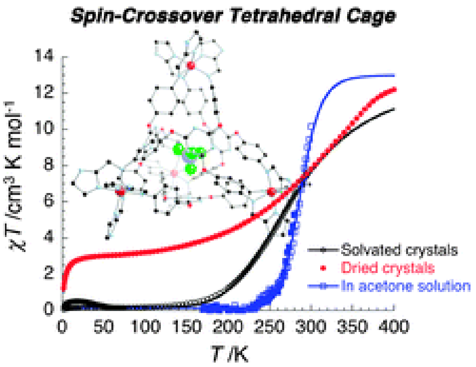
Mechanical responsiveness is essential to all biological systems down to the level of tissues and cells. The intra- and extracellular mechanics of such systems are governed by a series of proteins, such as microtubules, actin, intermediate filaments and collagen. As a general design motif, these proteins self-assemble into helical structures and superstructures that differ in diameter and persistence length to cover the full mechanical spectrum. Gels of cytoskeletal proteins display particular mechanical responses (stress stiffening) that until now have been absent in synthetic polymeric and low-molar-mass gels. Here we present synthetic gels that mimic in nearly all aspects gels prepared from intermediate filaments. They are prepared from polyisocyanopeptides grafted with oligo(ethylene glycol) side chains. These responsive polymers possess a stiff and helical architecture, and show a tunable thermal transition where the chains bundle together to generate transparent gels at extremely low concentrations. Using characterization techniques operating at different length scales (for example, macroscopic rheology, atomic force microscopy and molecular force spectroscopy) combined with an appropriate theoretical network model, we establish the hierarchical relationship between the bulk mechanical properties and the single-molecule parameters. Our results show that to develop artificial cytoskeletal or extracellular matrix mimics, the essential design parameters are not only the molecular stiffness, but also the extent of bundling. In contrast to the peptidic materials, our polyisocyanide polymers are readily modified, giving a starting point for functional biomimetic hydrogels with potentially a wide variety of applications, in particular in the biomedical field.

- A bolaamphiphilic sexithiophene with liquid crystalline triangular honeycomb phase
  Bu, W.; Gao, H.; Tan, X.; Dong, X.; Cheng, X.; Prehm, M.; Tschierske, C. *Chem. Commun*. **2013**, *49*, 1756-1758.
  Abstract:



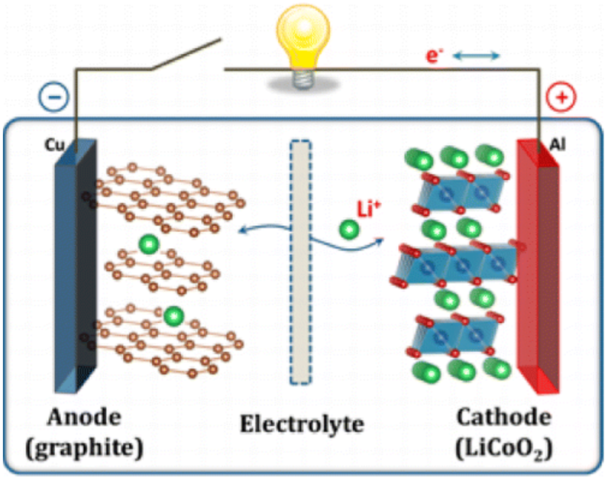
A new bolaamphiphile comprising a 5,5′′′′′-diphenyl-sexithiophene core with glycerol groups at each end and four lateral decyl chains was synthesized, which self-assembles into a liquid crystalline phase representing a nanoscale honeycomb composed of quasi-infinite triangular cylinders of π-conjugated sexithiophenes.

- A face-capped [Fe4L4]8+ spin crossover tetrahedral cage
  Ferguson, A.; Squire, M. A.; Siretanu, D.; Mitcov, D.; Mathonière, C.; Clérac, R.; Kruger, P. E. *Chem. Commun*. **2013**, *49*, 1597-1599.
  Abstract:



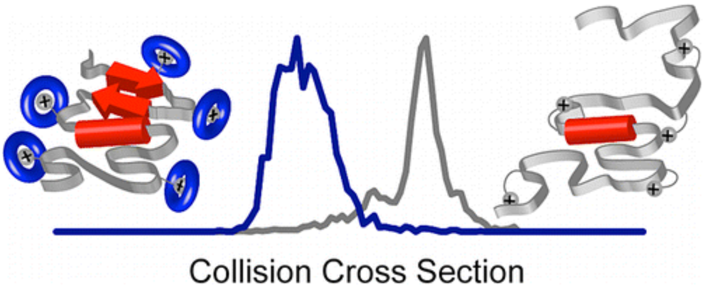
Reported here is a face-capped Fe(II) molecular tetrahedron, $[Fe_4L_4](BF_4)_8$, **1**. Single crystal X-ray diffraction at 153 and 293 K suggest spin crossover (SCO) and variable temperature magnetic susceptibility measurements confirm **1** displays thermally driven SCO behaviour in the solid state and in dilute acetone solution centred around 284–288 K.

- The Li-Ion Rechargeable Battery: A Perspective
  Goodenough, J. B.; Park, K.-S. *J. Am. Chem. Soc.* **2013**, *135*, 1167–1176.
  Abstract:



Each cell of a battery stores electrical energy as chemical energy in two electrodes, a reductant (anode) and an oxidant (cathode), separated by an electrolyte that transfers the ionic component of the chemical reaction inside the cell and forces the electronic component outside the battery. The output on discharge is an external electronic current *I* at a voltage *V* for a time Δ*t*. The chemical reaction of a rechargeable battery must be reversible on the application of a charging *I* and *V*. Critical parameters of a rechargeable battery are safety, density of energy that can be stored at a specific power input and retrieved at a specific power output, cycle and shelf life, storage efficiency, and cost of fabrication. Conventional ambient-temperature rechargeable batteries have solid electrodes and a liquid electrolyte. The positive electrode (cathode) consists of a host framework into which the mobile (working) cation is inserted reversibly over a finite solid–solution range. The solid–solution range, which is reduced at higher current by the rate of transfer of the working ion across electrode/electrolyte interfaces and within a host, limits the amount of charge per electrode formula unit that can be transferred over the time $\Delta t = \Delta t(I)$. Moreover, the difference between energies of the LUMO and the HOMO of the electrolyte, i.e., electrolyte window, determines the maximum voltage for a long shelf and cycle life. The maximum stable voltage with an aqueous electrolyte is 1.5 V; the Li-ion rechargeable battery uses an organic electrolyte with a larger window, which increase the density of stored energy for a given Δt. Anode or cathode electrochemical potentials outside the electrolyte window can increase V, but they require formation of a passivating surface layer that must be permeable to Li^+ and capable of adapting rapidly to the changing electrode surface area as the electrode changes volume during cycling. A passivating surface layer adds to the impedance of the Li^+ transfer across the electrode/electrolyte interface and lowers the cycle life of a battery cell. Moreover, formation of a passivation layer on the anode robs Li from the cathode irreversibly on an initial charge, further lowering the reversible Δt. These problems plus the cost of quality control of manufacturing plague development of Li-ion rechargeable batteries that can compete with the internal combustion engine for powering electric cars and that can provide the needed low-cost storage of electrical energy generated by renewable wind and/or solar energy. Chemists are contributing to incremental improvements of the conventional strategy by investigating and controlling electrode passivation layers, improving the rate of Li^+ transfer across electrode/electrolyte interfaces, identifying electrolytes with larger windows while retaining a Li^+ conductivity $\sigma_{Li} > 10^{-3}$ S cm^{-1}, synthesizing electrode morphologies that reduce the size of the active particles while pinning them on current collectors of large surface area accessible by the electrolyte, lowering the cost of cell fabrication, designing displacement-reaction anodes of higher capacity that allow a safe, fast charge, and designing alternative cathode hosts. However, new strategies are needed for batteries that go beyond powering hand-held devices, such as using electrode hosts with two-electron redox centers; replacing the cathode hosts by materials that undergo displacement reactions (e.g. sulfur) by liquid cathodes that may contain flow-through redox molecules, or by catalysts for air cathodes; and developing a Li^+ solid electrolyte separator membrane that allows an organic and aqueous liquid electrolyte on the anode and cathode sides, respectively. Opportunities exist for the chemist to bring together oxide and polymer or graphene chemistry in imaginative morphologies.

- Protein Structure in the Gas Phase: The Influence of Side-Chain Microsolvation
  Warnke, S.; von Helden, G.; Pagel, K. *J. Am. Chem. Soc.* **2013**, *135*, 1177–1180.
  Abstract:

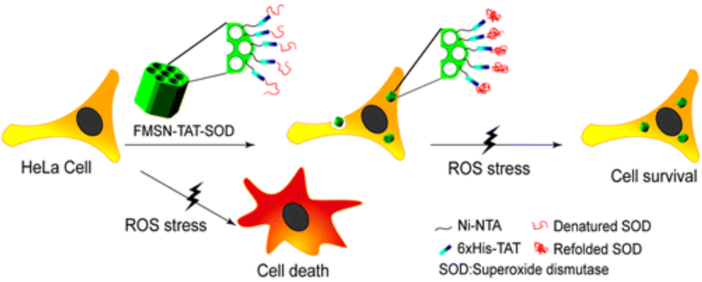


There is ongoing debate about the extent to which protein structure is retained after transfer into the gas phase. Here, using ion-mobility spectrometry, we investigated the impact of side-chain–backbone interactions on the structure of gas-phase protein ions by noncovalent attachment of crown ethers (CEs). Our results indicate that in the absence of solvent, secondary interactions between charged lysine side chains and backbone carbonyls can significantly influence the structure of a protein. Once the charged residues are capped with CEs, certain charge states of the protein are found to undergo significant structural compaction.

- A New Strategy for Intracellular Delivery of Enzyme Using Mesoporous Silica Nanoparticles: Superoxide Dismutase

Chen, Y.-P.; Chen, C.-T.; Hung, Y. ; Chou, C.-M.; Liu, T.-P.; Liang, M.-R.; Chen, C.-T. ; Mou, C.-Y. *J. Am. Chem. Soc.* **2013**, *135,* 1516–1523.

Abstract:

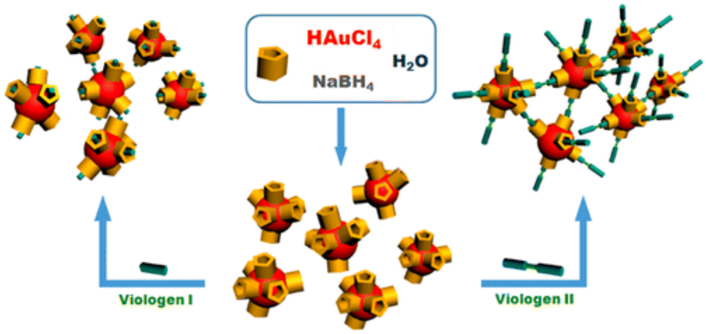


We developed mesoporous silica nanoparticle (MSN) as a multifunctional vehicle for enzyme delivery. Enhanced transmembrane delivery of a superoxide dismutase (SOD) enzyme embedded in MSN was demonstrated. Conjugation of the cell-penetrating peptide derived from the human immunodeficiency virus 1 (HIV) transactivator protein (TAT) to mesoporous silica nanoparticle is shown to be an effective way to enhance transmembrane delivery of nanoparticles for intracellular and molecular therapy. Cu,Zn-superoxide dismutase (SOD) is a key antioxidant enzyme that detoxifies intracellular reactive oxygen species, ROS, thereby protecting cells from oxidative damage. In this study, we fused a human Cu,Zn-SOD gene with TAT in a bacterial expression vector to produce a genetic in-frame His-tagged TAT-SOD fusion protein. The His-tagged TAT-SOD fusion protein was expressed in E. coli using IPTG induction and purified using FMSN-Ni-NTA. The purified TAT-SOD was conjugated to FITC-MSN forming FMSN-TAT-SOD. The effectiveness of FMSN-TAT-SOD as an agent against ROS was investigated, which included the level of ROS and apoptosis after free radicals induction and functional recovery after ROS damage. Confocal microscopy on live unfixed cells and flow cytometry analysis showed characteristic nonendosomal distribution of FMSN-TAT-SOD. Results suggested that FMSN-TAT-SOD may provide a strategy for the therapeutic delivery of antioxidant enzymes that protect cells from ROS damage.

- Viologen-Mediated Assembly of and Sensing with Carboxylatopillar[5]arene-Modified Gold Nanoparticles

  Li, H.; Chen, D.-X.; Sun, Y.-L.; Zheng, Y. B.; Tan, L.-L.; Weiss, P. S.; Yang, Y.-W. *J. Am. Chem. Soc.* **2013***, 135,* 1570–1576.

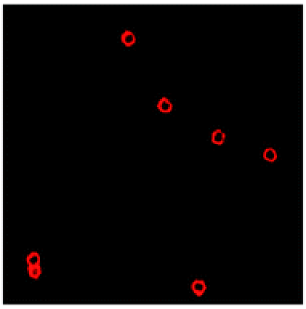
  Abstract:



Carboxylatopillar[5]arene (CP[5]A), a new water-soluble macrocyclic synthetic receptor, has been employed as a stabilizing ligand for in situ preparation of gold nanoparticles (AuNPs) to gain new insights into supramolecular host–AuNP interactions. CP[5]A-modified AuNPs with good dispersion and narrow size distributions (3.1 ± 0.5 nm) were successfully produced in aqueous solution, suggesting a green synthetic pathway for the application of AuNPs in biological systems.

Supramolecular self-assembly of CP[5]A-modified AuNPs mediated by suitable guest molecules was also investigated, indicating that the new hybrid material is useful for sensing and detection of the herbicide paraquat.

- Exploring locked nucleic acids as a bio-inspired materials assembly and disassembly tool
  Eze, N. A.; Milam, V. T. *Soft Matter* **2013,** *9*, 2403-2411.
  Abstract:

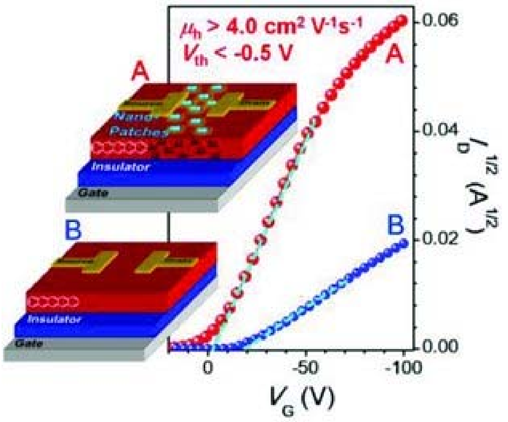


Oligonucleotides hold great promise as a recognition-based biomaterials assembly and disassembly tool. Chemically modified oligonucleotides such as locked nucleic acids (LNA) provide the added advantage of nuclease resistance. In the current study, we focus on programming the assembly and disassembly of LNA-linked colloidal particles as a function of sequence composition. We find that incorporation of LNA residues (∼30%) into either one or both primary hybridization partner strands results in a higher duplex density than for isosequential DNA strands. Mismatched primary hybridization partners with sequence length of 11–15 bases have similar initial primary duplex densities. The displacement of mismatched strands by 15 base-long, perfectly matched competitive target strands, however, does depend on the base length of the original mismatched partner strand. Confocal microscopy confirms that substantial colloidal assembly occurs for both perfectly matched and mismatched LNA sequences that are 9 bases in length. Extensive disassembly for the mismatched case is then triggered through the introduction of 15 base-long competitive target strands. Our work demonstrates that LNA can be used to programmatically assemble and disassemble colloidal particles.

- Stimuli-responsive surfactants
  Brown, P.; Butts, C. P.; Eastoe, J. *Soft Matter* **2013,** *9*, 2365-2374.
  Abstract:

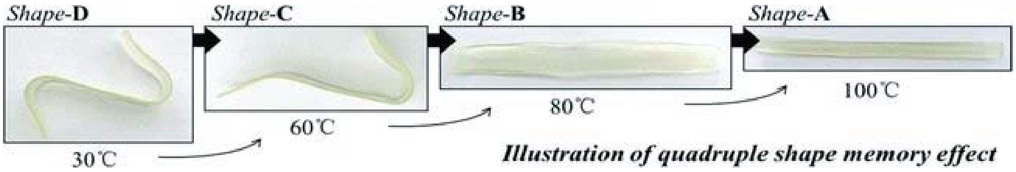
Recent progress in stimuli-responsive surfactants is reviewed, covering control of both interfaces and bulk solution properties. Particular attention is devoted to potential future directions and applications.

- Remarkable Mobility Increase and Threshold Voltage Reduction in Organic Field-Effect Transistors by Overlaying Discontinuous Nano-Patches of Charge-Transfer Doping Layer on Top of Semiconducting Film
  Kim, J. H.; Yun, S. W.; An, B.-K.; Han, Y.-D.; Yoon, S.-J.; Joo, J.; Park, S. Y. *Adv. Mater.* **2013**, *25*, 719–724.
  Abstract:



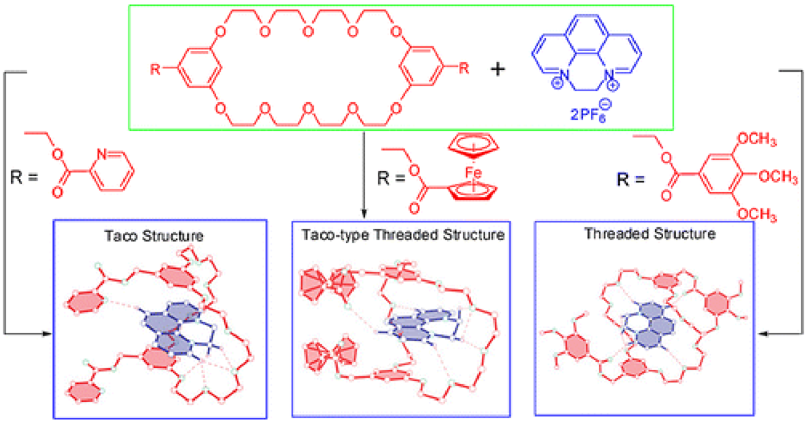
An effective strategy for significantly increasing the organic transistor mobility with simultaneous reduction of the threshold voltage utilizing discontinuous nano-patches of charge-transfer doping layer is demonstrated. By overlaying the nano-patches on top of a given semiconducting film, mobility and threshold voltage of *p*-type pentacene are remarkably improved to 4.52 $cm^2\ V^{-1}s^{-1}$ and −0.4 V, and those of *n*-type Hex-4-TFPTA are also improved to 2.57 $cm^2\ V^{-1}s^{-1}$ and 4.1 V.

- A General Approach Towards Thermoplastic Multishape-Memory Polymers via Sequence Structure Design
  Luo, Y.; Guo, Y.; Gao, X.; Li, B.-G; Xie, T. *Adv. Mater.* **2013**, *25*, 743–748.
  Abstract:



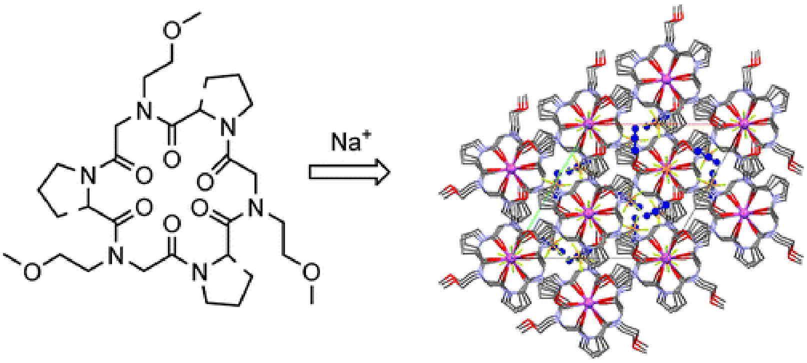
The chain sequence of a poly(styrene-*co*-methyl acrylate) copolymer is designed to form a V-shaped gradient sequence via controlled/living radical emulsion copolymerization. This specially designed chain sequence gives this common copolymer the capacity of multishape memory. The copolymer can sequentially recover to its permanent shape from three or more previously programmed temporary shapes with the stimulus of temperature.

- Chemically-Responsive Complexation of A Diquaternary Salt with Bis(*m*-phenylene)-32-Crown-10 Derivatives and Host Substituent Effect on Complexation Geometry
  Yan, X.; Li, Z.; Wei, P.; Huang, F. *Org. Lett.* **2013**, *15,* 534-537.
  Abstract:



A chemically responsive diquaternary salt with π-extended surface was made. The hostguest complexation with chemo-responsiveness between three bis(m-phenylene)-32-crown-10 (BMP32C10) derivatives and this diquaternary salt guest was studied through the sequential addition of basic and acidic reagents (diethylamine and trifluoroacetic acid, respectively). Furthermore, the host-substituent effect on the complexation geometries of these three hostguest complexes, from taco to taco-type threaded to threaded structures by changing the substituent on BMP32C10 as shown by crystal structures, was also addressed.

- Structural Effects of Proline Substitution andM etal Binding on Hexameric Cyclic Peptoids
  Izzo, I.; Ianniello, G.; De Cola, C.; Nardone, B; Erra, L.; Vaughan, G.; Tedesco, C.; De Riccardis, F. *Org. Lett.* **2013**, *15*, 598-601.
  Abstract:



L-Proline and N-methoxyethyl glycine have been included in novel cyclic hexameric peptoids. Supramolecular coordination with Na^+ triggered the formation of the first 1D metal-organic framework based on peptoids.