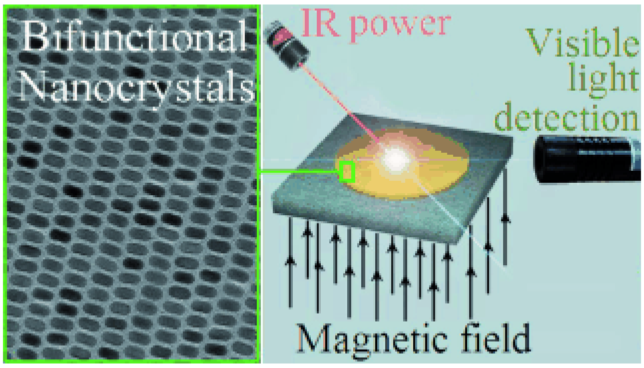
- Magnetic Tuning of Upconversion Luminescence in Lanthanide-Doped Bifunctional Nanocrystals

  Liu, Y.; Wang, D.; Shi, J.; Peng, Q.; Li, Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 4366 –4369.

  Abstract:

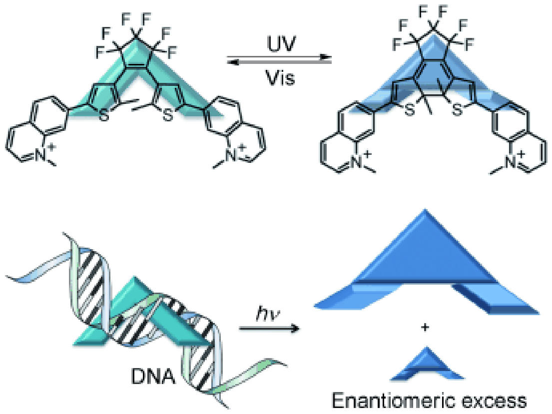


Nanocrystal clear: Optical-magnetic (OM) bifunctional $NaGdF_4$:Nd^{3+},Yb^{3+},Er^{3+}nanocrystals were successfully synthesized that consist of luminescent Er^{3+} ions and a coordinating magnetic Gd^{3+} ion. The luminescence of $NaGdF_4$:Nd^{3+},Yb^{3+},Er^{3+}nanocrystals was tuned by changing the applied magnetic field (see figure) both at room temperature and ultralow temperatures.

- Enantioselective Cyclization of Photochromic Dithienylethenes Bound to DNA

  Pace, T. C. S.; Müller, V.; Li, S.; Lincoln, P.; Andréasson, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 4393 –4396.

  Abstract:

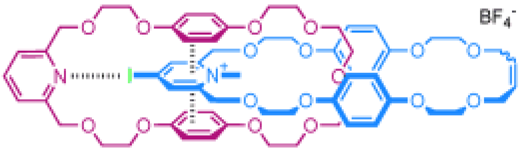


Guiding light: Enantioselectivity is obtained for the photocyclization of a photochromic dithienylethene when isomerization is carried out in the presence of DNA (see scheme).

- A Catenane Assembled through a Single Charge-Assisted Halogen Bond

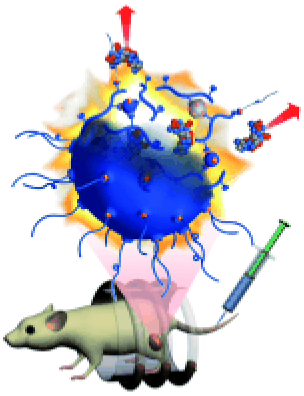
  Gilday, L. C.; Lang, T.; Caballero, A.; Costa, P. J.; Félix, V.; Beer, P. D. *Angew. Chem. Int. Ed.* **2013**, *52*, 4356-4360.

  Abstract:



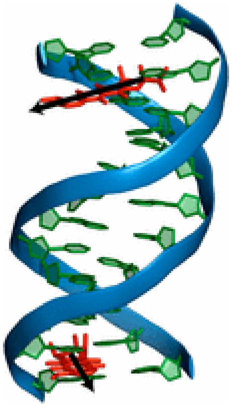
Getting connected: The formation of pseudorotaxane assemblies between a designed macrocyclic halogen bonding (XB) acceptor (red in scheme) and a series of XB donor threading components was templated by a single halogen bond. The strength of the XB assembly between the pyridine macrocycle and iodopyridinium thread was utilized in the ring-closing metathesis clipping synthesis of a [2]catenane.

- On-Demand Drug Release System for In Vivo Cancer Treatment through Self-Assembled Magnetic Nanoparticles
  Lee, J.-H.; Chen, K.-J.; Noh, S.-H.; Garcia, M. A.; Wang, H.; Lin, W.-Y.; Jeong, H.; Kong, B. J.; Stout, D. B.; Choen, J.; Tseng, H.-R. *Angew. Chem. Int. Ed.* **2013**, *52*, 4384-4388.
  Abstract:



On-demand drug release: Magnetothermally responsive drug-encapsulated supramolecular nanoparticles for on-demand drug release in vivo have been developed. The remote application of an alternative magnetic field heats the magnetic particles that effectively trigger the release of the drug. An acute drug concentration can be delivered to the tumor in vivo, resulting in an improved therapeutic outcome.

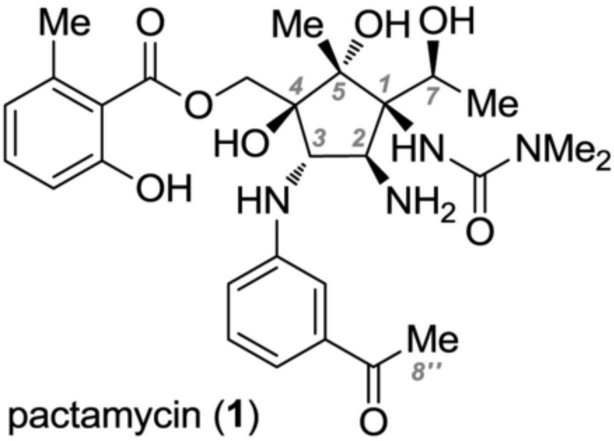
- Probing the relative orientation of molecules bound to DNA through controlled interference using second-harmonic generation
  Doughty, B.; Rao, Y.; Kazer, S. W.; Kwok, S. J. J.; Turro, N. J.; Eisenthal, K. B. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 5756-5758.
  Abstract:



A method is described in which the interference of radiated second-harmonic electric fields generated by a pair of oriented molecules intercalated into double-stranded DNA is controlled and measured. The results show that the relative molecular orientation of the two molecules significantly changes the magnitude of the observed second-harmonic generation intensity, which is described by a simple model that accounts for the interferences of the radiated fields. The technique presented shows promise for future experiments investigating structural changes induced by the formation of a

DNA–biomolecule complex.

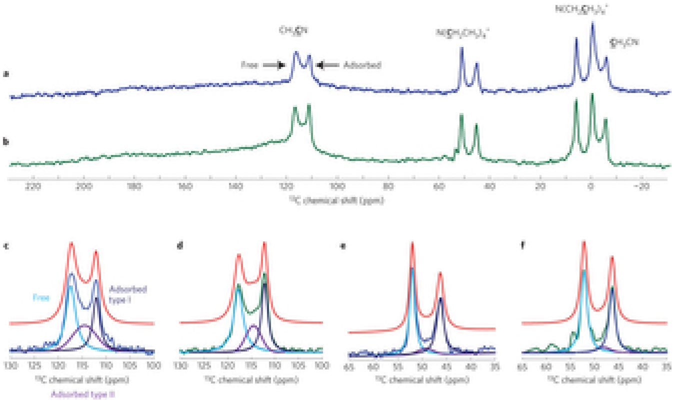
- Enantioselective Synthesis of Pactamycin, a Complex Antitumor Antibiotic
  Malinowski, J. T.; Sharpe, R. J.; Johnson, J. S. *Science* **2013**, *340*, 180-182.
  Abstract:



pactamycin (**1**)

Medicinal application of many complex natural products is precluded by the impracticality of their chemical synthesis. Pactamycin, the most structurally intricate aminocyclopentitol antibiotic, displays potent antiproliferative properties across multiple phylogenetic domains, but it is highly cytotoxic. A limited number of analogs produced by genetic engineering technologies show reduced cytotoxicity against mammalian cells, renewing promise for therapeutic applications. For decades, an efficient synthesis of pactamycin amenable to analog derivatizations has eluded researchers. Here, we present a short asymmetric total synthesis of pactamycin. An enantioselective Mannich reaction and symmetry-breaking reduction sequence was designed to enable assembly of the entire carbon core skeleton in under five steps and control critical three-dimensional (stereochemical) functional group relationships. This modular route totals 15 steps and is immediately amenable for structural analog synthesis.

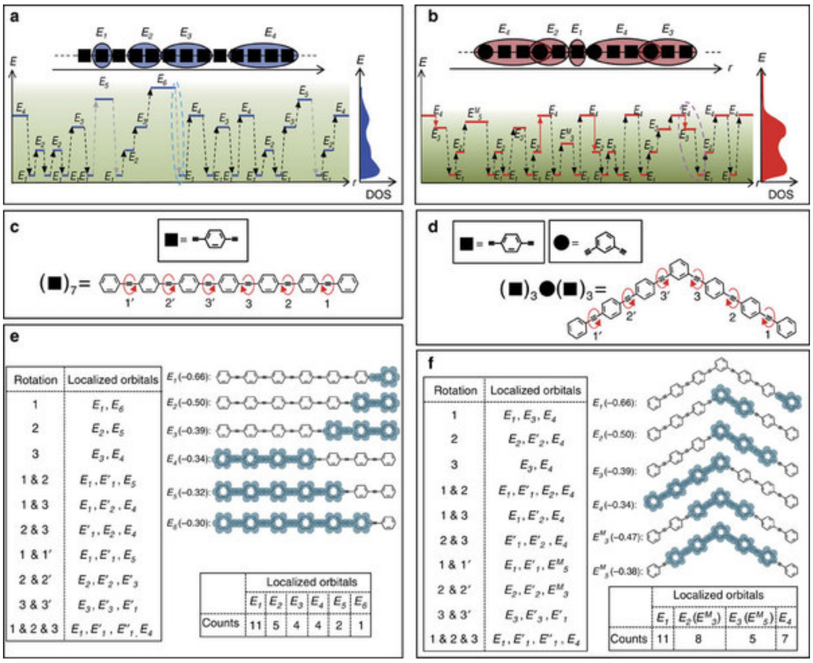
- Exploring electrolyte organization in supercapacitor electrodes with solid-state NMR
  Deschamps, M.; Gilbert, E.; Azais, P.; Raymundo-Piñero, E.; Ammar, M. R.; Simon, P.; Massiot, D.; Béguin, F. *Nature Mater.* **2013**, *12*, 351–358.
  Abstract:



Supercapacitors are electrochemical energy-storage devices that exploit the electrostatic interaction between high-surface-area nanoporous electrodes and electrolyte ions. Insight into the molecular mechanisms at work inside supercapacitor carbon electrodes is obtained with ^{13}C

and^{11}B *ex situ* magic-angle spinning nuclear magnetic resonance (MAS-NMR). In activated carbons soaked with an electrolyte solution, two distinct adsorption sites are detected by NMR, both undergoing chemical exchange with the free electrolyte molecules. On charging, anions are substituted by cations in the negative carbon electrode and cations by anions in the positive electrode, and their proportions in each electrode are quantified by NMR. Moreover, acetonitrile molecules are expelled from the adsorption sites at the negative electrode alone. Two nanoporous carbon materials were tested, with different nanotexture orders (using Raman and ^{13}C MAS-NMR spectroscopies), and the more disordered carbon shows a better capacitance and a better tolerance to high voltages.

- Design principle for increasing charge mobility of π-conjugated polymers using regularly localized molecular orbitals
  Terao, J.; Wadahama, A.; Matono, A.; Tada, T.; Watanabe, S.; Seki, S.; Fujihara, T.; Tsuji, Y. *Nature Commun.* **2013**, *4*, 1691.
  Abstract:



The feasibility of using π-conjugated polymers as next-generation electronic materials is extensively studied; however, their charge mobilities are lower than those of inorganic materials. Here we demonstrate a new design principle for increasing the intramolecular charge mobility of π-conjugated polymers by covering the π-conjugated chain with macrocycles and regularly localizing π-molecular orbitals to realize an ideal orbital alignment for charge hopping. Based on theoretical predictions, insulated wires containing *meta*-junctioned poly(phenylene–ethynylene) as the backbone units were designed and synthesized. The zigzag wires exhibited higher intramolecular charge mobility than the corresponding linear wires. When the length of the linear region of the zigzag wires was increased to 10 phenylene–ethynylene units, the intramolecular charge mobility increased to 8.5 $\mathrm{cm^{2}\,V^{-1}\,s^{-1}}$. Theoretical analysis confirmed that this design principle is suitable for obtaining ideal charge mobilities in π-conjugated polymer chains and that it provides the most effective pathways for inter-site hopping processes.

- Photo-induced covalent cross-linking for the analysis of biomolecular interactions

Preston, G. W.; Wilson, A. J. *Chem. Soc. Rev.* **2013**, *42*, 3289-3301.
Abstract:

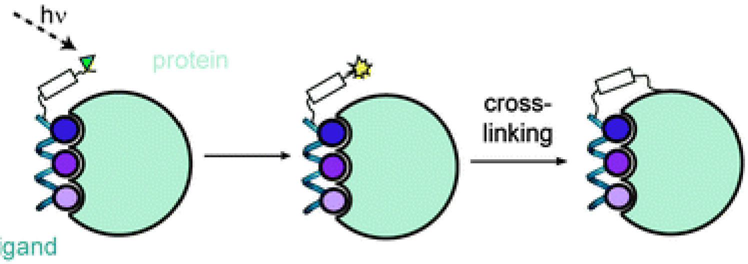
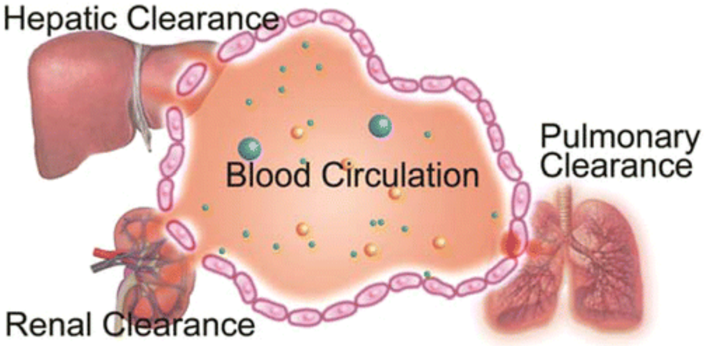


Photo-induced cross-linking (PIC) is a powerful strategy for generating information on biomolecular interactions. In PIC, the utility of traditional cross-linking methods is supplemented by the temporal control of photo-activation, enabling the study of non-covalent kinetic intermediates and heterogeneous mixtures. This tutorial review will introduce the photochemistry of activation, reactive intermediates, methods for the functionalisation of biomolecules and the installation of additional functionalities (*e.g.*, affinity tags). In doing so, we shall illustrate the wealth of data that can be obtained using this approach, ranging from the identification of interacting partners and structural data to temporal information. Alongside a discussion of the strengths and weaknesses of the various approaches, their applicability to different types of biological system will be described.

- Metabolism of Nanomaterials in Vivo: Blood Circulation and Organ Clearance
  Wang, B.; He, X.; Zhang, Z.; Zhao, Y.; Feng, W. *Acc. Chem. Res.* **2013**, *46*, 761–769.
  Abstract:



Before researchers apply nanomaterials (NMs) in biomedicine, they need to understand the blood circulation and clearance profile of these materials *in vivo.* These qualities determine the balance between nanomaterial-induced activity and unwanted toxicity. NMs have heterogeneous characteristics: they combine the bulk properties of solids with the mobility of molecules, and their highly active contact interfaces exhibit diverse functionalities. Any new and unexpected circulation features and clearance patterns are of great concern in toxicological studies and pharmaceutical screens. A number of studies have reported that NMs can enter the bloodstream directly during their application or indirectly via inhalation, ingestion, and dermal exposure. Due to the small size of NMs, the blood can then transport them throughout the circulation and to many organs where they can be stored.

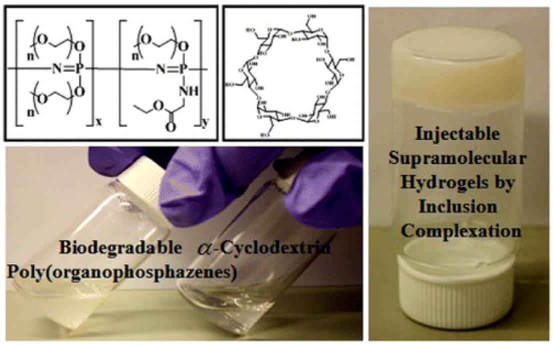
In this Account, we discuss the blood circulation and organ clearance patterns of NMs in the lung, liver, and kidney. The circulation of NMs in bloodstream is critical for delivery of inhalable NMs to extrapulmonary organs, the delivery of injectable NMs, the dynamics of tissue redistribution, and the overall targeting of drug carriers to specific cells and organs. The lung, liver, and kidney are the major distribution sites and target organs for NMs exposure, and the clearance patterns of NMs in these

organs are critical for understanding the *in vivo* fate of NMs.

Current studies suggest that multiple factors control the circulation and organ clearance of NMs. The size, shape, surface charge, surface functional groups, and aspect ratio of NMs as well as tissue microstructures strongly influence the circulation of NMs in bloodstream, their site-specific extravasation, and their clearance profiles within organs. Therefore structure design and surface modification can improve biocompatibility, regulate the *in vivo* metabolism, and reduce the toxicity of NMs.

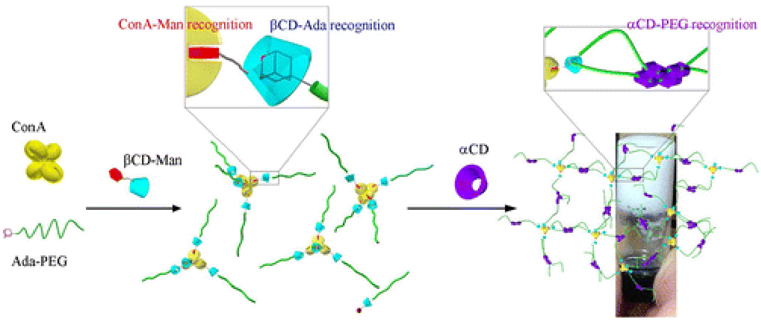
The biophysicochemical interactions occurring between NMs and between NMs and the biological milieu after the introduction of NMs into living systems may further influence the blood circulation and clearance profiles of NMs. These interactions can alter properties such as agglomeration, phase transformations, dissolution, degradation, protein adsorption, and surface reactivity. The physicochemical properties of NMs change dynamically *in vivo* thereby making the metabolism of NMs complex and difficult to predict. The development of *in situ*, real-time, and quantitative techniques, *in vitro* assays, and the adaptation of physiologically-based pharmacokinetic (PBPK) and quantitative structure–activity relationship (QNSAR) modeling for NMs will streamline future *in vivo* studies.

- Injectable and Biodegradable Supramolecular Hydrogels by Inclusion Complexation between Poly(organophosphazenes) and α-Cyclodextrin
  Tian, Z.; Chen, C.; Allcock, H. R. *Macromolecules* **2013**, *46*, 2715-2724.
  <u>Abstract:</u>



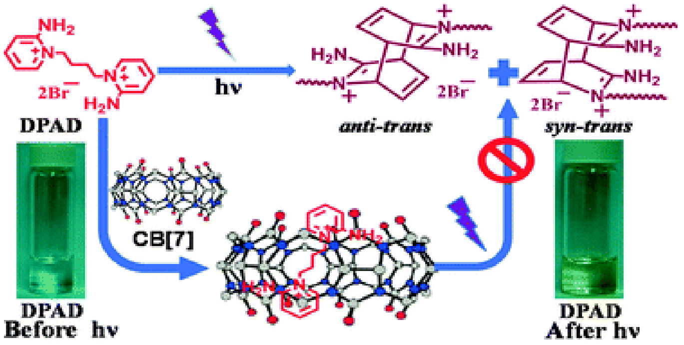
Biodegradable poly(organophosphazenes) containing side chains of various oligo(ethylene glycol) methyl ethers (mPEGs) and glycine ethyl ester units were synthesized and characterized. Novel supramolecular-structured hydrogel systems based on the inclusion complex between the mPEG grafted polyphosphazenes and α-cyclodextrin were prepared in aqueous media. The gelation time depended on the length of the mPEG side chains, the molar ratio between mPEG repeat units and α-cyclodextrin, and the concentration of the polymeric gel precursors. The rheological measurements of the supramolecular hydrogels indicate a fast gelation process and flowable character under a large strain. The hydrogel systems demonstrate unique structure-related reversible gel–sol transition properties at a certain temperature due to the reversible supramolecular assembly. The formation of a channel-type inclusion complex induced gelation mechanism was studied by DSC, TGA, ^{13}C CP/MAS NMR, and X-ray diffraction techniques. The strong potential of the system for injectable drug delivery applications was explored with the use of bovine serum albumin as a model protein for in vitro release studies. All the supramolecular hydrogels studied showed disintegration by dethreading of the α-cyclodextrin. Polymers with longer poly(ethylene glycol) side chains had better stability and slower protein release profiles. The molecular weights of the polymers were monitored by GPC to show the biodegradability of the hydrogel system.

- Dual Molecular Recognition Leading to a Protein-Polymer Conjugate and Further Self-Assembly
  Wei, K.; Li, J.; Chen, G.; Jiang, M. *ACS Macro Lett*. **2013**, *2*, 278-283.
  Abstract:



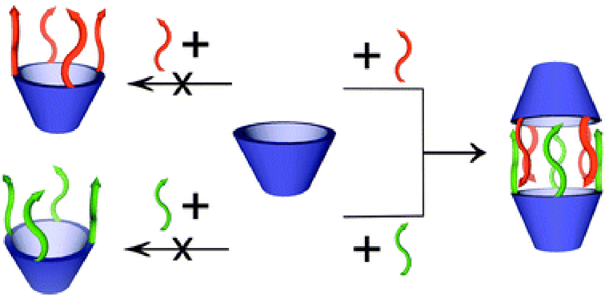
Supramolecular conjugation between native protein concanavalin A (ConA) and synthetic polymer PEG (polyethylene glycol) was achieved by dual molecular recognition interactions via a linker, βCD-Man, of which β-cyclodextrin (βCD) and α-mannopyranoside (Man) recognized the adamantane (Ada) end of PEG and lectin ConA orthogonally. Further self-assembly of the resultant supra-conjugates of ConA-PEG was induced by the addition of αCD, which was selectively threaded by PEG chains, leading to nanoparticles in dilute solution or hydrogel at a higher concentration. The moduli of the obtained hydrogel were three magnitudes higher than those of the control sample without ConA, showing the dramatic cross-linking effect of ConA achieved by its rather weak interaction with α-D-mannopyranoside.

- Cucurbit[7]uril as a "protective agent": controlling photochemistry and detecting 1-adamantanamine
  Yang, H.; Liu, Y.; Yang, L.; Liu, K.; Wang, Z.; Zhang, X. *Chem. Commun.* **2013**, *49*, 3905-3907.
  Abstract:



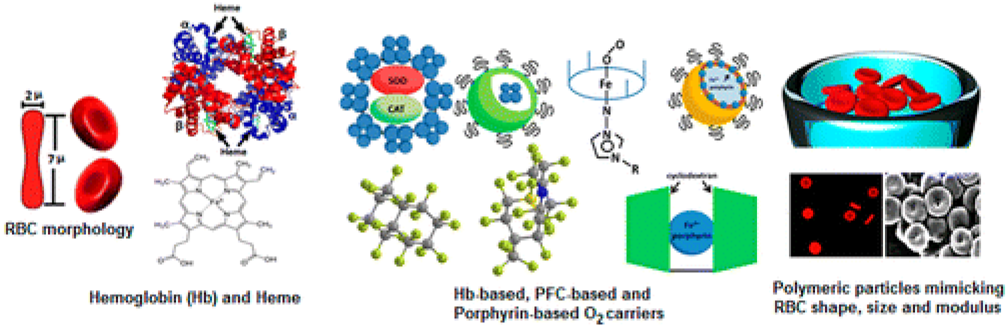
Cucurbit[7]uril (CB[7]) as a "protective agent" can effectively inhibit the [4+4] photochemical reaction of 1,1′-(butane-1,4-diyl)bis(2-aminopyridine)bromide (DPAD) by host–guest interaction between CB[7] and DPAD. In addition, the host–guest complex DPAD–CB[7] as a supramolecular sensor can detect the concentration of 1-adamantanamine with good sensitivity and selectivity because of the guest competitive complexation.

- Assembly-driven synthesis of hybrid molecular capsules controlled by chiral sorting
  Wierzbicki, M.; Szumna, A. *Chem. Commun*. **2013**, *49*, 3860-3862.
  Abstract:



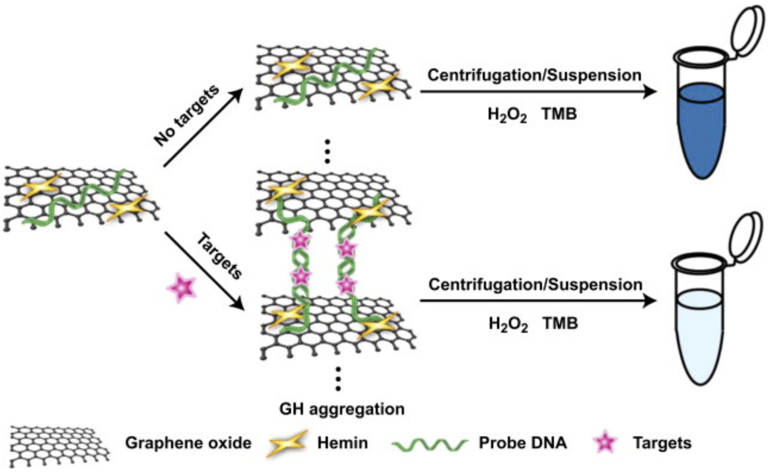
Chiral capsules with polar interiors (reversed capsules) undergo heterochiral sorting and exhibit positive mutalism – both hemispheres mutually benefit from the association. This feature can be coupled with partial reversibility of the formation reaction and utilized to amplify synthesis of hybrid capsules made of hemispheres that cannot be formed independently.

- Synthetic Approaches to RBC Mimicry and Oxygen Carrier Systems
  Modery-Pawlowski, C. L.; Tian, L. L.; Pan, V.; Sen Gupta, A. *Biomacromolecules* **2013**, *14*, 939-948.
  <u>Abstract:</u>



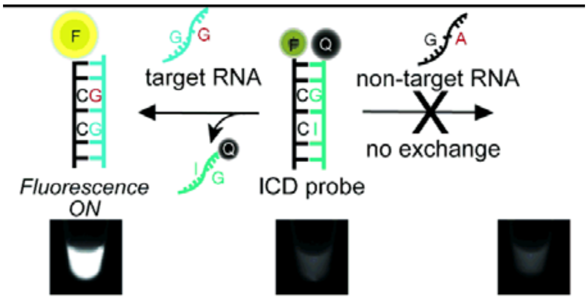
Whole blood or red blood cell (RBC) transfusions are highly significant, clinically, for blood replacement therapies in traumatic injuries, presurgical conditions, and anemias. However, natural RBC-based products suffer from limited shelf life due to pathological contamination and also present risks of refractoriness, graft-versus-host disease, immunosuppression, and acute lung injury. These issues can be only partially resolved by pathogen reduction technologies, serological blood testing, leukoreduction, and specialized storage; hence, they severely affect the efficacy and safety of the blood products. Consequently, there is a significant interest in synthetic RBC analogues that can mimic its oxygen-transport properties while allowing convenient manufacture, reproducibility, long shelf life, and reduced biological risks. To this end, the current Review provides a comprehensive description and discussion of the various research approaches and current state-of-the-art in synthetically mimicking RBC's oxygen-carrying biochemical properties, as well as the biophysical parameters (shape, size and mechanical modulus) that influence RBCs' hemodynamic transport properties in blood flow.

- Self-assembled, functionalized graphene and DNA as a universal platform for colorimetric assays
  Tao, Y.; Lin, Y.; Ren, J.; Qu, X. *Biomaterials* **2013**, *34*, 4810–4817.
  <u>Abstract:</u>



We have demonstrated a robust sensing strategy by employing single-stranded probe DNA and the hemin-graphene hybrid (GH) to detect a broad range of targets including metal ions, DNA and small molecules. This nearly “universal” biosensor approach is based on the DNA-mediated assembly of the hemin-graphene composite upon addition of the targets. Afterwards, GH aggregate resulting from DNA hybridization will occur. The DNA-GH hybrids will settle on the bottom of the vial after centrifugation, leaving behind a transparent supernatant. After incubation with TMB and H_2O_2, the colorimetric signal of the centrifugal supernatant will be significantly lower compared to that in the absence of targets. Therefore, mediation of the assembly of DNA on GH by targets can yield a facile means with tunable optical properties in response to concentration changes of the targets. This colorimetric “readout” offers great advantages such as the simple operation process, low-cost portable instrument and easy-to-use applications. Therefore, we believe that this method promises a great potential of becoming a routine tool for quantitative detection of a wide spectrum of analytes for specific applications in biodiagnostics, nanoelectronics, and bionanotechnology.

- A Peptide Nucleic Acid (PNA) Heteroduplex Probe Containing an Inosine–Cytosine Base Pair Discriminates a Single-Nucleotide Difference in RNA
  Matsumoto, K.; Nakata, E.; Tamura, T.; Saito, I.; Aizawa, Y.; Morii, T. *Chem. Eur. J.* **2013**, *19*, 5034–5040.
  Abstract:

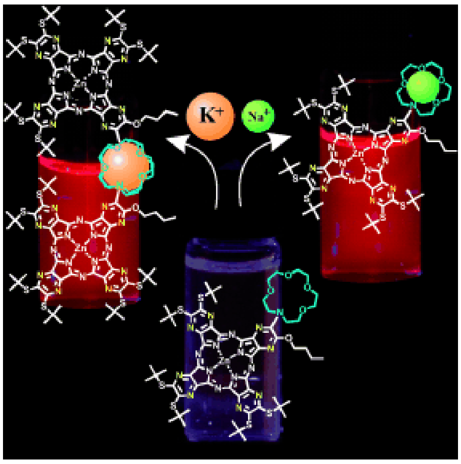


Selective discrimination of a single-nucleotide difference in single-stranded DNA or RNA remains a challenge with conventional DNA or RNA probes. A peptide nucleic acid (PNA)-derived probe, in which PNA forms a pseudocomplementary heteroduplex with inosine-containing DNA or RNA, effectively discriminates a single-nucleotide difference in a closely related group of sequences of single-stranded DNA and/or RNA. The pseudocomplementary PNA heteroduplex is easily converted to a fluorescent probe that distinctively detects a member of highly homologous let-7 microRNAs.

- Azaphthalocyanines: Red Fluorescent Probes for Cations

  Novakova, V.; Lochman, L.; Zajícová, I.; Kopecky, K.; Miletin, M.; Lang, K.; Kirakci, K.; Zimcik, P. *Chem. Eur. J.* **2013**, *19*, 5025–5028.

  Abstract:

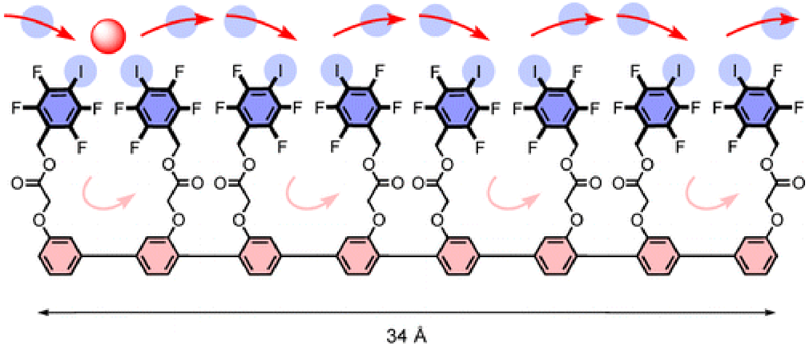


Light up a red crown: Chelation of sodium and potassium cations by aza[15]crown-5 switches on strong red fluorescence in azaphthalocyanines. This is due to an inhibition of ultrafast intramolecular charge transfer by coordination of the cations to the donor center. Sodium cations fit well into a cavity of the recognition moiety, while potassium forms supramolecular assemblies of azaphthalocyanines with 1:2 stoichiometry.

- Transmembrane Halogen-Bonding Cascades

  Vargas Jentzsch, A.; Matile,S. *J. Am. Chem. Soc.* **2013**, *135,* 5302–5303.

  Abstract:

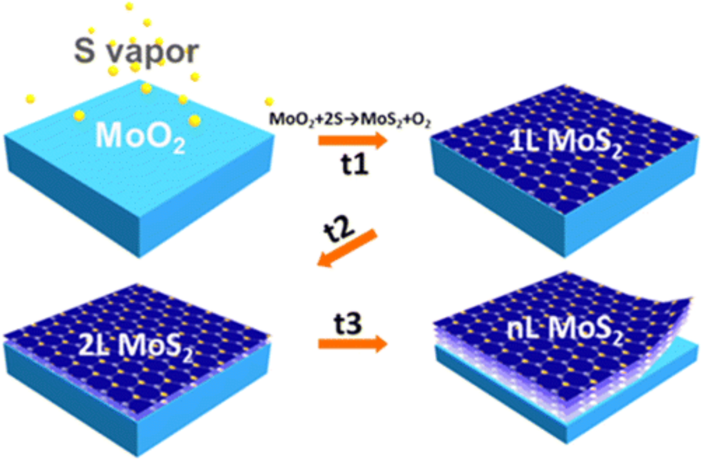


Halogen bonds have recently been introduced as ideal to transport anions across lipid bilayer membranes. However, activities obtained with small transporters were not impressive, and cyclic arrays of strong halogen-bond donors above a calix[4]arene scaffold gave even weaker activities. Here, we report that their linear alignment for anion hopping along transmembrane rigid-rod scaffolds gives excellent activities with an unprecedented cooperativity coefficient m = 3.37.

- Controlled Synthesis of Highly Crystalline

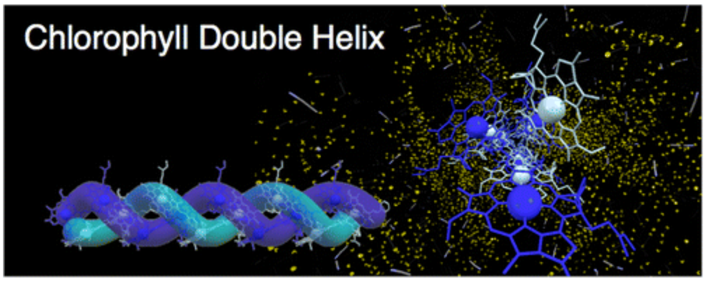
  Wang, X.; Feng, H.; Wu, Y.; Jiao, L. *J. Am. Chem. Soc.* **2013**, *135*, 5304–5307.

  Abstract:



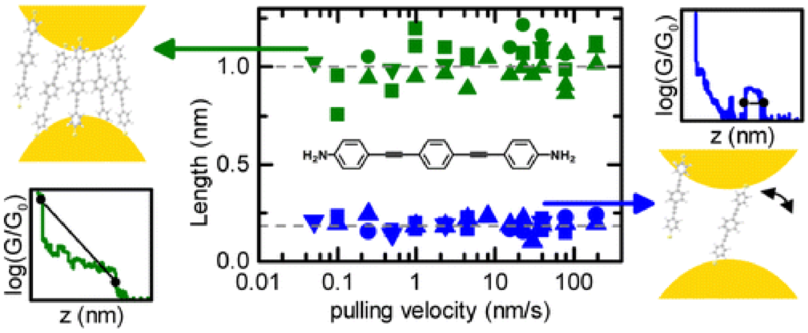
The controlled synthesis of highly crystalline MoS_2 atomic layers remains a challenge for the practical applications of this emerging material. Here, we developed an approach for synthesizing MoS_2 flakes in rhomboid shape with controlled number of layers by the layer-by-layer sulfurization of MoO_2 microcrystals. The obtained MoS_2 flakes showed high crystallinity with crystal domain size of ~10 µm, significantly larger than the grain size of MoS_2 grown by other methods. As a result of the high crystallinity, the performance of back-gated field effect transistors (FETs) made on these MoS_2 flakes was comparable to that of FETs based on mechanically exfoliated flakes. This simple approach opens up a new avenue for controlled synthesis of MoS_2 atomic layers and will make this highly crystalline material easily accessible for fundamental aspects and various applications.

- Double Helices of a Pyridine-Appended Zinc Chlorophyll Derivative
  Shinozaki, Y.; Richards, G.; Ogawa, K.; Yamano, A.; Ohara, K.; Yamaguchi, K.; Kawano, S.; Tanaka, K.; Araki, Y.; Wada, T. ; Otsuki, J. *J. Am. Chem. Soc.* **2013***, 135*, 5262–5265.
  Abstract:



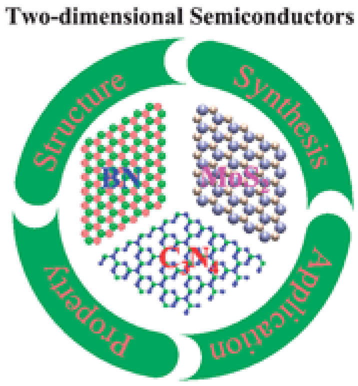
Self-assembled structures formed from a pyridine-appended zinc chlorophyll derivative are reported. While the zinc complex forms cyclic oligomers in chloroform solution, as indicated by 1H NMR studies (including diffusion-ordered spectroscopy), vapor pressure osmometry, and cold-spray ionization mass spectrometry, it forms double-stranded helical coordination polymers in the solid state, as revealed by single-crystal X-ray analysis.

- Stability of Single- and Few-Molecule Junctions of Conjugated Diamines
  González, M. T.; Díaz, A.; Leary, E.; García, R.; Herranz, M. Á.; Rubio-Bollinger, G.; Martín, N.; Agraït, N. *J. Am. Chem. Soc.* **2013***, 135,* 5420–5426.
  Abstract:



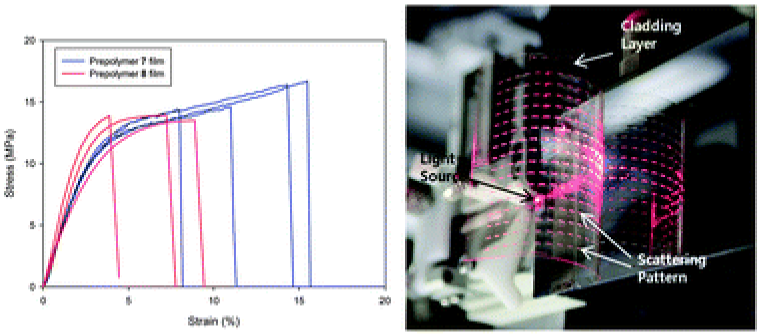
We study the stability of molecular junctions based on an oligo(phenylenethynylene) (OPE) diamine using a scanning tunneling microscope at room temperature. In our analysis, we were able to differentiate between junctions most probably formed by either one or several molecules. Varying the stretching rate of the junctions between 0.1 and 100 nm/s, we observe practically no variation of the length over which both kinds of junction can be stretched before rupture. This is in contrast with previously reported results for similar compounds. Our results suggest that, over the studied speed range, the junction breakage is caused purely by the growth of the gap between the gold electrodes and the elastic limit of the amine–gold bond. On the other hand, without stretching, junctions would survive for periods of time longer than our maximum measurement time (at least 10 s for multiple-molecule junctions) and can be considered, hence, very stable.

- Two-dimensional semiconductors: recent progress and future perspectives
  Song, X.; Hu, J.; Zeng, H. *J. Mater. Chem. C* **2013**, *1*, 2952-2969.
  Abstract:



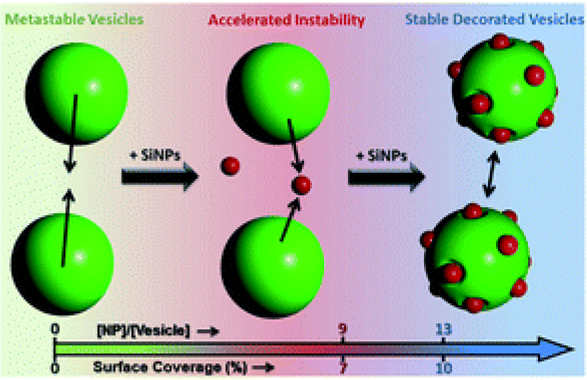
Graphene with a sp^2-honeycomb carbon lattice has drawn a large amount of attention due to its excellent properties and potential applications in many fields. Similar to the structure of graphene, two-dimensional semiconductors are its two-dimensional and isostructural counterparts based on the typical layer-structured semiconductors, such as boron nitride (h-BN) and transition metal dichalcogenides (*e.g.* MoS_2 and WS_2), whose layers are bound by weak van der Waals forces. Unlike the semi-metal features of graphene, the two-dimensional semiconductors are natural semiconductors with thicknesses on the atomic scale. When one of the dimensions is extremely reduced, the two-dimensional semiconductors exhibit some unique properties, such as a transition from indirect to direct semiconductor properties, and hence have great potential for applications in electronics, energy storage, sensors, catalysis and composites, which arise both from the dimension-reduced effect and from the modified electronic structure. In this feature article, recent developments in the synthesis, properties and applications of two-dimensional semiconductors are discussed. The reported virtues and novelties of two-dimensional semiconductors are highlighted and the current problems in their developing process are clarified, in addition to their challenges and future prospects.

- Photocrosslinkable liquid prepolymers for flexible waveguide display applications
  Park, S. K.; Ju, J. J.; Ki, J. T.; Kim, M.-S.; Moon, J.; Lee, J.-I.; Chu, H. Y.; Kim, D. W.; Kyung, K.-U.; Park, S. *J. Mater. Chem. C* **2013**, *1*, 2983-2989.
  Abstract:



We have prepared and evaluated two liquid prepolymers and their UV-cured films for flexible display applications. 2,3,5,6,2′,3′,5′,6′-Octafluoro-4,4′-bis-[2-(2-{2-[2-(2,3,5,6-tetrafluoro-4-vinyl-phenoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-biphenyl (**7**) and 2,3,5,6,2′,3′,5′,6′-octafluoro-4,4′-bis-[2-(2-{2-[1,1-difluoro-2-(2,3,5,6-tetrafluoro-4-vinyl-phenoxy)-ethoxy]-1,1,2,2-tetrafluoro-ethoxy}-1,1,2,2-tetrafluoro-ethoxy)-2,2-difluoro-ethoxy]-biphenyl (**8**) are synthesized with decafluorobiphenyl, 2,3,4,5,6-pentafluorostyrene, and tetraethylene glycol or fluorinated tetraethylene glycol. The UV-cured films prepared from these prepolymers show mechanical flexibility and optical transparency. The refractive indices and optical losses of the films prepared from prepolymers **7** and **8** are around 1.51 and 1.43, and 1.03 and 1.06 dB cm^{-1} at a wavelength of 633 nm. The films are thermostable at high temperature over 350 °C. The ultimate stress, initial modulus, and elongation of the films prepared from prepolymers **7** and **8** are 15.5 MPa, 0.42 GPa, and 12.2%, and 13.8 MPa, 0.49 GPa, and 6.8%, respectively. Finally, we have demonstrated a flexible waveguide display film fabricated from our prepolymers and identified the liquid prepolymers as possible good candidate materials for flexible display applications.

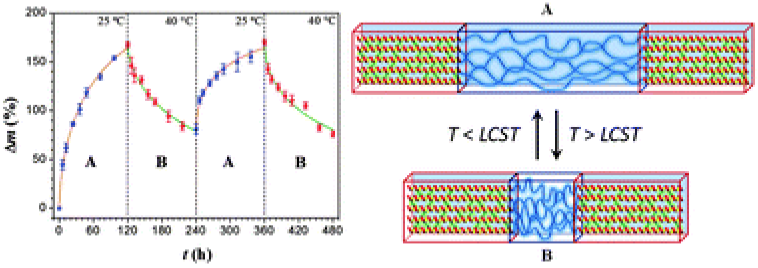
- Control of the stability and structure of liposomes by means of nanoparticles
  Michel, R.; Plostica, T.; Abezgauz, L.; Danino, D.; Gradzielski, M. *Soft Matter* **2013**, *9*, 4167-4177.
  Abstract:



The interaction of bilayer vesicles with hard nanoparticles is of great relevance to the field of nanotechnology, *e.g.*, its impact on health and safety matters, and also as vesicles are important as

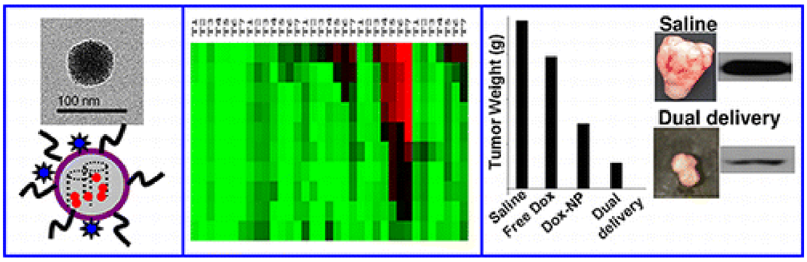
delivery vehicles. In this work we describe hybrid systems composed of zwitterionic phospholipid vesicles (DPPC), which are below the phase transition temperature, and added silica nanoparticles (SiNPs) of much smaller size. The initial DPPC unilamellar vesicles, obtained by extrusion, are rather unstable and age but the rate of ageing can be controlled over a large time range by the amount of added SiNPs. For low addition they become destabilized whereas larger amounts of SiNPs enhance the stability largely as confirmed by dynamic light scattering (DLS). ζ-Potential and DSC measurements confirm the binding of the SiNPs onto the phospholipid vesicles, which stabilizes the vesicles against flocculation by rendering the ζ-potential more negative. This effect appears above a specific SiNP concentration, and is the result of the adsorption of the negatively charged nanoparticles onto the outer surface of the liposome leading to decorated vesicles as proven by cryogenic transmission electron microscopy (cryo-TEM). Small amounts of surface-adsorbed SiNPs initially lead to a bridging of vesicles thereby enhancing flocculation, while higher amounts render the vesicles much more negatively charged and thereby long-time stable. This stability has an optimum at neutral pH and for low ionic strength. Thus we show that the addition of the SiNPs is a versatile way to control the stability of gel-state phospholipid vesicles and also to modulate their surface structure in a systematic fashion. This is not only of importance for understanding the fundamental interaction between SiNPs and bilayer vesicles, but also with respect to using silica particles as formulation aids for phospholipid dispersions.

- Thermo-responsive peptide-based triblock copolymer hydrogels
  Sanchez-Ferrer, A.; Kotharangannagari, V. K.; Ruokolainen, J.; Mezzenga, R. *Soft Matter* **2013**, *9*, 4304-4311.
  Abstract:



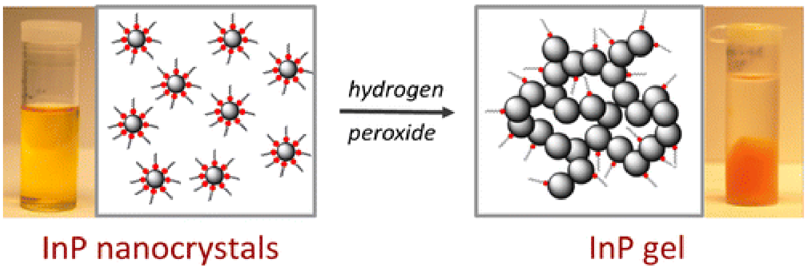
A series of novel thermo-responsive peptide-based triblock copolymers, poly(L-glutamic acid)-*b*-poly(*N*-isopropylacrylamide)-*b*-poly(L-glutamic acid) (PLGA-*b*-PNIPAM-*b*-PLGA), were successfully synthesized *via* ring opening polymerization (ROP) of the γ-benzyl L-glutamate derivative (BLG-NCA) using a diamino-terminated PNIPAM as a macroinitiator, followed by de-protection of the benzyl groups. These triblock copolymers form physically crosslinked networks after complexation with a diamino-terminated poly(ethylene oxide) (PEO) in an organic solvent through acid–base proton transfer and successive ionic-bonding confirmed by Fourier transform infrared (FTIR) spectroscopy. The secondary structure of the peptide block, before and after complexation, was confirmed by circular dichroism (CD) experiments, showing an α-helix conformation of the PLGA segments. Swelling experiments on the ionic-bonded networks showed that the water uptake process strongly depends on the temperature and relative humidity conditions. Thus, higher humidity and temperatures below the lower critical solubility temperature (LCST) of the PNIPAM block increase the amount of water absorbed into the network. These swollen ionic complexes contract and reject water when these thermo-responsive peptide-based hydrogels are heated up above their LCST, making them promising for biomedical applications and drug delivery systems.

- Codelivery of an Optimal Drug/siRNA Combination Using Mesoporous Silica Nanoparticles To Overcome Drug Resistance in Breast Cancer in Vitro and in Vivo
  Meng, H.; Mai, W. X.; Zhang, H.; Xue, M.; Xia, T.; Lin, S.; Wang, X.; Zhao, Y.; Ji, Z.; Zink, J. I.; Nel, A. E. *ACS Nano* **2013**, *7*, 994-1005.
  Abstract:



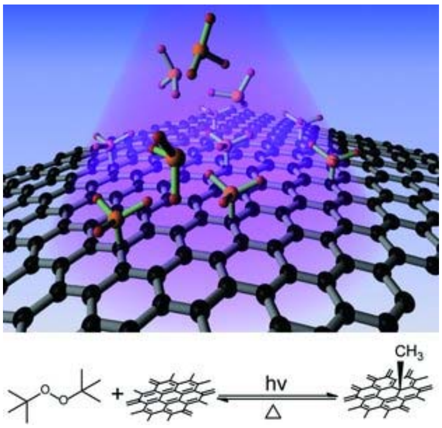
We used a multifunctional mesoporous silica nanoparticle (MSNP) carrier to overcome doxorubicin (Dox) resistance in a multidrug resistant (MDR) human breast cancer xenograft by codelivering Dox and siRNA that targets the P-glycoprotein (Pgp) drug exporter. The Pgp siRNA selection from among a series of drug resistance targets was achieved by performing high throughput screening in a MDR breast cancer cell line, MCF-7/MDR. Following the establishment of a MCF-7/MDR xenograft model in nude mice, we demonstrated that a 50 nm MSNP, functionalized by a polyethyleneimine–polyethylene glycol (PEI-PEG) copolymer, provides protected delivery of stably bound Dox and Pgp siRNA to the tumor site. The effective biodistribution and reduced reticuloendothelial uptake, as a result of our nanocarrier design, allowed us to achieve an 8% enhanced permeability and retention effect at the tumor site. Compared to free Dox or the carrier loaded with either drug or siRNA alone, the dual delivery system resulted in synergistic inhibition of tumor growth in vivo. Analysis of multiple xenograft biopsies demonstrated significant Pgp knockdown at heterogeneous tumor sites that correspond to the regions where Dox was released intracellularly and induced apoptosis. We emphasize that the heterogeneity originates in the tumor microenvironment, which influences the vascular access, rather than heterogeneous Pgp expression in the MDR cells. Taken together, these data provide proof-of-principle testing of the use of a dual drug/siRNA nanocarrier to overcome Dox resistance in a xenograft. The study also provides the first detailed analysis of the impact of heterogeneity in the tumor microenvironment on the efficacy of siRNA delivery in vivo.

- Assembly of Phosphide Nanocrystals into Porous Networks: Formation of InP Gels and Aerogels
  Hitihami-Mudiyanselage, A.; Senevirathne, K.; Brock, S. L. *ACS Nano* **2013**, *7*, 1163-1170.
  Abstract:



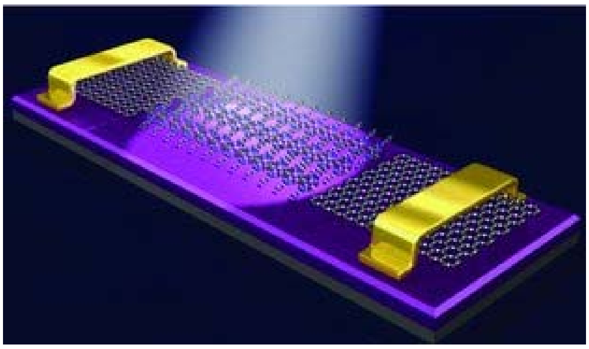
The applicability of sol–gel nanoparticle assembly routes, previously employed for metal chalcogenides, to phosphides is reported for the case of InP. Two different sizes (3.5 and 6.0 nm) of InP nanoparticles were synthesized by solution-phase arrested precipitation, capped with thiolate ligands, and oxidized with H_2O_2 or O_2/light to induce gel formation. The gels were aged, solvent-exchanged, and then supercritically dried to obtain aerogels with both meso- (2–50 nm) and macropores (>50 nm) and accessible surface areas of 200 m2/g. Aerogels showed higher band gap values relative to precursor nanoparticles, suggesting that during the process of assembling nanoparticles into 3D architectures, particle size reduction may have taken place. In contrast to metal chalcogenide gelation, InP gels did not form using tetranitromethane, a non-oxygen-transferring oxidant. The requirement of an oxygen-transferring oxidant, combined with X-ray photoelectron spectroscopy data showing oxidized phosphorus, suggests gelation is occurring due to condensation of phosphorus oxoanionic moieties generated at the interfaces. The ability to link discrete InP nanoparticles into a 3D porous network while maintaining quantum confinement is expected to facilitate exploitation of nanostructured InP in solid-state devices.

- Photoinduced Methylation of Graphene
  Liao, L.; Song, Z.; Zhou, Y.; Wang, H.; Xie, Q.; Peng, H. ; Liu, Z. *Small* **2013**, *9*, 1348–1352.
  Abstract:



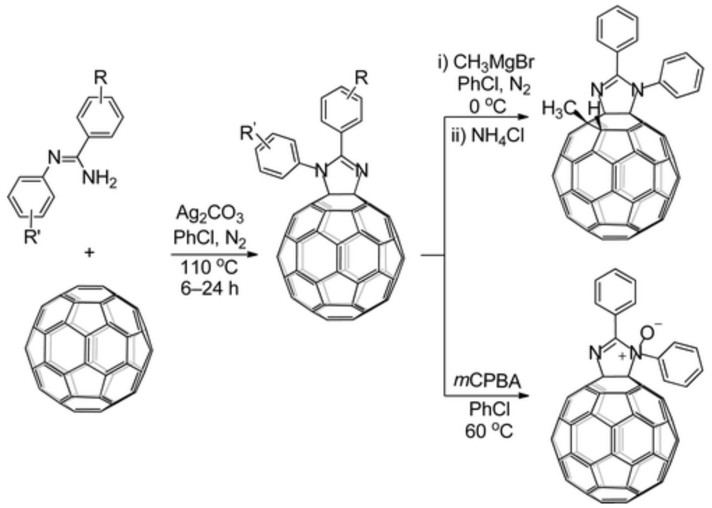
Covalent grafting of methyl groups onto the basal plane of graphene is achieved through a photochemical reaction between graphene and di-tert-butyl peroxide. The methylation of graphene is found to be reversible. The edge of single-layer graphene shows the largest methylation reactivity, which provides a route to tailor the edge state of graphene.

- Unique Role of Self-Assembled Monolayers in Carbon Nanomaterial-Based Field-Effect Transistors
  Chen, H.; Guo, X. *Small* **2013**, *9*, 1144–1159.
  Abstract:



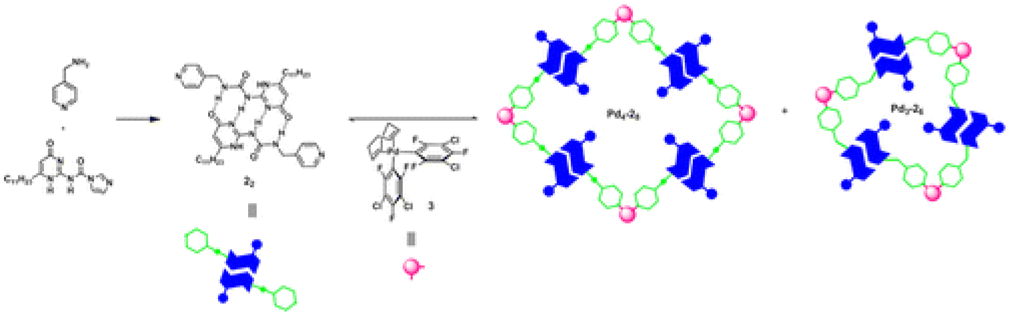
Molecular self-assembly is a promising technology for creating reliable functional films in optoelectronic devices with full control of thickness and even spatial resolution. In particular, rationally designed self-assembled monolayers (SAMs) play an important role in modifying the electrode/semiconductor and semiconductor/dielectric interfaces in field-effect transistors. Carbon nanomaterials, especially single-walled carbon nanotubes and graphene, have attracted intense interest in recent years due to their remarkable physicochemical properties. The combination of the advantages of both SAMs and carbon nanomaterials has been opening up a thriving research field. In this Review article, the unique role of SAMs acting as either active or auxiliary layers in carbon nanomaterials-based field-effect transistors is highlighted for tuning the substrate effect, controlling the carrier type and density in the conducting channel, and even installing new functionalities. The combination of molecular self-assembly and molecular engineering with materials fabrication could incorporate diverse molecular functionalities into electrical nanocircuits, thus speeding the development of nanometer/molecular electronics in the future.

- Synthesis and Functionalization of [60]Fullerene-Fused Imidazolines
  He, C.-L.; Liu, R.; Li, D.-D. Zhu; S. E.; Wang, G.-W. *Org. Lett.* **2013***, 15*, 1532-1535.
  <u>Abstract:</u>



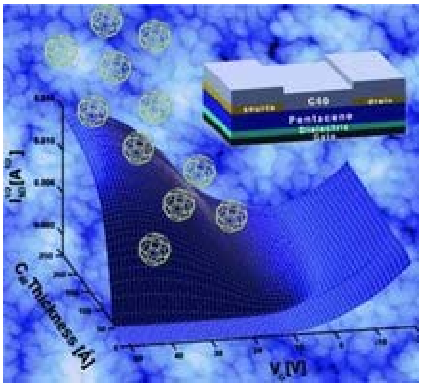
The silver carbonate promoted reaction of [60]fullerene with (Z)-N-arylbenzamidines afforded the unprecedented C60-fused imidazoline derivatives in high yields. Substrates with both electron-donating and -withdrawing groups on aromatic rings could be employed. In addition, the electrochemistry and further selective functionalization of the obtained C60-fused imidazolines were investigated.

- Self-Assembled Squares and Triangles by Simultaneous Hydrogen Bonding and Metal Coordination
  Marshall, L.-J.; de Mendoza, J. *Chem. Asian J.* **2013***, 8*, 1548-1555.
  <u>Abstract:</u>



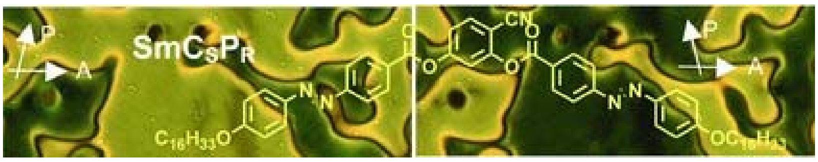
Through the combination of hydrogen bonding and metal-templated self-assembly, molecular squares and molecular triangles are observed in chloroform solution upon the complexation of hydrogen-bonded dimers of para-pyridyl-substituted 2-ureido-4-[1H]-pyrimidinone (UPy) and an appropriate cis-substituted palladium complex. Molecular modeling studies and NMR analysis confirmed the presence of two distinct structures in solution: the tubular structure of the molecular square and propeller-bowl structure of the molecular triangle.

- Dual Channel Operation Upon n-Channel Percolation in a Pentacene-C_{60} Ambipolar Organic Thin Film Transistor
  Noever, S. J.; Fischer, S.; Nickel, B. *Adv. Mater.* **2013**, *25*, 2147–2151.
  Abstract:



Thickness resolved measurements of ambipolar thin-film transistor characteristics track the charging of an organic–organic heterojunction. Combined with structural investigation methods such as AFM and GIXS, this leads to a better understanding of the physics in state of the art devices such as organic solar cells, organic light emitting diodes and light emitting TFTs.

- A Liquid Crystalline Phase with Uniform Tilt, Local Polar Order and Capability of Symmetry Breaking
  Alaasar, M.; Prehm, M.; Nagaraj, M.; Vij, J. K.; Tschierske, C. *Adv. Mater.* **2013**, *25*, 2186–2191.
  Abstract:



A new liquid crystalline (LC) phase with uniform tilt, local polar order and capability of symmetry breaking is found for a bent-core mesogen combining a 4-cyanoresorcinol unit with two azobenzene wings. The combination of local polar order and long range synclinic tilt in this SmC_sP_R phase leads, under special conditions, to macroscopic domains with opposite chirality, though the molecules themselves are achiral.