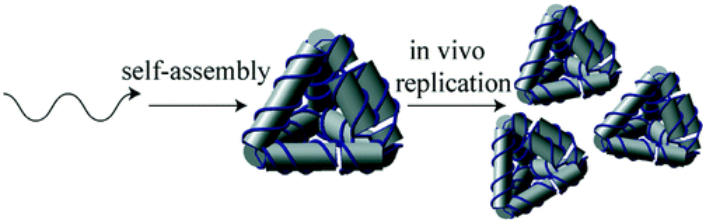
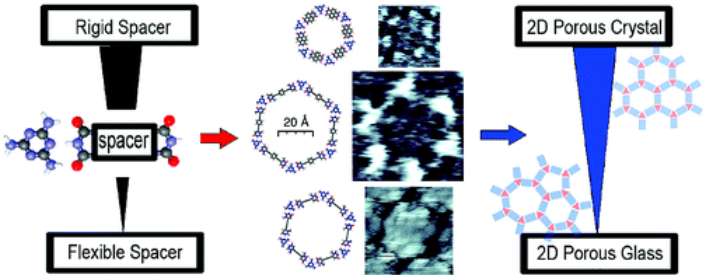
- A Replicable Tetrahedral Nanostructure Self-Assembled from a Single DNA Strand
  Li, Z. Wei, B.; Nangreave, J.; Lin, C.; Liu, Y.; Mi, Y.; Yan, H. *J. Am. Chem. Soc.* **2009**, *131*, 13093–13098.
  Abstract:



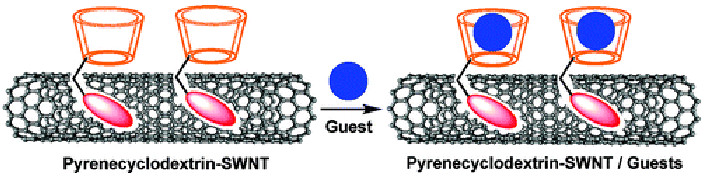
We report the design and construction of a nanometer-sized tetrahedron from a single strand of DNA that is 286 nucleotides long. The formation of the tetrahedron was verified by restriction enzyme digestion, Ferguson analysis, and atomic force microscopy (AFM) imaging. We further demonstrate that synthesis of the tetrahedron can be easily scaled up through in vivo replication using standard molecular cloning techniques. We found that the in vivo replication efficiency of the tetrahedron is significantly higher in comparison to in vitro replication using rolling-circle amplification (RCA). Our results suggest that it is now possible to design and replicate increasingly complex, single-stranded DNA nanostructures in vivo.

- Tailoring Bicomponent Supramolecular Nanoporous Networks: Phase Segregation, Polymorphism, and Glasses at the Solid−Liquid Interface
  Palma, C. A.; Bjork, J.; Bonini, M.; Dyer, M. S.; Llanes-Pallas, A.; Bonifazi, D.; Persson, M.; Samori, P. *J. Am. Chem. Soc.* **2009**, *131*, 13093–13098.
  Abstract:



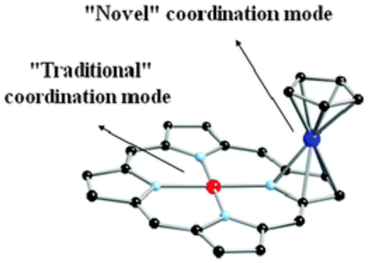
We study the formation of four supramolecular bicomponent networks based on four linear modules (linkers) bridging melamine via triple hydrogen-bonds. We explore at the nanoscale level the phenomena of polymorphism and phase segregation which rule the generation of highly crystalline nanoporous patterns self-assembled at the solid−liquid interface. The investigated linkers include two systems exposing diuracil groups in the α and ω position, naphthalene tetracarboxylic diimide and pyromellitic diimide. In situ scanning tunneling microscopy (STM) investigations revealed that, when blended with melamine, out of the four systems, three are able to form two-dimensional (2D) porous architectures, two of which exhibit highly ordered hexagonal structures, while pyromellitic diimide assembles only into one-dimensional (1D) supramolecular arrays. These bicomponent self-assembled monolayers are used as a test bed to gain detailed insight into phase segregation and polymorphism in 2D supramolecular systems by exploring the contribution of hydrogen-bond energy and periodicity, molecular flexibility, concentration and ratio of the components in solution as well as the effect of annealing via time-dependent and temperature-modulated experiments. These comparative studies, obtained through a joint experimental and computational analysis, offer new insights into strategies toward the bottom-up fabrication of highly ordered tunable nanopatterning at interfaces mediated by hydrogen bonds.

- Noncovalent Functionalization of Single-Walled Carbon Nanotubes
  Zhao, Y.-L.; Stoddart, J. F. *Acc. Chem. Res.* **2009**, *42*, 1161–1171.
  Abstract:



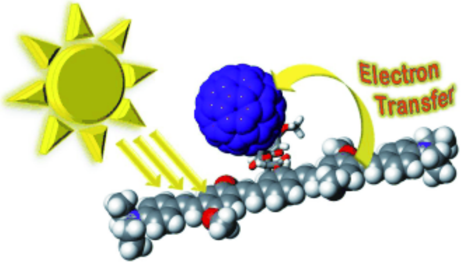
Single-walled carbon nanotubes (SWNTs) have attracted much attention on account of their potential to be transformed into new materials that can be employed to address a wide range of applications. The insolubility of the SWNTs in most solvents and the difficulties of handling these highly intractable carbon nanostructures, however, are restricting their real-life applications at the present time. To improve upon the properties of the SWNTs, low-cost and industrially feasible approaches to their modifications are constantly being sought by chemists and materials scientists. Together, they have shown that noncovalent functionalization of the SWNTs can do much to preserve the desired properties of the SWNTs while remarkably improving their solubilities. This Account describes recent advances in the design, synthesis, and characterization of SWNT hybrids and evaluates applications of these new hybrid materials based on noncovalently functionalized SWNTs. Their solubilization enables the characterization of these hybrids as well as the investigation of the properties of the SWNTs using solution-based techniques. Cognizant of the structural properties of the functional molecules on the SWNTs, we present some of the recent work carried out by ourselves and others under the umbrella of the following three subtopics: (i) aromatic small-molecule-based noncovalent functionalization, (ii) biomacromolecule-based noncovalent functionalization, and (iii) polymer-based noncovalent functionalization. Several examples for the applications of noncovalently functionalized SWNT hybrids in the fabrication of field-effect transistor (FET) devices, chemical sensors, molecular switch tunnel junctions (MSTJs), and photovoltaic devices are highlighted and discussed. The blossoming of new methods for the noncovalent functionalization of the SWNTs promises a new generation of SWNT hybrid-based integrated multifunctional sensors and devices, an outcome which is essential for the development of carbon nanotube chemistry that interfaces with physics, materials, biology, and medical science.

- π-Metal complexes of tetrapyrrolic systems. A novel coordination mode in "porphyrin-like" chemistry
  Cuesta, L.; Sessler, J. L. *Chem. Soc. Rev.* **2009**, *38*, 2716 – 2729.
  Abstract:



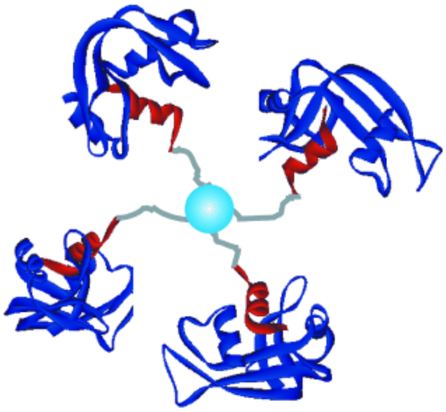
The coordination chemistry of porphyrins and related tetrapyrrolic ligands has traditionally centered around the ability of these systems to form pyrrole N-ligated complexes *via* the formation of σ bonds, either within the N_4 core or displaced above it. In fact, such σ-complexes are known with almost every metal cation in the periodic table. However, a growing number of π-complexes derived from tetrapyrrolic ligands have been reported in recent years. The underlying coordination mode, while still novel in the context of ‟porphyrin-like˝ chemistry, is already being recognized for the effects it can impart over the reactivity, as well as the spectroscopic, redox, electronic, and optical properties of various oligopyrrolic macrocycles. This *critical review* summarizes accomplishments made in this fast-emerging field (59 references).

- Fullerene Derivatives Functionalized with Diethylamino-Substituted Conjugated Oligomers: Synthesis and Photoinduced Electron Transfer
  Gégout, A.; Nierengarten, J.-F.; Delavaux-Nicot, B.; Duhayon, C.; Saquet, A.; Listorti, A.; Belbakra, A.; Chiorboli, C.; Armaroli, N. *Chem. Eur. J.* **2009**, *15*, 8825 – 8833.
  Abstract:



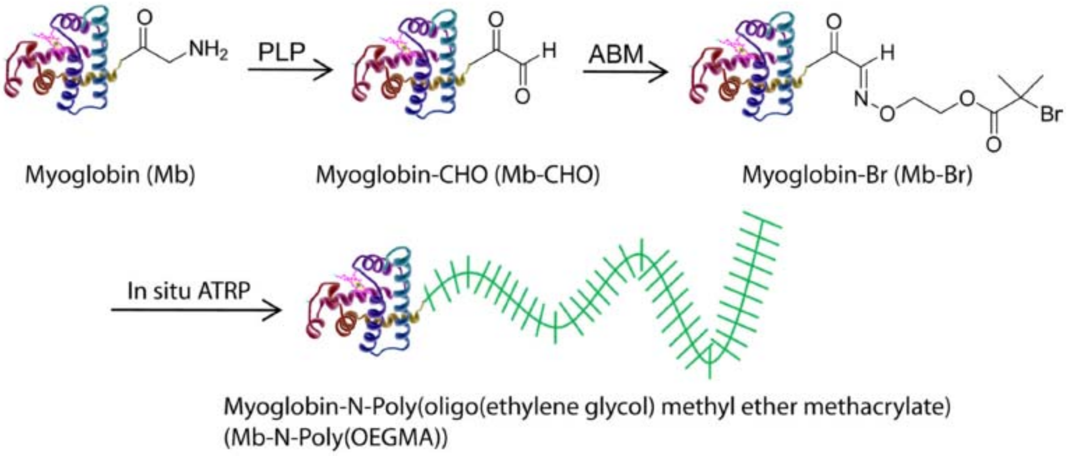
Diethylamino-substituted oligophenylenevinylene (OPV) building blocks have been prepared and used for the synthesis of two [60]fullerene-OPV dyads, **F-D1** and **F-D2**, which exhibit different conjugation length of the OPV fragments. The electrochemical properties of these acceptor-donor dyads have been studied by cyclic voltammetry. The first reduction is always assigned to the fullerene moiety and the first oxidation centered on the diethylaniline groups of the OPV rods, thus making these systems suitable candidates for photoinduced electron transfer. Both the OPV and the fullerene-centered fluorescence bands are quenched in toluene and benzonitrile, which suggests the occurrence of photoinduced electron transfer from the amino-substituted OPVs to the carbon sphere in the dyads in both solvents. By means of bimolecular quenching experiments, transient absorption spectral fingerprints of the radical cationic species are detected in the visible (670 nm) and near-IR (1300-1500 nm) regions, along with the much weaker fullerene anion band at λ_{max}=1030 nm. Definitive evidence for photoinduced electron transfer in **F-D1** and **F-D2** comes from transient absorption measurements. A charge-separated state is formed within 100 ps and decays in less than 5 ns.

- Noncovalent Synthesis of Protein Dendrimers
  Lempens, E. H. M.; van Baal, I.; van Dongen, J. L. J. ; Hackeng, T. M.; Merkx, M.; Meijer, E. W. *Chem. Eur. J.* **2009**, *15*, 8760 – 8767.
  Abstract :



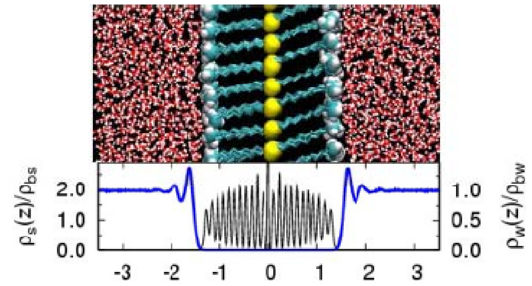
The covalent synthesis of complex biomolecular systems such as multivalent protein dendrimers often proceeds with low efficiency, thereby making alternative strategies based on noncovalent chemistry of high interest. Here, the synthesis of protein dendrimers using a strong but noncovalent interaction between a peptide and complementary protein is proposed as an efficient strategy to arrive at dendrimers fully functionalized with protein domains. The association of S-peptide to S-protein results in the formation of an active enzyme (ribonuclease S) and therefore serves as an ideal system to explore this synthetic approach. Native chemical ligation was used to couple four S-peptides by means of their C-terminal thioester to a cysteine-functionalized dendritic scaffold, thus yielding a tetravalent S-peptide wedge. A fully functional ribonuclease S tetramer was prepared by addition of four equivalents of S-protein. Biophysical techniques (isothermal titration calorimetry (ITC), surface plasmon resonance (SPR), and mass spectrometry) and an enzymatic activity assay were used to verify the formation of the multivalent complex. The noncovalent synthetic strategy presented here provides access to well-defined, dynamic, semisynthetic protein assemblies in high yield and is therefore of interest to the field of nanomedicine as well as biomaterials.

- In situ growth of a stoichiometric PEG-like conjugate at a protein's N-terminus with significantly improved pharmacokinetics
  Gao, W.; Liu, W.; Mackay, J. A.; Zalutsky, M. R.; Toone, E. J.; Chilkoti, A. *Proc. Nat. Acad. Sci.* **2009**, *106*, 15231–15236.
  Abstract:



The challenge in the synthesis of protein-polymer conjugates for biological applications is to synthesize a stoichiometric (typically 1:1) conjugate of the protein with a monodisperse polymer, with good retention of protein activity, significantly improved pharmacokinetics and increased bioavailability, and hence improved in vivo efficacy. Here we demonstrate, using myoglobin as an example, a general route to grow a PEG-like polymer, poly(oligo(ethylene glycol) methyl ether methacrylate) [poly(OEGMA)], with low polydispersity and high yield, solely from the N-terminus of the protein by in situ atom transfer radical polymerization (ATRP) under aqueous conditions, to yield a site-specific (N-terminal) and stoichiometric conjugate (1:1). Notably, the myoglobin-poly(OEGMA) conjugate [hydrodynamic radius (Rh): 13 nm] showed a 41-fold increase in its blood exposure compared to the protein (Rh: 1.7 nm) after IV administration to mice, thereby demonstrating that comb polymers that present short oligo-(ethylene glycol) side chains are a class of PEG-like polymers that can significantly improve the pharmacological properties of proteins. We believe that this approach to the synthesis of N-terminal protein conjugates of poly(OEGMA) may be applicable to a large subset of protein and peptide drugs, and thereby provide a general methodology for improvement of their pharmacological profiles.

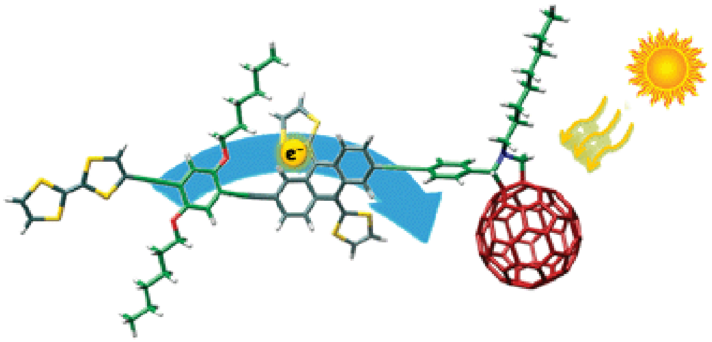
- Characterizing hydrophobicity of interfaces by using cavity formation, solute binding, and water correlations.
  Godawat, R.; Jamadagni, S. N.; Garde, S *Proc. Nat. Acad. Sci.* **2009**, *106*, 15119–15124.
  Abstract:



Hydrophobicity is often characterized macroscopically by the droplet contact angle. Molecular signatures of hydrophobicity have, however, remained elusive. Successful theories predict a drying transition leading to a vapor-like region near large hard-sphere solutes and interfaces. Adding attractions wets the interface with local density increasing with attractions. Here we present extensive molecular simulation studies of hydration of realistic surfaces with a wide range of chemistries from hydrophobic ($-CF_3$, $-CH_3$) to hydrophilic ($-OH$, $-CONH_2$). We show that the water density near weakly attractive hydrophobic surfaces (e.g., $-CF_3$) can be bulk-like or larger, and provides a poor quantification of surface hydrophobicity. In contrast, the probability of cavity formation or the free energy of binding of hydrophobic solutes to interfaces correlates quantitatively with the macroscopic wetting properties and serves as an excellent signature of hydrophobicity. Specifically, the probability of cavity formation is enhanced in the vicinity of hydrophobic surfaces, and water–water correlations correspondingly display characteristics similar to those near a vapor–liquid interface. Hydrophilic surfaces suppress cavity formation and reduce the water–water correlation length. Our results suggest a potentially robust approach for characterizing hydrophobicity of more complex and heterogeneous surfaces of proteins and biomolecules, and other nanoscopic objects.

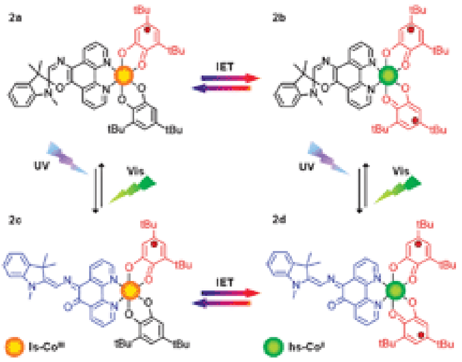
- Electron transfer through exTTF bridges in electron donor–acceptor conjugates.
  Illescas, B. M.; Santos, J.; Wielopolski, M.; Atienza, C. M.; Martín, N.; Guldi, D. M. *Chem. Commun.* **2009**, 5374 – 5376.

Abstract:



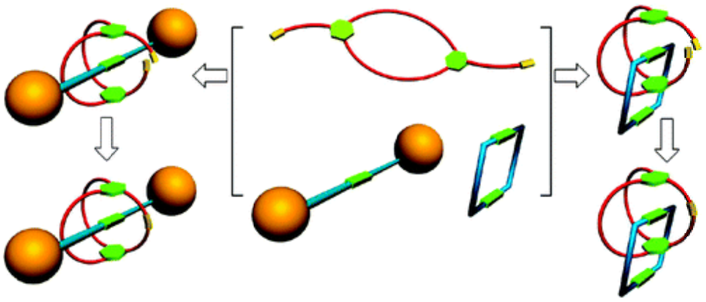
Rigid and soluble electron donor–acceptor conjugates combining exTTF and/or TTF as donors and C_{60} as acceptor have been synthesized; fluorescence and transient absorption measurements confirm the generation of charge-separated radical-ion pairs with lifetimes in the s timescale.

- Incorporating optical bistability into a magnetically bistable system: a photochromic redox isomeric complex.
  Paquette, M. M.; Kopelman, R. A.; Beitler, E.; Frank, N. L. *Chem. Commun.* **2009**, 5424 – 5426.
  Abstract:



A photochromic cobalt–bis(dioxolene)spirooxazine metal complex has been synthesized which exhibits both photochromic and redox-active behavior, providing a potentially powerful approach to the development of optically induced changes in redox, magnetic, or optical properties of a metal center.

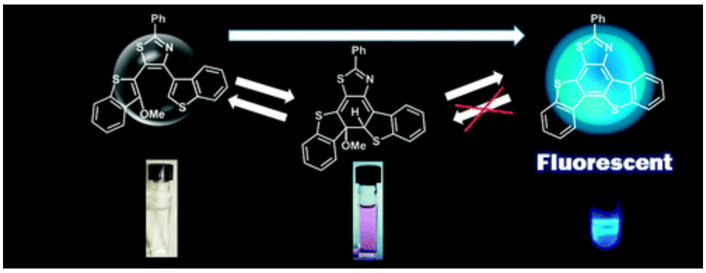
- Taco Complex Templated Syntheses of a Cryptand/Paraquat [2]Rotaxane and a [2]Catenane by Olefin Metathesis
  Li, S.; Liu, M.; Zheng, B.; Zhu, K.; Wang, F.; Li, N.; Zhao, X.-L.; Huang, F. *Org. Lett.* **2009**, *11*, 3350–3353.
  Abstract:



Taco complex templation based on the bis(*m*-phenylene)-32-crown-10/paraquat recognition motif is used to develop a general method for preparing mechanically interlocked molecules. A

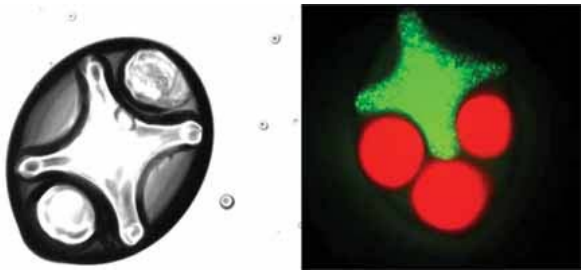
[2]rotaxane and a [2]catenane were synthesized in high yields by a ring-closing metathesis reaction, which was owed to the impactful template effect. Due to the high symmetry of (5,5′)-difunctional bis(*m*-phenylene)-32-crown-10 derivatives, this taco complex templated synthesis has potential to be a tempting method to solve a symmetry-based problem in the fabrication of complicated mechanically interlocked structures.

- Synthesis and Photochemical Reactions of Photochromic Terarylene Having a Leaving Methoxy Group
  Nakagawa, H.; Kawai, S.; Nakashima, T.; Kawai, T. *Org. Lett.* **2009**, *11*, 1475–1478.
  Abstract:



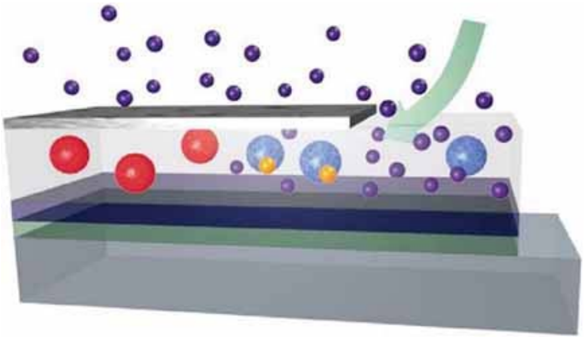
Photochromic terarylene having a methoxy group and hydrogen as the leaving units at the photochemical reaction center carbon atoms has been synthesized. This molecule shows irreversible photochemical reaction affording a highly fluorescent condensed aromatic molecule.

- Hydrogels in Regenerative Medicine
  Slaughter, B. V.; Khurshid, S. S.; Fisher, O. Z.; Khademhosseini, A.; Peppas, N. A. *Adv. Mater.* **2009,** 3307-3329.
  Abstract:



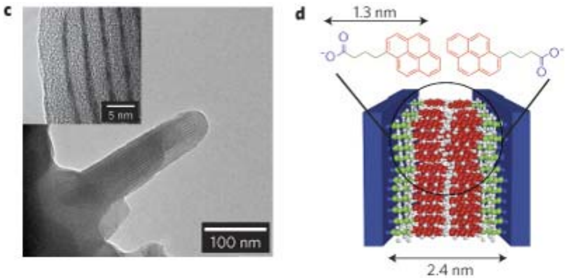
Applications of hydrogels in tissue engineering and regenerative medicine are reviewed. Physical properties of gels, synthesis methods from synthetic and natural monomers and macromers, and design considerations including vascularization and biocompatibility are specifically highlighted. Emerging techniques to microengineer hydrogels for increased tissue scaffold complexity are also discussed.

- SensLED: An Electro-Optical Active Probe for Oxygen Determination
  Sax, A.; Fisslthaler, E.; Kappaun, S.; Konrad, C.; Waich, K.; Mayr, T.; Slugovc, C.; Klimant, I.; List E. J. W. *Adv. Mater.* **2009,** 3483-3487.
  Abstract:



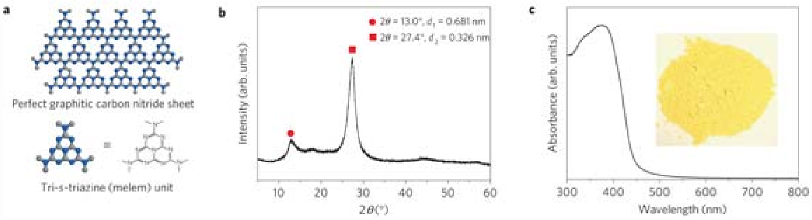
A novel concept for an electro-optical active gas probe capable of oxygen detection is presented. Based on a modified organic light-emitting device, we demonstrate that a reversible analyte-indicator interaction can be used for analyte determination.

- A synergistic assembly of nanoscale lamellar photoconductor hybrids
  Sofos, M.; Goldberger, J.; Stone, D. A.; Allen, J. E.; Ma, Q.; Herman, D. J.; Tsai, W.-W.; Lauhon, L. J.; Stupp, S. I. *Nature Materials* **2009**, *8*, 68-75.
  Abstract:



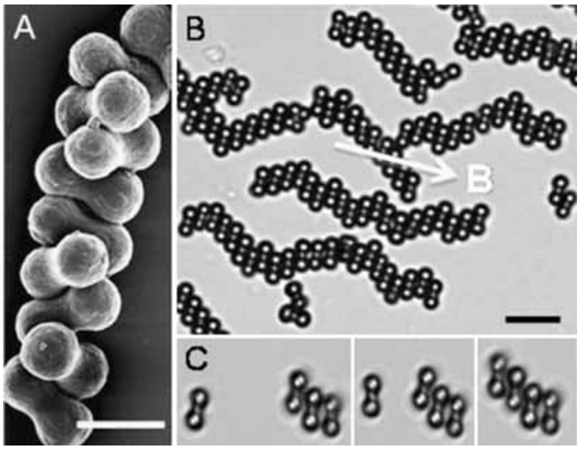
Highly ordered nanostructured organic/inorganic hybrids offer chemical tunability, novel functionalities and enhanced performance over their individual components. Hybrids of complementary p-type organic and n-type inorganic components have attracted interest in optoelectronics, where high-efficiency devices with minimal cost are desired. We demonstrate here self-assembly of a lamellar hybrid containing periodic and alternating 1-nm-thick sheets of polycrystalline ZnO separated by 2–3 nm layers of conjugated molecules, directly onto an electrode. Initially the electrodeposited inorganic is $Zn(OH)_2$, but π–π interactions among conjugated molecules stabilize synergistically the periodic nanostructure as it converts to ZnO at 150 °C. As photoconductors, normalized detectivities (D*) greater than 2times1010 Jones, photocurrent gains of 120 at 1.2 V μm^{-1} and dynamic ranges greater than 60 dB are observed on selective excitation of the organic. These are among the highest values measured for organic, hybrid and amorphous silicon, making them technologically competitive as low-power, wavelength-tunable, flexible and environmentally benign photoconductors.

- A metal-free polymeric photocatalyst for hydrogen production from water under visible light
  Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. *Nature Materials* **2009**, *8*, 76-80.
  Abstract:



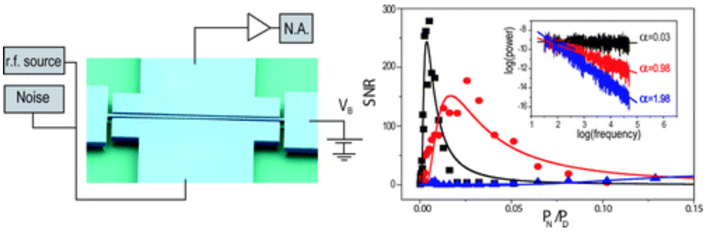
The production of hydrogen from water using a catalyst and solar energy is an ideal future energy source, independent of fossil reserves. For an economical use of water and solar energy, catalysts that are sufficiently efficient, stable, inexpensive and capable of harvesting light are required. Here, we show that an abundant material, polymeric carbon nitride, can produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor. Contrary to other conducting polymer semiconductors, carbon nitride is chemically and thermally stable and does not rely on complicated device manufacturing. The results represent an important first step towards photosynthesis in general where artificial conjugated polymer semiconductors can be used as energy transducers.

- Anisotropic Magnetic Colloids: A Strategy to Form Complex Structures Using Nonspherical Building Blocks
  Lee, S. H.; Liddell, C. M. *Small* **2009**, *5*, 1957 – 1962.
  Abstract:



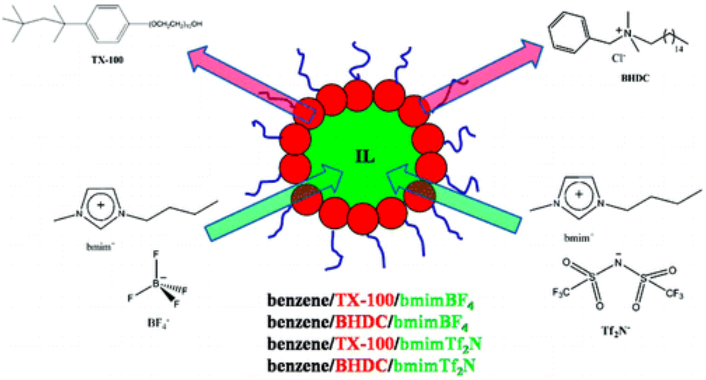
Hierarchical microstructure and magnetic anisotropy of peanut-shaped colloids promotes a permanent transverse magnetic dipole, leading to rich self-assembly behavior. Crisscross and planar zigzag chains (see image; scale bar = 2 µm in A and 5 µm in B), as well as a molecular crystal-type phase with oblique symmetry in 2D are observed.

- Signal Amplification by 1/*f* Noise in Silicon-Based Nanomechanical Resonators
  Guerra, D. N.; Dunn, T.; Mohanty, P. *Nano Lett.* **2009**, *9*, 3096–3099.
  Abstract:



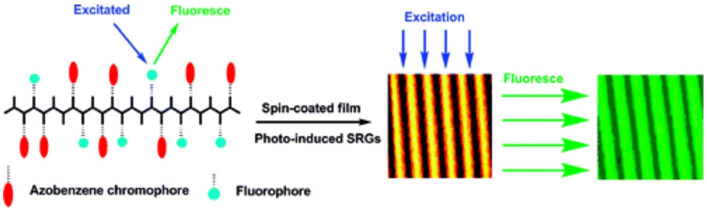
We report signal amplification by $1/f^{\alpha}$ noise with stochastic resonance in a nonlinear nanomechanical resonator. The addition of $1/f^{\alpha}$ noise to a subthreshold modulation signal enhances the probability of an electrostatically driven resonator switching between its two vibrational states in the hysteretic region. Considering the prevalence of $1/f$ noise in the materials in integrated circuits, signal enhancement demonstrated here, using a fully on-chip electronic actuation/detection scheme, suggests beneficial use of the otherwise detrimental noise.

- On the Formation of New Reverse Micelles: A Comparative Study of Benzene/Surfactants/Ionic Liquids Systems Using UV-Visible Absorption Spectroscopy and Dynamic Light Scattering
  Falcone, R. D.; Correa, N. M.; Silber, J. J. *Langmuir* **2009**, *25*, 10426–10429.
  Abstract:



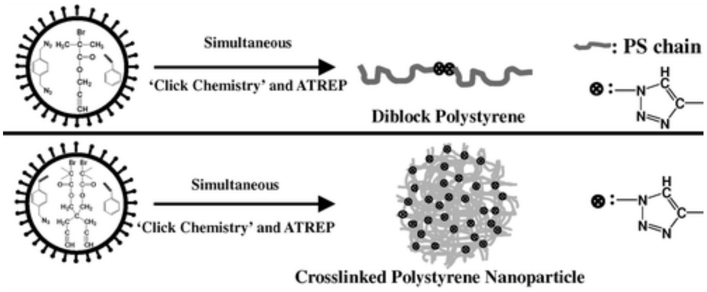
The microenvironment of the polar core generated in different ionic liquid reverse micelle (IL RM) systems were investigated using the solvatochromic behavior of 1-methyl-8-oxyquinolinium betaine (QB) as an absorption probe and dynamic light scattering (DLS) technique. The novel RM systems consist of two different ILs;1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF4) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmim- Tf2N);sequestrated by two different surfactants;Triton X-100 (TX-100) and benzyl-n-hexadecyldimethylammonium chloride (BHDC);in order to make IL/surfactant/benzene RMs. The effect of the variation of Ws (Ws = [IL]/[surfactant]) on the QB spectroscopy was used to characterize these nonaqueous RMs. DLS results confirm the formation of these IL RM systems because increasing Ws increases the droplet sizes. Moreover it is demonstrated that the structure of the sequestrated ILs depends strongly on the type of surfactant use to create the RMs.

- Fabrication of Fluorescent Holographic Micropatterns Based on Azobenzene-Containing Host-Guest Complexes
  Chen, X.; Liu, B.; Zhang, H.; Guan, S.; Zhang, J.; Zhang, W.; Chen, Q.; Jiang, Z.; Guiver, M. D. *Langmuir* **2009**, *25*, 10444–10446.
  Abstract:



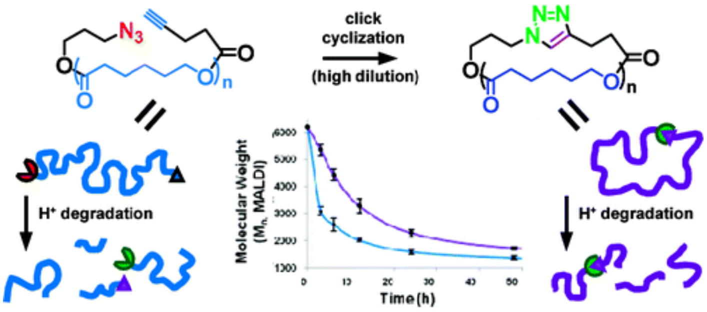
On the basis of photoinduced surface relief gratings (SRGs) with fluorophore/azo-complexes, a novel and facile method for fabricating stable and bright fluorescent two-dimensional micropatterns, whose color could be easily adjusted by changing the corresponding fluorophores, was developed for the first time.

- Simultaneous “Click Chemistry” and Atom Transfer Radical Emulsion Polymerization and Prepared Well-Defined Cross-Linked Nanoparticles.
  Xu, L. Q.; Yao, F.; Fu, G.-D. *Macromolecules* **2009**, *42*, 6385–6392.
  Abstract:



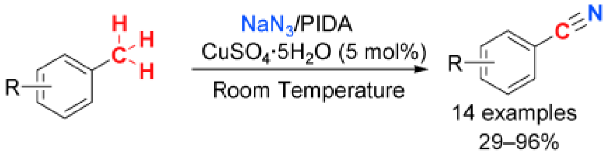
Simultaneous “click chemistry” and atom transfer radical emulsion polymerization (ATREP) to prepare well-defined macromolecules and cross-linked nanoparticles are first reported in this work. First, simultaneous “click chemistry” and ATREP of styrene were conducted in the presence of p-xylylene diazide, using propargyl 2-bromoisobutyrate (PBiB) as initiator, Tween-20 as emulsifier, copper(I) bromideas catalyst, and pentamethyldiethylenetriamine (PMDETA) as ligand. The simultaneous reactions sharing a same catalyst system gave rise to diblock polystyrene (PS) with controlled molecular weight and narrow molecular weight distribution. The resulting polymers were characterized by gel permeation chromatography (GPC), FT-IR, and 1H NMR spectroscopy. Then, well-defined cross-linked PS nanoparticles with diameter in the range of 50-150 nm were prepared from a simultaneous “click chemistry” and ATREP of a mixed styrene and 4-vinylbenzyl azide using 4,4-bis((20-bromo-20-methylpropionyloxy)methyl)-1,6-heptadiyne (BMP) as initiator, Tween-20 as emulsifier, copper(I) bromide as catalyst, and PMDETA as ligand. Wellpreserved nanostructures of particles in tetrahydrofuran (THF) and dimethylformamide (DMF) solvents reveal the nanoparticles have a cross-linked structure. The size and morphology of nanoparticles were also characterized by photon correlation spectroscopy and transmission electron microscope. The size of nanoparticles is very uniform and can be regulated by changing the ratio of monomer and initiator as well as the amount of emulsifiers. The cross-linked PS nanoparticles were more thermally stabile than PS from ATREP.

- Synthesis and Degradation Behavior of Cyclic Poly(ε-caprolactone).
  Hoskins, J. N.; Grayson, S. M. *Macromolecules* **2009**, *42*, 6406–6413.
  Abstract:



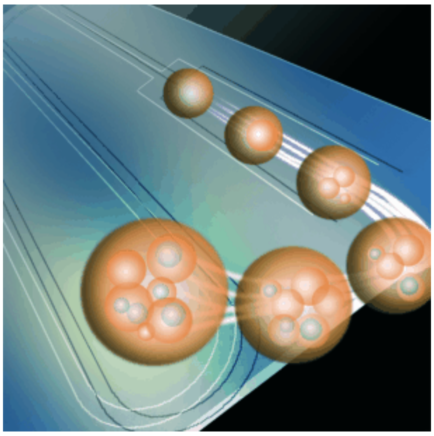
Narrow polydisersity cyclic poly(caprolactone) was synthesized by cyclization of linear R, ω-functionalized poly(caprolactone). The linear precursors were prepared via ring-opening polymerization from an azido-functionalized initiator, followed by end group modification to attach a terminal alkyne. Click coupling afforded the cyclic polymer in high yields and provided linear and cyclic poly(caprolactone) with exactly identical molecular weight distributions. The thermal and acid-catalyzed degradation of analogous linear and cyclic poly(caprolactone) samples were investigated to determine the effect of architecture.

- Direct Transformation of Methyl Arenes to Aryl Nitriles at Room Temperature
  Zhou, W.; Zhang, L.; Jiao, N. *Angew. Chem. Int. Ed*. **2009**, *48*, 7094-7097.
  Abstract :



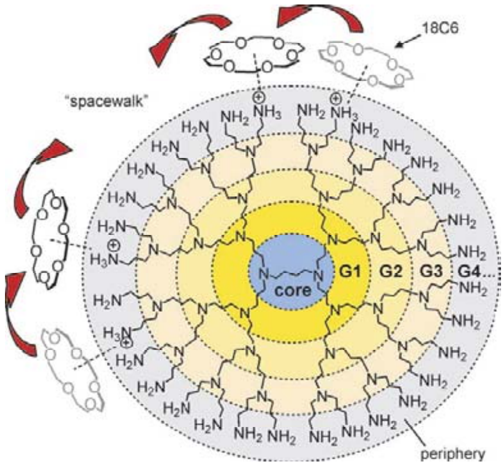
Three C—H bonds are cleaved in the direct transformation of methyl arenes to aryl nitriles under mild and neutral conditions (see scheme). This new synthetic tool may not only be used to construct synthetically and medicinally important aryl nitriles, it also achieves C—H functionalization under mild conditions. PIDA=phenyliodonium diacetate.

- Microfluidic Mass-Transfer Control for the Simple Formation of Complex Multiple Emulsions
  Zhao, C.-X.; Middelberg, A. P. J. *Angew. Chem. Int. Ed*. **2009**, *48*, 7208 –7211.
  Abstract:



Transforming emulsions: A straightforward method for turning a single emulsion into multiple emulsions in a common T-junction microfluidic device has been achieved. Water is introduced into oil using a cosolvent; a single emulsion then forms at a T junction, which is followed by the autocatalytic formation of a multiple emulsion by cosolvent shifting into the continuous phase.

- Dynamic Motion in Crown Ether Dendrimer Complexes: A “Spacewalk” on the Molecular Scale
  Winkler, H. D. F.; Weimann, D. P.; Springer, A.; Schalley, C. A. *Angew. Chem. Int. Ed*. **2009**, *48*, 7246 –7250.
  Abstract:



Walking on the edge: Mass spectrometry aided by H/D exchange experiments provides evidence for a surprisingly quick movement of [18]crown-6 units across the periphery of POMAM dendrimers (see picture). In the diluted gas phase, dissociation/reassociation equilibria do not play any role. The movement of the crown ether units resembles that of astronauts on the outside of a space station.