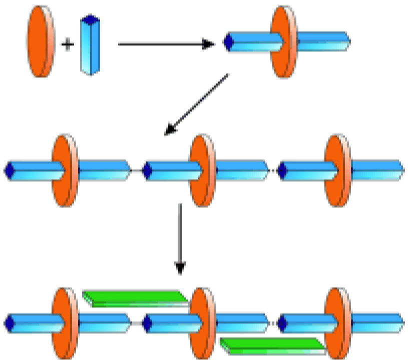
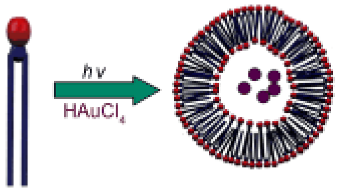
- One-Pot Mechanosynthesis with Three Levels of Molecular Self-Assembly: Coordination Bonds, Hydrogen Bonds and Host-Guest Inclusion
  Friščić, T.; Meštrović, E.; Škalec Šamec, D.; Kaitner, B.; Fábián, L. *Chem. Eur. J.* **2009**, *15*, 12653-12662.
  Abstract:



Liquid-assisted grinding (LAG) was used to combine three levels of molecular self-assembly into a one-pot mechanochemical approach for the construction of metal-organic materials. The approach was applied for the construction of three adducts of cobalt(II) dibenzoylmethanate with isonicotinamide, nicotinamide and imidazole, to screen for their inclusion compounds. The one-pot process consists of: i) The coordination-driven binding of addends to the equatorially-protected metal ion, resulting in "wheel-and-axle"-shaped complexes; ii) self-assembly of resulting complexes by way of hydrogen-bonded synthons to form metal-organic inclusion hosts; iii) in situ inclusion of the grinding liquid in the resulting host. This approach provided quantitatively and within 20 min the known inclusion compounds of the bis(isonicotinamide) adduct in a single synthetic step. Changing the liquid phase in LAG was used to explore the inclusion behaviour of new wheel-and-axle adducts with nicotinamide and imidazole, revealing several inclusion compounds, as well as two polymorphs, of the bis(nicotinamide) host. Preliminary results suggest that one-pot LAG is superior to solution synthesis in screening for metal-organic inclusion compounds. The difference between the methods is rationalised in terms of reactant solubility and solvent competition. In contrast to the nicotinamide adduct, the bis(imidazole) adduct did not form inclusion compounds. The difference in the inclusion properties of the two adducts is rationalised by structural information gathered by single crystal and powder X-ray diffraction.

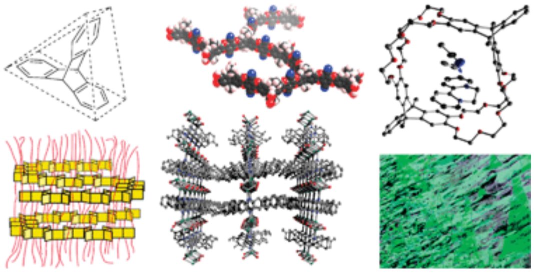
- Liposomes by Polymerization of an Imidazolium Ionic Liquid: Use as Microreactors for Gold-Catalyzed Alcohol Oxidation
  Buaki, M.; Aprile, C.; Dhakshinamoorthy, A.; Álvaro, M.; García, H. *Chem. Eur. J.* **2009**, *15*, 13082-13089.
  Abstract:



The bipodal ionic liquid *N*,*N*′-bis(10-undecenyl)-2-methylimidazolium underwent polymerization in aqueous media with potassium persulfate to form submicrometric liposomes. A TEM study indicated that the liposomes are the result of several morphological transformations of the polymer particles. Photopolymerization at room temperature led to spherical particles with some internal voids and

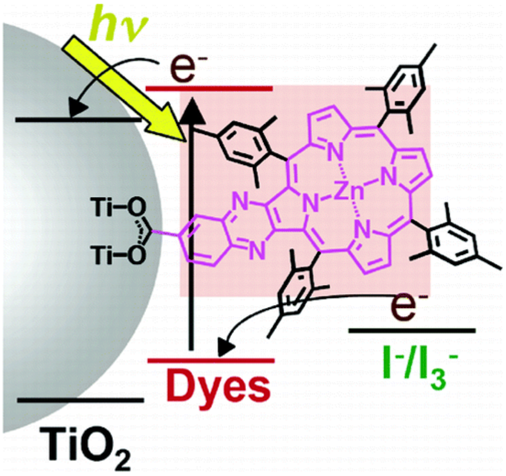
polymer chains. We took advantage of the positive charge on the imidazolium rings and used a photocuring agent to form in a single step starting from the imidazolium monomer and $NaAuCl_4$ spherical polymer particles containing gold nanoparticles (10-15 nm) in their interior. This system was found to promote the selective aerobic oxidation of 2-hydroxybenzyl alcohol to salicylaldehyde.

- Iptycenes in supramolecular and materials chemistry
  Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301 – 3315.
  Abstract:



Iptycenes, including triptycene as the smallest member, are rigid molecules with shapes that lead them to form open structures with substantial ‟free volume˝. There is a great deal of excitement in the application of these molecules to supramolecular chemistry, where researchers have taken advantage of their unique properties to construct new molecules and materials, including molecular machines, novel liquid crystals, and porous polymers for chemical sensing. This *tutorial review* highlights the application of iptycenes to the supramolecular chemistry of crystal engineering, host–guest complexes, molecular machines, polymers, and liquid crystals.

- Large π-Aromatic Molecules as Potential Sensitizers for Highly Efficient Dye-Sensitized Solar Cells
  Imahori, H.; Umeyama, T.; Ito, S. *Acc. Chem. Res.* **2009**, *42*, 1809–1818.
  Abstract:



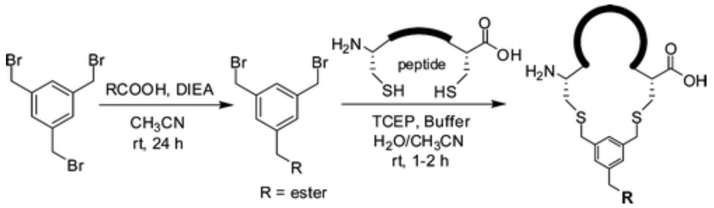
Recently, dye-sensitized solar cells have attracted much attention relevant to global environmental issues. Thus far, ruthenium(II) bipyridyl complexes have proven to be the most efficient TiO_2 sensitizers in dye-sensitized solar cells. However, a gradual increment in the highest power conversion efficiency has been recognized in the past decade. More importantly, considering that ruthenium is a rare metal, novel dyes without metal or using inexpensive metal are desirable for highly efficient dye-sensitized solar cells. Large π-aromatic molecules, such as porphyrins, phthalocyanines, and perylenes, are important classes of potential sensitizers for highly efficient dye-sensitized solar cells, owing to their photostability and high light-harvesting capabilities that can allow applications in thinner, low-cost dye-sensitized solar cells.

Porphyrins possess an intense Soret band at 400 nm and moderate Q bands at 600 nm. Nevertheless, the poor light-harvesting properties relative to the ruthenium complexes have limited the cell performance of porphyrin-sensitized TiO_2 cells. Elongation of the π conjugation and loss of symmetry in porphyrins cause broadening and a red shift of the absorption bands together with an increasing intensity of the Q bands relative to that of the Soret band. On the basis of the strategy, the cell performance of porphyrin-sensitized solar cells has been improved intensively by the enhanced light absorption. Actually, some push−pull-type porphyrins have disclosed a remarkably high power conversion efficiency (6−7%) that was close to that of the ruthenium complexes.

Phthalocyanines exhibit strong absorption around 300 and 700 nm and redox features that are similar to porphyrins. Moreover, phthalocyanines are transparent over a large region of the visible spectrum, thereby enabling the possibility of using them as “photovoltaic windows”. However, the cell performance was poor, owing to strong aggregation and lack of directionality in the excited state. Novel unsymmetrical zinc phthalocyanine sensitizers with “push” and “pull” groups have made it possible to reduce the aggregation on a TiO_2 surface, tune the level of the excited state, and strengthen the electronic coupling between the phthalocyanine core and the TiO_2 surface. As a result, the power conversion efficiency of up to 3.5% has been achieved.

Perylenes are well-known as chemically, thermally, and photophysically stable dyes and have been used in various optical devices and applications. Nevertheless, the power conversion efficiency remained low compared to other organic dyes. The origin of such limited cell performance is the poor electron-donating abilities of the perylenes, which makes it difficult to inject electrons from the excited singlet state of the perylenes to the conduction band of the TiO_2 electrode efficiently. Strongly electron-donating perylene carboxylic acid derivatives with amine substituents at their perylene core have allowed us to increase the power conversion efficiency of up to ∼7% in perylene-sensitized solar cells. The efficiency of large π-aromatic molecule-sensitized solar cells could be improved significantly if the dyes with larger red and near-infrared absorption could be developed.

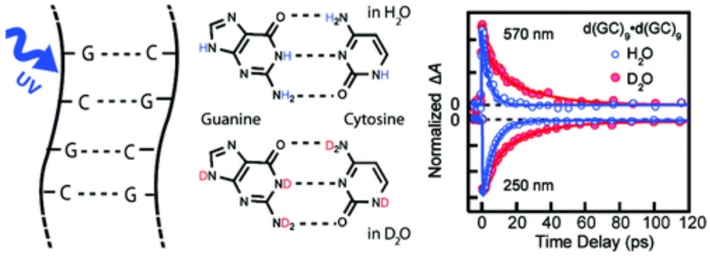
- Synthesis of Novel Peptide Linkers: Simultaneous Cyclization and Labeling
  Dewkar, G. K.; Carneiro, P. B.; Hartman, M. C. T. *Org. Lett.* **2009**, *11*, 4708–4711.
  Abstract:



Synthesis of novel peptide linkers was accomplished by monocarboxylation of 1,3,5-tris(bomomethyl)benzene with a wide variety of carboxylic acids in the presence of diisopropylethylamine. These reagents can be used to simultaneously cyclize and label peptides containing two cysteines. Many labels are compatible with this method including lipids, fluorescent groups, and biotin.

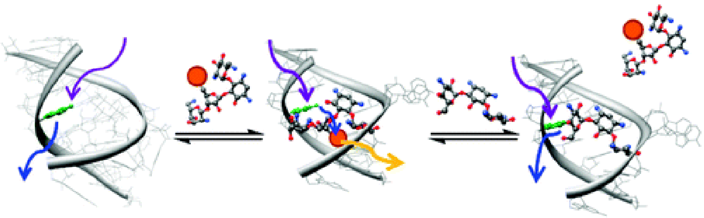
- Deuterium Isotope Effect on Excited-State Dynamics in an Alternating GC Oligonucleotide
  de La Harpe, K.; Crespo-Hernández, C. E.; Kohler, B. *J. Am. Chem. Soc.* **2009**, *131*, 17557–17559.

Abstract:



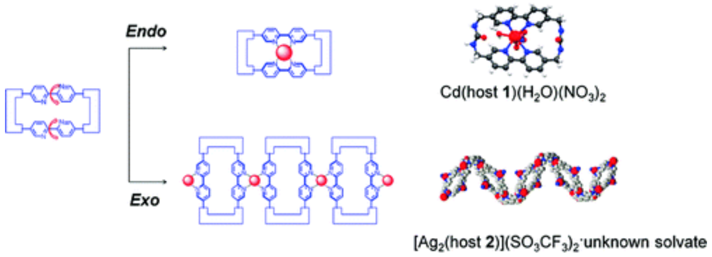
Isotope effects on the excited-state dynamics of single- and double-stranded GC-containing DNAs were studied by femtosecond transient absorption spectroscopy. A pronounced deuterium isotope effect was observed in alternating $d(GC)_9 \cdot d(GC)_9$, but none was seen in the nonalternating or single-stranded variations investigated. These findings demonstrate that an interstrand process involving proton-coupled electron transfer contributes to the excited-state dynamics in DNAs having an appropriate base sequence.

- FRET Enabled Real Time Detection of RNA-Small Molecule Binding
  Xie, Y.; Dix, A. V.; Tor, Y. *J. Am. Chem. Soc.* **2009**, *131*, 17605–17614.
  Abstract:



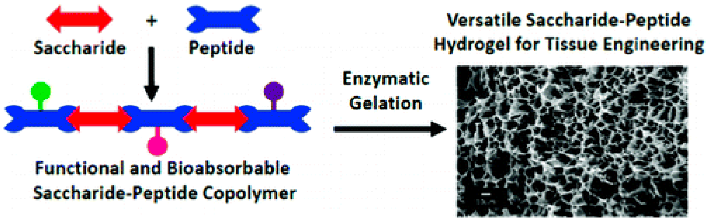
A robust analysis and discovery platform for antibiotics targeting the bacterial rRNA A-site has been developed by incorporating a new emissive U surrogate into the RNA and labeling the aminoglycosides with an appropriate fluorescence acceptor. Specifically, a 5-methoxyquinazoline-2,4(1*H*,3*H*)-dione-based emissive uracil analogue was identified to be an ideal donor for 7-diethylaminocoumarin-3-carboxylic acid. This donor/acceptor pair displays a critical Förster radius (R_0) of 27 Å, a value suitable for an A-site-aminoglycoside assembly. Titrating the coumarin labeled aminoglycosides into the emissive A-site construct, labeled at position U1406, shows a decrease in donor emission (at 395 nm) and concurrent increase of the acceptor emission (at 473 nm). Titration curves, obtained by fitting the donor's emission quenching or the augmentation of the acceptor's sensitized emission, faithfully generate EC_{50} values. Titration of unlabeled ligands into the preformed FRET complex showed a continuous increase of the donor emission, with a concurrent decrease of the acceptor emission, yielding valuable data regarding competitive displacement of aminoglycosides by A-site binders. Detection of antibiotic binding is therefore not dependent on changes in the environment of a single fluorophore, but rather on the responsive interaction between two chromophores acting as a FRET pair, facilitating the determination of direct binding and competitive displacement events with FRET accuracy.

- Macrocycles with Switchable *exo*/*endo* Metal Binding Sites
  Tian, L.-L.; Wang, C.; Dawn, S.; Smith, M. D.; Krause, J. A.; Shimizu, L. S. *J. Am. Chem. Soc.* **2009**, *131*, 17620–17629.
  Abstract:



We report herein the synthesis and metal complexation properties of two macrocyclic hosts that contain two 2,2′-bipyridines and two urea groups. These hosts take advantage of the conformationally mobile 5,5′-positions of the bipyridines to give metal binding sites that are dynamic. By simple bond rotation, these hosts can exchange an interior (*endo*) situated metal binding site for an exterior (*exo*) binding site. We examine the solid-state structures of the two free hosts and two coordination complexes ([Cd(host **1**)(H_2O)(NO_3)$_2$] and [Ag_2(host **2**)](SO_3CF_3)$_2$) using X-ray crystallography. Analysis of these crystal structures suggests that the bipyridine groups within the hosts are able to rotate to access multiple conformations including the desired *exo* and *endo* conformations. We also investigate the binding affinity of these new ligands in solution by UV−vis titrations with a series of metal nitrate salts (Ag, Cd, Zn, Ni, Mn, Fe, Co, Cr, and Cu) to afford discrete metal complexes. Some complexes showed a slow subsequent assembly to yield coordination polymers. Thus, these systems may afford unique insights into the process of metal organic framework formation.

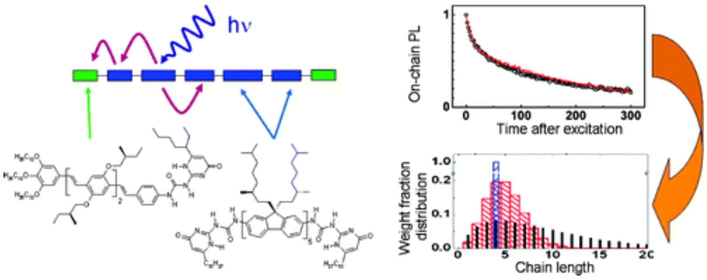
- De Novo Design of Saccharide−Peptide Hydrogels as Synthetic Scaffolds for Tailored Cell Responses
  Liao, S. W.; Yu, T.-B.; Guan, Z. *J. Am. Chem. Soc.* **2009**, *131*, 17638–17646.
  Abstract:



A new class of functional saccharide−peptide copolymer-based hydrogels was synthesized and investigated as synthetic extracellular matrices for regenerative medicine applications. The polymer was composed entirely of natural building blocks, namely, galactaric acid and lysine on the backbone, with tyrosine grafted onto the side chain as a handle for enzyme-catalyzed hydrogelation. The resulting hydrogels are degradable under simulated physiological conditions and exhibit minimal cytotoxicity on dermal fibroblast and PC-12 cells. As a demonstration of the versatility of the system, the mechanical properties of the gels can be independently controlled without changing the polymer chemical composition. Using an identical copolymer solution, by simply allowing different lengths of cross-linking time, a series of hydrogels was obtained with different mechanical moduli at constant chemical structure. The moduli of the resulting hydrogels varied stepwise from 1.7, 4.1, 6.9, and 12.5 kPa to allow for systematic studies on the effects of modulus on cell behavior. It was exciting to observe that a simple change in hydrogel physical properties could induce a direct phenotypic change in cell adhesion and proliferation. Depending on the substrate mechanical modulus, the cell morphology changed and proliferation rate differed by an order of magnitude for different cell lines.

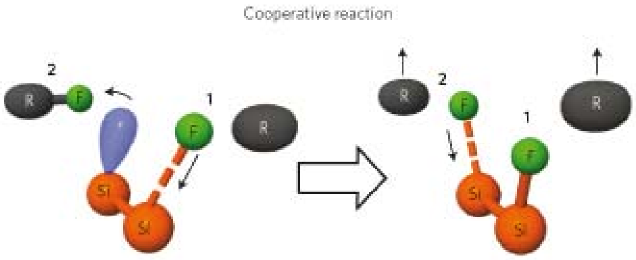
These data suggest our saccharide–peptide hydrogels as promising synthetic extracellular matrices for cell culture and tissue regeneration.

- Analyzing the Molecular Weight Distribution in Supramolecular Polymers
  Schmid, S. A.; Abbel, R.; Schenning, A. P. H.; Meijer, E. W.; Sijbesma, R. P.; Herz, L. M. *J. Am. Chem. Soc.* **2009**, *131*, 17696–17704.
  Abstract:



We have investigated the formation process of supramolecular linear polymer chains and its influence on the resulting chain length distribution function. For this purpose, we explored the migration of excitation energy between oligofluorene units coupled together through quadruple hydrogen-bonding groups to form linear chains that are terminated by oligophenylene vinylene end-caps acting as energy traps. The energy transfer dynamics from the main chain to the chain end was monitored experimentally using time-resolved PL spectroscopy and compared to an equivalent Monte Carlo simulation incorporating information on the structure of the chains, the transition transfer rates, and various weight distribution trial functions. We find that the assumption of a Flory distribution of chain lengths leads to excellent agreement between experimental and simulated data for a wide range of end-cap concentrations. On the other hand, both a Poisson function and a simplified assumption of a monodisperse distribution significantly underestimate the presence of long chains in the ensemble. Our results therefore show that supramolecular polymerization is a steplike process equivalent to polycondensation reactions in linear covalent polymers. These findings emphasize that equal reactivity of the supramolecular building blocks leads to a dynamic growth process for the supramolecular chain involving all chain components at all times.

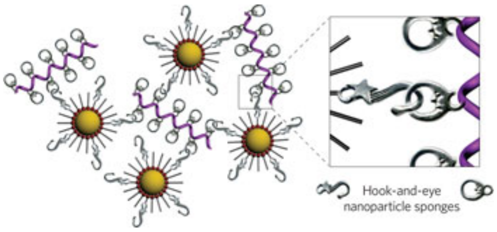
- Cooperative molecular dynamics in surface reactions
  Harikumar, K. R.; Leung, L.; McNab, I. R.; Polanyi, J. C.; Lin, H.; Hofer, W. A. *Nature Chem.* **2009**, *1*, 716-721.
  Abstract:



The controlled imprinting of surfaces with specified patterns is important in the development of nanoscale devices. Previously, such patterns were created using self-assembled physisorbed adsorbate molecules that can be stabilized on the surface by subsequent chemical bonding. Here we show a first step towards use of the bonding within a surface to propagate reactions for patterning, namely the cooperative reaction of adjacent silicon atoms. We exploit the doublebonded silicon

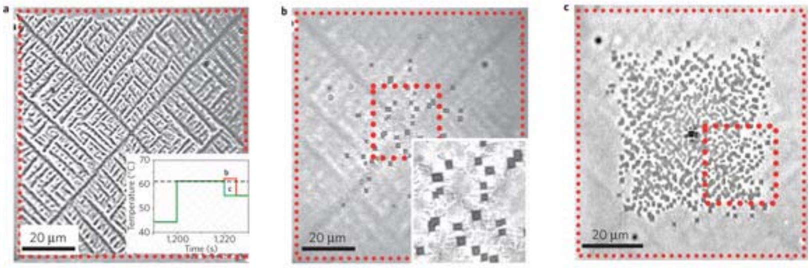
dimer pairs present on the surface of Si(100)-231 and show that the halogenation of one silicon atom (induced by electrons or heat) results in cooperative halogenation of the neighbouring silicon atom with unit efficiency. The reactants used were two 1 halopentane molecules physisorbed over a pair of silicon atoms. This cooperative pair of halogenation reactions was shown by ab initio calculation to be sequential on a timescale of femtoseconds.

- Dynamic hook-and-eye nanoparticle sponges
  Klajn, R.; Olson, M. A.; Wesson, P. J.; Fang, L.; Coskun, A.; Trabolsi, A.; Soh, S.; Stoddart, J. F.; Grzybowski, B. A. *Nature Chem.* **2009**, *1*, 733-738.
  Abstract:



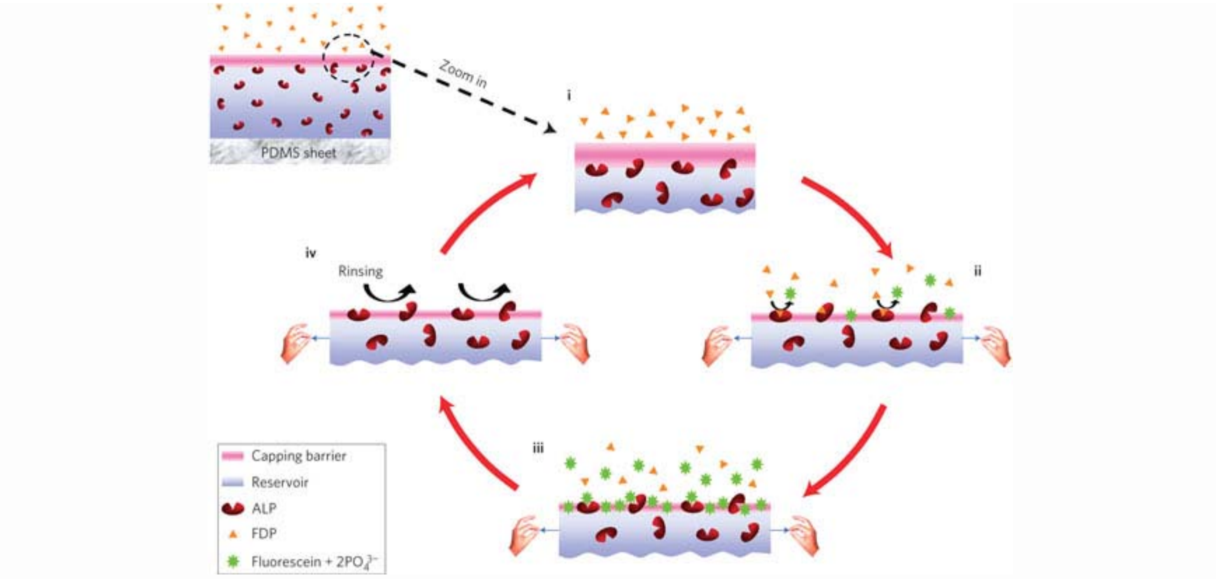
Systems in which nanoscale components of different types can be captured and/or released from organic scaffolds provide a fertile basis for the construction of dynamic, exchangeable functional materials. In such heterogeneous systems, the components interact with one another by means of programmable, noncovalent bonding interactions. Herein, we describe polymers that capture and release functionalized nanoparticles selectively during redox-controlled aggregation and disaggregation, respectively. The interactions between the polymer and the NPs are mediated by the reversible formation of polypseudorotaxanes, and give rise to architectures ranging from short chains composed of few nanoparticles to extended networks of nanoparticles crosslinked by the polymer. In the latter case, the polymer/nanoparticle aggregates precipitate from solution such that the polymer acts as a selective 'sponge' for the capture/release of the nanoparticles of different types.

- Cloning polymer single crystals through self-seeding
  Xu, J.; Ma, Y.; Hu, W.; Rehahn, M.; Reiter, G. *Nature Materials* **2009**, *8*, 348-353.
  Abstract:



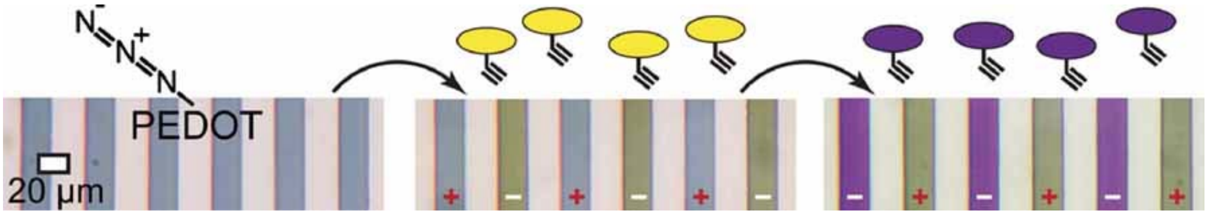
In general, when a crystal is molten, all molecules forget about their mutual correlations and long-range order is lost. Thus, a regrown crystal does not inherit any features from an initially present crystal. Such is true for materials exhibiting a well-defined melting point. However, polymer crystallites have a wide range of melting temperatures, enabling paradoxical phenomena such as the coexistence of melting and crystallization. Here, we report a self-seeding technique that enables the generation of arrays of orientation-correlated polymer crystals of uniform size and shape ('clones') with their orientation inherited from an initial single crystal. Moreover, the number density and locations of these cloned crystals can to some extent be predetermined through the thermal history of the starting crystal. We attribute this unique behaviour of polymers to the coexistence of variable fold lengths in metastable crystalline lamellae, typical for ordering of complex chain-like molecules.

- Mechanotransductive surfaces for reversible biocatalysis activation
  Mertz, D.; Vogt, C.; Hemmerlé, J.; Mutterer, J.; Ball, V.; Voegel, J.-C.; Schaaf, P.; Lavalle, P. *Nature Materials* **2009**, *8*, 731-738.
  Abstract:



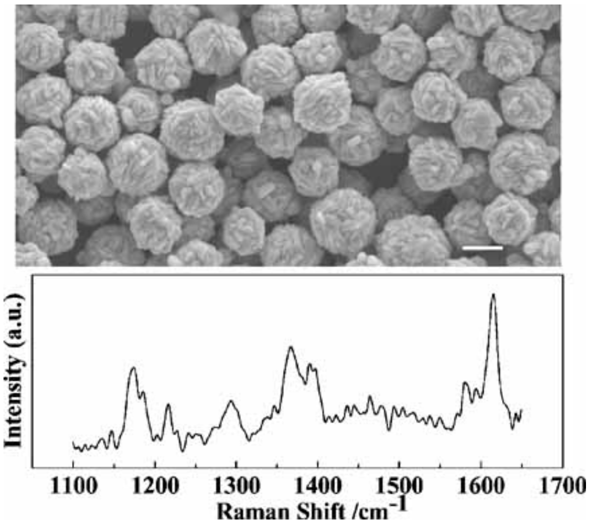
Fibronectin, like other proteins involved in mechanotransduction, has the ability to exhibit recognition sites under mechanical stretch. Such cryptic sites are buried inside the protein structure in the native fold and become exposed under an applied force, thereby activating specific signalling pathways. Here, we report the design of new active polymeric nanoassembled surfaces that show some similarities to these cryptic sites. These nanoassemblies consist of a first polyelectrolyte multilayer stratum loaded with enzymes and capped with a second polyelectrolyte multilayer acting as a mechanically sensitive nanobarrier. The biocatalytic activity of the film is switched on/off reversibly by mechanical stretching, which exposes enzymes through the capping barrier, similarly to mechanisms involved in proteins during mechanotransduction. This first example of a new class of biologically inspired surfaces should have great potential in the design of various devices aimed to trigger and modulate chemical reactions by mechanical action with applications in the field of microfluidic devices or mechanically controlled biopatches for example.

- Spatially Selective Functionalization of Conducting Polymers by “Electroclick” Chemistry
  Hansen, T.S.; Daugaard, A.E.; Hvilsted, S.; Larsen N.B. *Adv. Mater.* **2009,** 4483-4486.
  Abstract:



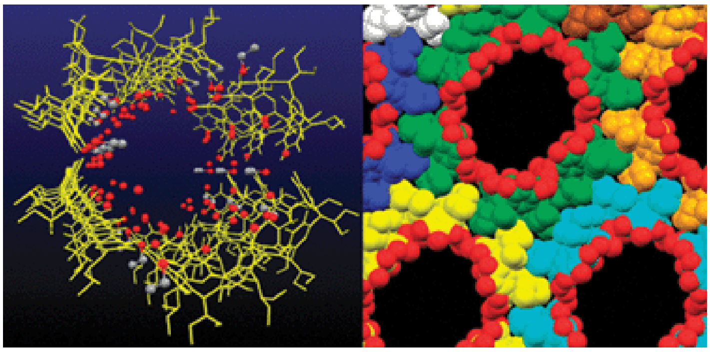
Conducting polymer microelectrodes can electrochemically generate the catalyst required for their own functionalization by “click chemistry” with high spatial resolution. Interdigitated microelectrodes prepared from an azide-containing conducting polymer are selectively functionalized in sequence by two alkyne-modified fluorophores by control of the applied potentials.

- Highly Surface-roughened "Flower-like" Silver Nanoparticles for Extremely Sensitive Substrates of Surface-enhanced Raman Scattering
  Liang, H.; Li, Z.; Wang, W.; Wu, Y.; Xu, H. *Adv. Mater.* **2009,** 4614-4618.
  Abstract:



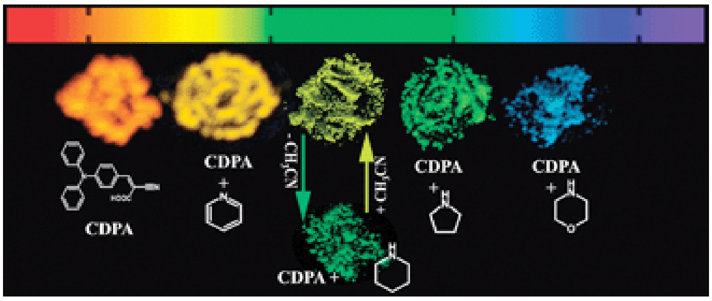
Monodispersed silver particles with a novel, highly roughened, "flower-like" morphology have been synthesized by reducing silver nitrate with ascorbic acid in aqueous solution. The nanometer-scale surface roughness of the particles can provide several "hot spots" on a single particle, which significantly increases the enhancement of surface-enhanced Raman scattering.

- Self-assembled, cogged hexameric nanotubes formed from pyrogallol[4]arenes with a unique branched side chain.
  Kulikov, O. V.; Daschbach, M. M.; Yamnitz, C. R.; Rath, N.; Gokel, G. W. *Chem. Commun.* **2009**, 7497 – 7499.
  Abstract:



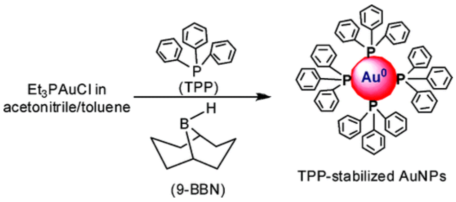
A branched side chain pyrogallol[4]arene self-assembles into a previously-unreported cogged hydrogen-bonded nanotube structure in the solid state and self-assembles at the air–water interface on the Langmuir trough.

- Switching and tuning organic solid-state luminescence via a supramolecular approach.
  Anthony, S. P.; Varughese, S.; Draper, S. V. *Chem. Commun.* **2009**, 7500 – 7502.
  Abstract:



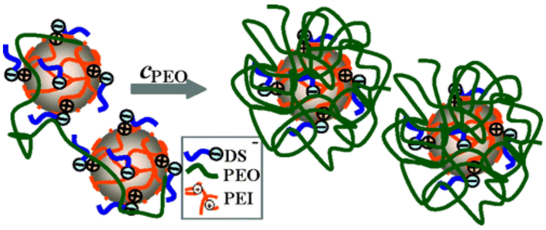
Unusual intermolecular interactions of organic luminescent acid, 2-cyano-3(4-(diphenylamino)phenyl)acrylic acid (CDPA), with amines lead to the formation of supramolecular luminescence systems with switchable and tunable solid-state luminescence.

- One-Step Synthesis of Phosphine-Stabilized Gold Nanoparticles Using the Mild Reducing Agent 9-BBN.
  Shem, P. M.; Sardar, R.; Shumaker-Parry, J. S. *Langmuir* **2009**, *25*, 13279–13283.
  Abstract:



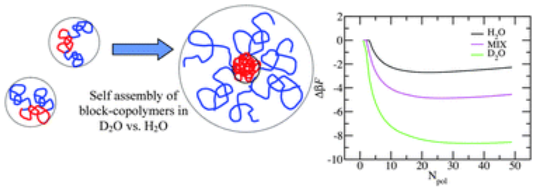
A simple method to synthesize phosphine-stabilized gold nanoparticles (AuNPs) of narrow size dispersion using the mild reducing agent 9-borabicyclo[3.3.1]nonane (9-BBN) is described. The methodology produces particles 1.2-2.8 nm in size depending on the reaction conditions and the phosphine ligand used. The phosphine-stabilized AuNPs exhibit size dependent localized surface plasmon resonance (LSPR) behavior as measured by UV-visible spectroscopy. 31P NMR spectroscopy analysis of triphenylphosphine-AuNPs (TPP-AuNPs) shows a peak shift to 63.0 ppm compared to pure TPP at -5.4 ppm which is attributed to adsorption of TPP on the AuNP surface. Synthesis of trioctylphosphine-stabilized AuNPs demonstrates the versatility of the 9-BBN-based method. We present initial investigations of using TPP-AuNPs as precursor materials for nanoparticles functionalized with other ligands through ligand exchange reactions with dodecanethiol (DDT) and 11-mercaptoundecanoic acid (MUA).

- Novel Self-Assemblies of Oppositely Charged Polyelectrolytes and Surfactants in the Presence of Neutral Polymer
  Pojjak, K.; Meszaros, R. *Langmuir* **2009**, *25*, 13336–13339.
  Abstract:



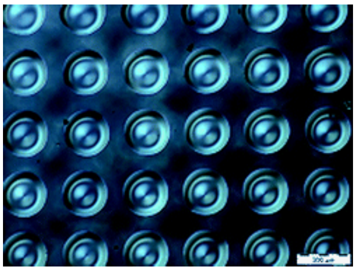
In this Letter, the effect of addition of poly(ethylene oxide) (PEO) on the nature of the self-assemblies of sodium dodecyl sulfate (SDS) and branched poly(ethyleneimine) (PEI) is investigated. We demonstrate that the neutral polymer adsorbs onto the surface of the polyelectrolyte/surfactant nanoparticles, which may result in sterically stabilized colloidal dispersions of the nanoparticles with hydrophobic core and hydrophilic corona. The kinetic stability is maintained even at high ionic strengths, where the charge stabilization of the PEI/SDS dispersions is inefficient. These results might be exploited to improve the efficiency of those formulations, which contain oppositely charged macromolecules and amphiphiles.

- An isotopic effect in self-assembly of amphiphilic block copolymers: the role of hydrogen bonds
  Shvartzman-Cohen, R.; Ren, C.; Szleifer, I.; Yerushalmi-Rozen, R. *Soft Matter* **2009**, *5*, 5003 – 5011.
  <u>Abstract:</u>



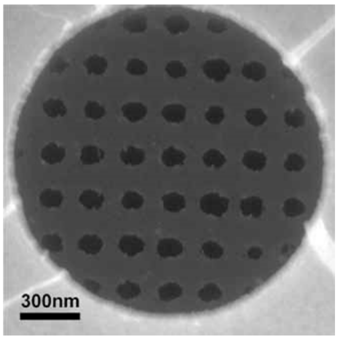
An isotopic effect was observed in solutions of self-assembling (SA) amphiphilic block copolymers: it was found that the micellization enthalpy, temperature and the size of the formed micelles are affected by replacing H_2O by D_2O. The SA of solvated block-copolymers (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)) in H_2O, D_2O and their mixtures was investigated as a function of temperature. High sensitivity differential scanning calorimetry revealed that the micellization temperature is reduced, and the enthalpic penalty of the transition and size of the formed micelles increase when H_2O is exchanged by D_2O. Molecular theory calculations suggest that the difference in the hydrogen bond strength of the solvent, H_2O or D_2O, is the origin of the different structural and conformational properties of the solvated block copolymers. The differences in the solvent properties were predicted to modify the solubility and consequently the SA of the polymers in the two solvents, as experimentally measured. The study provides an insight into the role of hydrogen bonding in systems of amphiphilic block copolymers, and suggests that in SA polymers small differences in hydrogen-bonding strength of the solvent may result in observable macroscopic effects.

- Inkjet printing of proteins
  Delaney Jr., J. T.; Smith, P. J.; Schubert, U. S. *Soft Matter* **2009**, *5*, 4866 – 4877.
  <u>Abstract:</u>



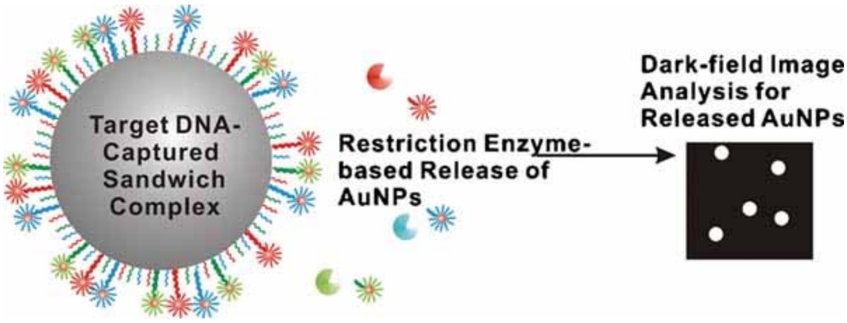
This article presents a review of the current status of the use of inkjet technology with protein-related applications. It includes a brief history of inkjet printing, discusses the advantages of employing the technology with proteins, using a number of selected applications as illustration, and concludes with a view of future research directions.

- Chemically Functionalized Carbon Nanosieves with 1-nm Thickness
  Schnietz, M.; Turchanin, A.; Nottbohm, C. T.; Beyer, A.; Solak, H. H.; Hinze, P.; Weimann, T.; Gölzhäuser, A. *Small* **2009**, *5*, 2651-2655.
  Abstract:



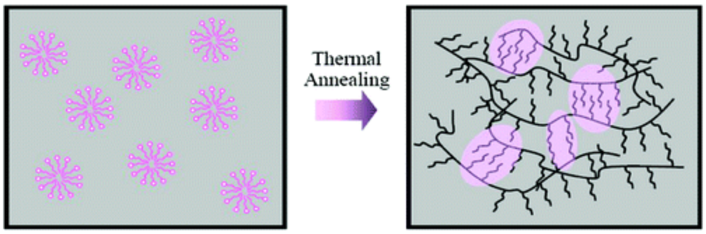
A route to produce novel chemically functionalized carbon nanosieves with a thickness of only ≈1nm is presented. The nanosieves (see image) have areas of up to ≈1mm^2 with regular openings down to ≈30nm. Carbon nanosieves are made via nanopatterning of self-assembled monolayers of 4’-nitro-1,1’-biphenyl-4-thiols by extreme UV interference lithography

- Restriction-Enzyme-Coded Gold-Nanoparticle Probes for Multiplexed DNA Detection
  Jang, K.-J.; Lee, H.; Jin, H.-L.; Park, Y.; Nam, J.-M. *Small* **2009**, *5*, 2665-2668.
  Abstract:



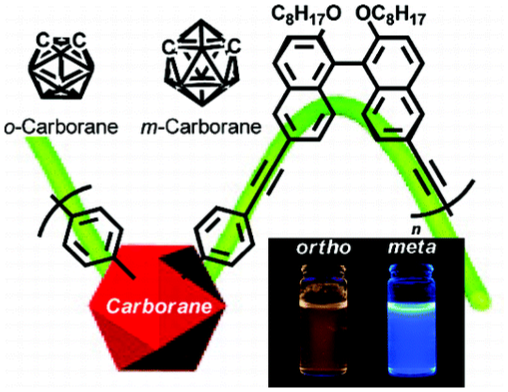
A highly sensitive multiplexed DNA detection assay uses restriction-enzyme-encoded, DNA-modified magnetic microparticle and gold nanoparticle probes combined with dark-field nanoparticle imaging analysis (see picture). A sensitivity of 100 fM and high specificity of the detection targets are achieved.

- Epoxy Networks with Physical Cross-Links Produced by Tail-to-Tail Associations of Alkyl Chains
  Puig, J.; Zucchi, I. A.; Hoppe, C. E.; Perez,C. J.; Galante, M. J.; Williams, R. J. J.; Rodríguez-Abreu, C. *Macromolecules* **2009**, *42*, 9344–9350.
  Abstract:



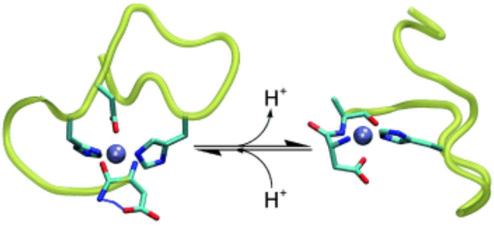
In a recent paper, we showed that linear amphiphilic epoxy polymers synthesized by the polyaddition of diglycidyl ether of bisphenol A (DGEBA) with dodecylamine (DA) could undergo a physical gelation process through tail-to-tail association of dodecylchains. The aim of the present study was to analyze in more detail conditions leading to the formation of epoxy networks with physical cross-links by the reaction of DGEBA with alkylamines of different chain lengths: octylamine (OA), dodecylamine (DA), and hexadecylamine (HA). SAXS spectra showed that tail-totail associations of alkyl chains were present since the beginning of polymerization and remained in the final materials. Initially, these associations correspond to micelles of the alkylamines dispersed in the solvent =(DGEBA). In the course of polymerization, micelles are disaggregated as the individual alkylamine chains become part of the linear amphiphilic polymer. However, tail-to-tail associations among alkyl chains attached to the polymer backbone persisted in the final materials. Reactions were followed by rheometry at 100 _C. For every system, a significant discontinuity in the increase in the storage modulus observed at advanced conversions was assigned to a phase inversion process produced by solvent depletion. By annealing prolonged times at the reaction temperature, a crossover of storage and loss modulus was observed because of the increase in the extent of associations among alkyl chains leading to a physical gel. Times for physical gelation varied in the order OA < DA < HA. Both DGEBA-DA and DGEBA-HA polymers could be reversibly transformed from gel to liquid states by appropriate heating-cooling cycles; however, the DGEBA-OA polymer showed no thermoreversibility. Physical gels exhibited a high swelling capacity in THF (HA > DA > OA). These amphiphilic gels could be used as dispersion media for a variety of nanoparticles stabilized with alkyl chains. They can also be the basis of single-component thermally remendable epoxy networks.

- Luminescent and Axially Chiral π-Conjugated Polymers Linked by Carboranes in the Main Chain.
  Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 9238–9242.
  Abstract:



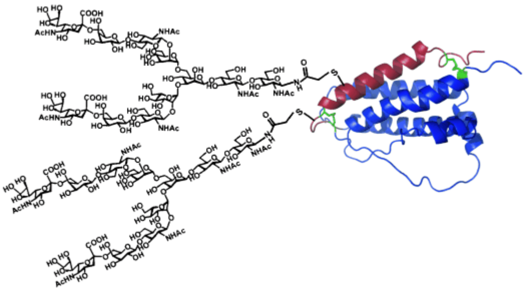
Sonogashira-Hagihara polycondensations of two bis(4-iodophenyl)carborane compounds with axially chiral diyne monomers having binaphthyl unit were carried out to obtain the corresponding chiral π-conjugated polymers having o- or m-carborane segment in the main chain. The polymer structures and their optical properties were characterized by 1H, 13C, and 11B NMR, FT-IR, UV-vis absorption, photoluminescence, and circular dichroism spectroscopies. Photoluminescence study revealed that the polymer having m-carborane exhibited intense blue emission in solution state, whereas polymers having o-carborane exhibited aggregation-induced emission (AIE). All polymers showed strong CD signals, indicating the construction of highly ordered conformation.

- Deprotonation of the Asp1-Ala2 Peptide Bond Induces Modificationof the Dynamic Copper(II) Environment in the Amyloid-β Peptide near Physiological pH
  Hureau, C.; Coppel, Y.; Dorlet, P.; Solari, P. L.; Sayen, S.; Guillon, E.; Sabater, L.; Faller, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 9522–9525.
  Abstract:



Premium bonds: The pH-dependent coordination of Cu^{II} to the Alzheimer's disease amyloid-β peptide has been studied by NMR spectroscopy. Several equivalent ligands are in equilibrium for Cu^{II} binding near pH 6.6 and 8.7. Fewer conformers are detected at high pH, in line with a reshuffling of the Cu^{II} binding site induced by deprotonation of the Asp1-Ala2 peptide bond (see picture).

- Design and Synthesis of a Homogeneous Erythropoietin Analogue with Two Human Complex-Type Sialyloligosaccharides: Combined Use of Chemical and Bacterial Protein Expression Methods
  Hirano, K.; Macmillan, D.; Tezuka, K.; Tsuji, T.; Kajihara, Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 9557–9560.
  Abstract:



Highly expressive: Cell proliferation was observed with concentrations of an erythropoietin (EPO) analogue above 50 pg mL^{-1}. The EPO analogue has two human complex-type sialyloligosaccharides (see picture) and was formed by the combined use of chemical synthesis and protein expression in *E. coli.* Both the 24- and 30-positions are glycosylated, but the two sialyloligosaccharides do not interfere with binding of the EPO analogue to a receptor.