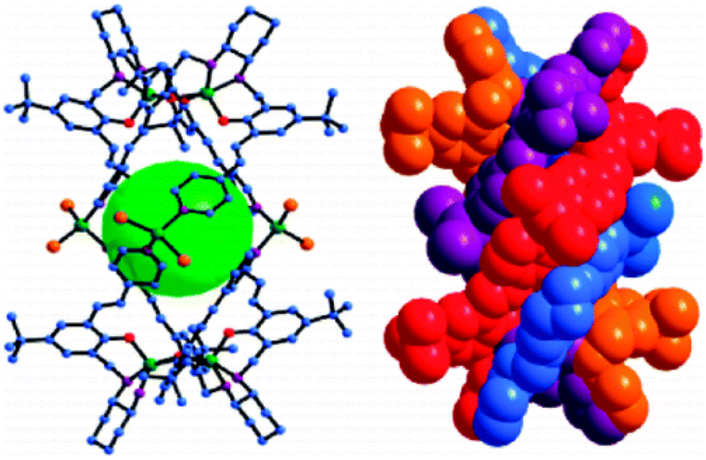
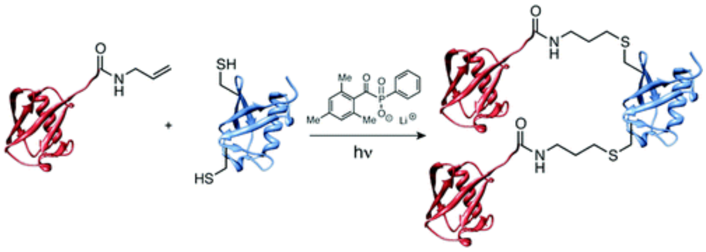
- A Chiral Quadruple-Stranded Helicate Cage for Enantioselective Recognition and Separation
  Xuan, W.; Zhang, M.; Liu, Y.; Chen, Z.; Cui, Y. *J. Am. Chem. Soc.* **2012**, *134*, 6904–6907.
  Abstract:



The self-assembly of enantiopure pyridyl-functionalized metallosalan units affords a homochiral helicate cage, $[Zn_8L_4Cl_8]$, in which the optical rotation of each ligand is increased by a factor of 10 upon coordination. The octanuclear cage featuring a chiral amphiphilic cavity exhibits enantioselective luminescence enhancement by amino acids in solution. The cage exists in two different crystalline polymorphic forms that possess porous structures built of helicate cages interconnected by 1D channels or pentahedral cages and have the ability to separate small racemic molecules by adsorption but with different enantioselectivities.

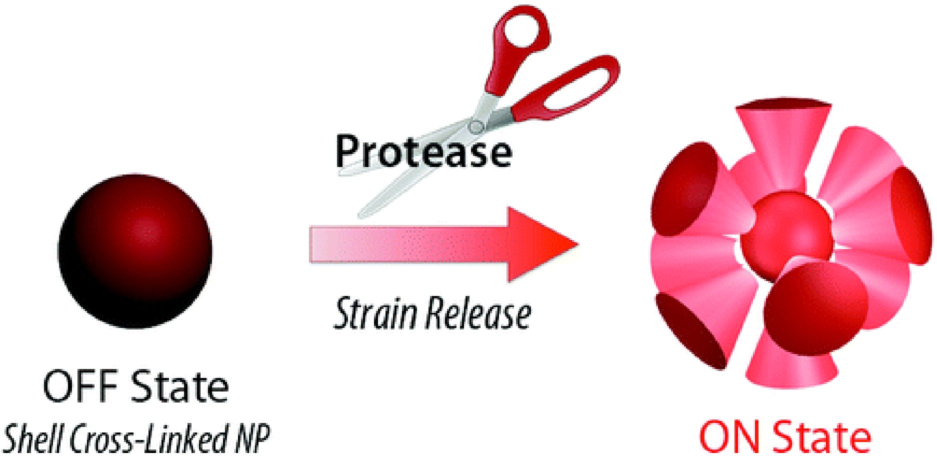
- Forging Isopeptide Bonds Using Thiol–Ene Chemistry: Site-Specific Coupling of Ubiquitin Molecules for Studying the Activity of Isopeptidases
  Valkevich, E. M.; Guenette, R. G.; Sanchez, N. A.; Chen, Y.-c.; Ge, Y.; Striete, E. R. *J. Am. Chem. Soc.* **2012**, *134*, 6916–6919.
  Abstract:



Chemical methods for modifying proteins can enable studies aimed at uncovering biochemical function. Herein, we describe the use of thiol–ene coupling (TEC) chemistry to report on the function of branched (also referred to as forked) ubiquitin trimers. We show how site-specific isopeptide (Nε-Gly-l-homothiaLys) bonds are forged between two molecules of Ub, demonstrating the power of TEC in protein conjugation. Moreover, we demonstrate that the Nε-Gly-l-homothiaLys isopeptide bond is processed to a similar extent by deubiquitinases (DUBs) as that of a native Nε-Gly-l-Lys isopeptide bond, thereby establishing the utility of TEC in the generation of Ub-Ub linkages. TEC is then applied to the synthesis of branched Ub trimers. Interrogation of these branched derivatives with DUBs reveals that the relative orientation of the two Ub units has a dramatic impact on how they are hydrolyzed. In particular, cleavage of K48C-linkages is suppressed when the central Ub unit is also conjugated through K6C, whereas cleavage proceeds normally when the central unit is conjugated

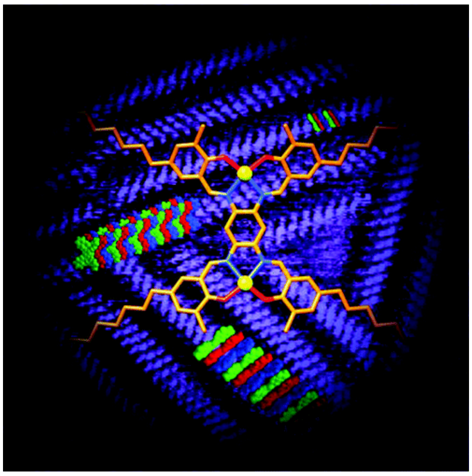
through either K11C or K63C. The results of this work presage a role for branched polymeric Ub chains in regulating linkage-selective interactions.

- Strain Release in Organic Photonic Nanoparticles for Protease Sensing
  Cordovilla, C.; Swager, T. M. *J. Am. Chem. Soc.* **2012**, *134*, 6932–6935.
  Abstract:



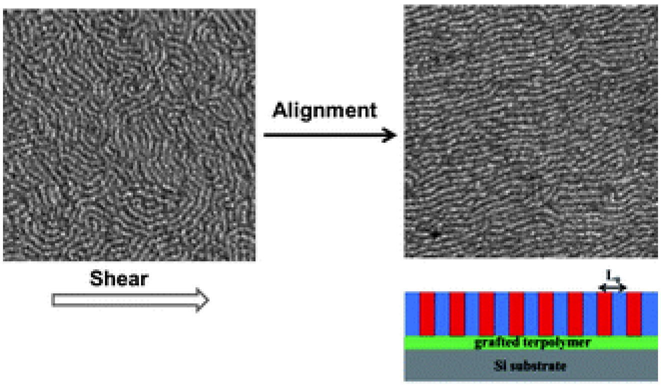
Proteases are overexpressed in most cancers and proteolytic activity has been shown to be a viable marker for cancer imaging in vivo. Herein, we describe the synthesis of luminescence-quenched shell cross-linked nanoparticles as photonic nanoprobes for protease sensing. Protease sensing scheme is based on a “turn-on” mechanism where the protease cleaves peptide cross-linkers of the fluorescence-quenched shell cross-linked NP (OFF state) leading to a highly emissive non-cross linked NP (ON state). The cross-linked particles can be strained by exposure to a good solvent and proteolysis allows for particle expansion (swelling) and a recovery of the luminescence.

- Extremely Strong Self-Assembly of a Bimetallic Salen Complex Visualized at the Single-Molecule Level
  Salassa, G.; Coenen, M. J. J.; Wezenberg, S. J.; Hendriksen, B. L. M.; Speller, S.; Elemans, J. A. A. W.; Kleij, A. W. *J. Am. Chem. Soc.* **2012**, *134*, 186–7192.
  Abstract:



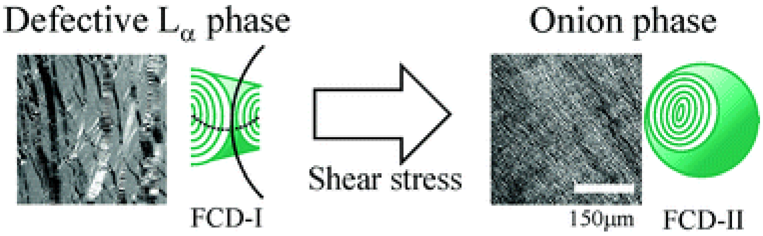
A bis-Zn(salphen) structure shows extremely strong self-assembly both in solution as well as at the solid–liquid interface as evidenced by scanning tunneling microscopy, competitive UV–vis and fluorescence titrations, dynamic light scattering, and transmission electron microscopy. Density functional theory analysis on the $Zn_2$ complex rationalizes the very high stability of the self-assembled structures provoked by unusual oligomeric $(Zn–O)_n$ coordination motifs within the assembly. This coordination mode is strikingly different when compared with mononuclear Zn(salphen) analogues that form dimeric structures having a typical $Zn_2O_2$ central unit. The high stability of the multinuclear structure therefore holds great promise for the development of stable self-assembled monolayers with potential for new opto-electronic materials.

- Alignment of perpendicular lamellae in block copolymer thin films by shearing
  Pujari, S.; Keaton, M. A.; Chaikin, P. M.; Register, R. A. *Soft Matter* **2012**, *8*, 5358-5363.
  Abstract:



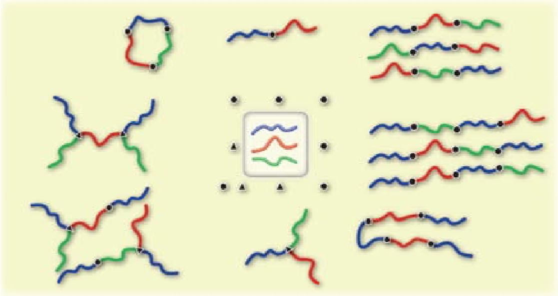
Lamellar block copolymers, with the lamellae standing perpendicular to the substrate, are attractive candidates as templates for nanostructure array fabrication. However, no process currently exists to impose long-range in-plane alignment of such perpendicular lamellae on simple unpatterned substrates—to align the lamellar normal over macroscopic distances. Here, we have generated such aligned films of perpendicular lamellae in a polystyrene-poly(methylmethacrylate) diblock, PS-PMMA, by neutralizing the substrate with a random terpolymer brush and shearing the film with a moving polydimethylsiloxane (PDMS) pad in contact with the film surface. At sufficiently high shear stresses, the lamellae align over the entire ($cm^2$) area of the pad; the perpendicular orientation of the lamellae is preserved, although for films thicker than the lamellar spacing, a "capping layer" of PS forms in contact with the PDMS pad. However, when compared with typical shear-aligned block copolymers having a morphology of in-plane cylinders, a significantly higher stress is required to align the lamellar PS-PMMA, and the orientational order is poorer and the dislocation density higher; a limiting order parameter $\psi_2 \approx 0.8$ is achieved at high stresses.

- Shear-induced onion formation of polymer-grafted lamellar phase
  Fujii, S.; Mitsumasu, D.; Isono, Y.; Richtering, W. *Soft Matter* **2012**, *8*, 5381-5390.
  Abstract:



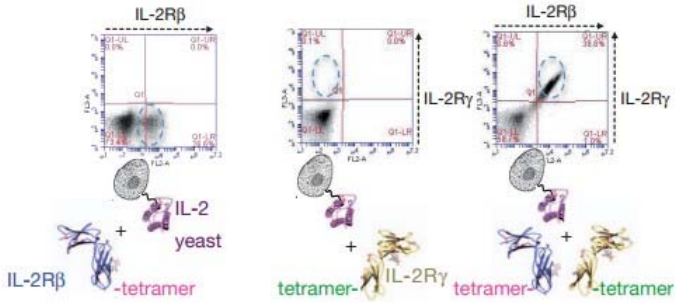
We study the shear-induced lamellar/onion transformation of the polymer-grafted lamellar phase composed of nonionic surfactant and amphiphilic triblock copolymers. Increase in the mole fraction of polymer $X_P$ and the degrees of polymerization of hydrophilic chain $N_{EO}$ remarkably affects the shear-induced onion phase formation behavior. From the viewpoint of the defect-mediated rheology, the shear modulus $G'$ is attributed to the oily streak network density. Linear increase in $G'$ with preshear rate prior to the onion formation indicates that the increase in the oily streak network density is essential as a pretransition. The oily streak is composed of the focal conic domains (FCDs), which locally have inhomogeneous layer spacing. The critical shear stress $\sigma_c$ is well scaled by the effective increment of the bending modulus theoretically predicted for the polymer-grafted membranes, $\Delta\kappa \sim X_{P}N^{1.27}_{EO}$. Experimental results suggest that the shear-induced onion phase is achieved by reorganizing the layer orientation of FCDs with the negative Gaussian curvature in order to eliminate the inhomogeneous layer spacing.

- Multiblock Polymers: Panacea or Pandora's Box?
  Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H.
  *Science* **2012***, 336*, 434-440.
  Abstract:



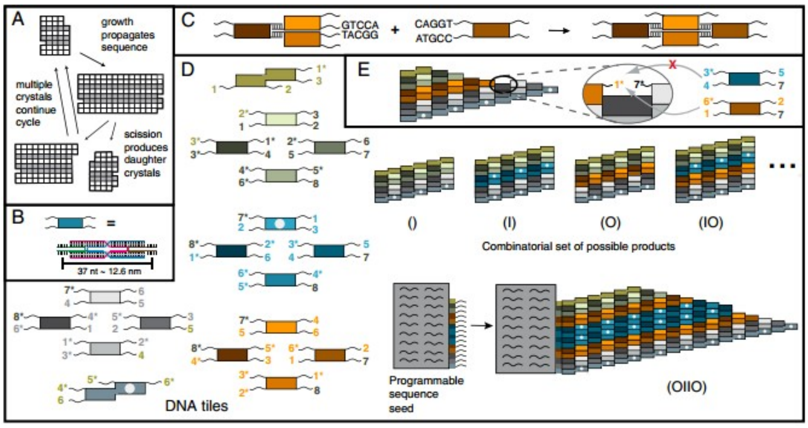
Advances in synthetic polymer chemistry have unleashed seemingly unlimited strategies for producing block polymers with arbitrary numbers (n) and types (k) of unique sequences of repeating units. Increasing (k, n) leads to a geometric expansion of possible molecular architectures, beyond conventional ABA-type triblock copolymers (k = 2, n = 3), offering alluring opportunities to generate exquisitely tailored materials with unparalleled control over nanoscale-domain geometry, packing symmetry, and chemical composition. Transforming this potential into targeted structures endowed with useful properties hinges on imaginative molecular designs guided by predictive theory and computer simulation. Here, we review recent developments in the field of block polymers.

- Exploiting a natural conformational switch to engineer an interleukin-2 'superkine'
  Levin, A. M.; Bates, D. L.; Ring, A. M.; Krieg, C.; Lin, J. T.; Su, L.; Moraga, I.; Raeber, M. E.; Bowman, G. R.; Novick, P.; Pande, V. S.; Fathman, C. G.; Boyman, O.; Garcia, K. C. *Nature* **2012***, 484*, 529-533.
  Abstract:



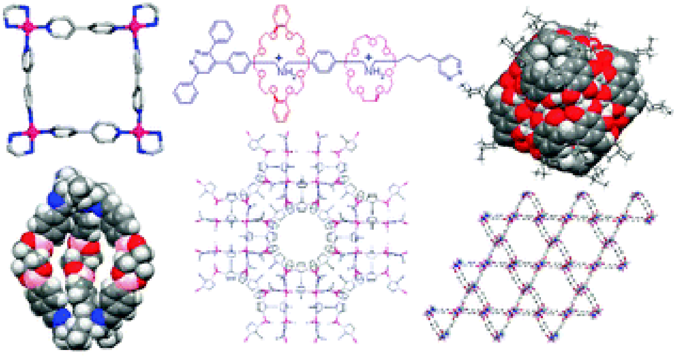
The immunostimulatory cytokine interleukin-2 (IL-2) is a growth factor for a wide range of leukocytes, including T cells and natural killer (NK) cells. Considerable effort has been invested in using IL-2 as a therapeutic agent for a variety of immune disorders ranging from AIDS to cancer. However, adverse effects have limited its use in the clinic. On activated T cells, IL-2 signals through a quaternary ‘high affinity’ receptor complex consisting of IL-2, IL-2Ra (termed CD25), IL-2Rb and IL-2Rc. Naive T cells express only a low density of IL-2Rb and IL-2Rc, and are therefore relatively insensitive to IL-2, but acquire sensitivity after CD25 expression, which captures the cytokine and presents it to IL-2Rb and IL-2Rc. Here, using in vitro evolution, we eliminated the functional requirement of IL-2 for CD25 expression by engineering an IL-2 ‘superkine’ (also called super-2) with increased binding affinity for IL-2Rb. Crystal structures of the IL-2 superkine in free and receptor-bound forms showed that the evolved mutations are principally in the core of the cytokine, and molecular dynamics simulations indicated that the evolved mutations stabilized IL-2, reducing the flexibility of a helix in the IL-2Rb binding site, into an optimized receptor-binding conformation resembling that when bound to CD25. The evolved mutations in the IL-2 superkine recapitulated the functional role of CD25 by eliciting potent phosphorylation of STAT5 and vigorous proliferation of T cells irrespective of CD25 expression. Compared to IL-2, the IL-2 superkine induced superior expansion of cytotoxic T cells, leading to improved antitumour responsesin vivo, and elicited proportionally less expansion of T regulatory cells and reduced pulmonary oedema. Collectively, we show thatin vitro evolution has mimicked the functional role of CD25 in enhancing IL-2 potency and regulating target cell specificity, which has implications for immunotherapy.

- Robust self-replication of combinatorial information via crystal growth and scission
  Schulman, R.; Yurke, B.; Winfree, E. *Proc. Nat. Acad. Sci. USA* **2012***, 109*, 6405-6410.
  Abstract:



Understanding how a simple chemical system can accurately replicate combinatorial information, such as a sequence, is an important question for both the study of life in the universe and for the development of evolutionary molecular design techniques. During biological sequence replication, a nucleic acid polymer serves as a template for the enzyme-catalyzed assembly of a complementary sequence. Enzymes then separate the template and complement before the next round of replication. Attempts to understand how replication could occur more simply, such as without enzymes, have largely focused on developing minimal versions of this replication process. Here we describe how a different mechanism, crystal growth and scission, can accurately replicate chemical sequences without enzymes. Crystal growth propagates a sequence of bits while mechanically-induced scission creates new growth fronts. Together, these processes exponentially increase the number of crystal sequences. In the system we describe, sequences are arrangements of DNA tile monomers within ribbon-shaped crystals. 99.98% of bits are copied correctly and 78% of 4-bit sequences are correct after two generations; roughly 40 sequence copies are made per growth front per generation. In principle, this process is accurate enough for 1,000-fold replication of 4-bit sequences with 50% yield, replication of longer sequences, and Darwinian evolution. We thus demonstrate that neither enzymes nor covalent bond formation are required for robust chemical sequence replication. The form of the replicated information is also compatible with the replication and evolution of a wide class of materials with precise nanoscale geometry such as plasmonic nanostructures or heterogeneous protein assemblies.

- Supramolecular concepts and new techniques in mechanochemistry: cocrystals, cages, rotaxanes, open metal–organic frameworks
  Friščić, T. *Chem. Soc. Rev.* **2012**, *41*, 3493-3510.
  Abstract:

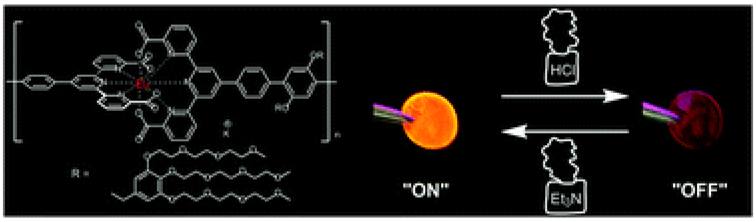


Mechanochemical reactions effected by milling or grinding are an attractive means to conduct chemical reactions dependent on molecular recognition and to systematically explore different modes of molecular self-assembly. The natural relationship between milling mechanochemistry and supramolecular chemistry arises primarily from the ability to avoid bulk solvent, which simultaneously avoids limitations of solution-based chemistry, such as solubility, solvent complexation, or solvolysis, and makes the resulting process highly environmentally friendly. This *tutorial review* highlights the use of mechanochemistry for the synthesis of supramolecular targets in the solid state, such as molecular hydrogen- or halogen-bonded complexes, molecular and supramolecular cages, open frameworks and interlocked architectures. It is also demonstrated that the molecular self-assembly phenomena that are well-established in solution chemistry, such as reversible binding through covalent or non-covalent bonds, thermodynamic equilibration and structure templating, are also accessible in milling mechanochemistry through recently developed highly efficient methodologies such as liquid-assisted grinding (LAG) or ion- and liquid-assisted grinding (ILAG). Also highlighted are the new opportunities arising from the marriage of concepts of supramolecular and mechanochemical synthesis, including organocatalysis, deracemisation and discovery of new molecular recognition motifs.

- Functionalized mesoporous silica materials for controlled drug delivery
  Yang, P.; Gai, S.; Lin, J. *Chem. Soc. Rev.* **2012**, *41*, 3679-3698.
  Abstract:

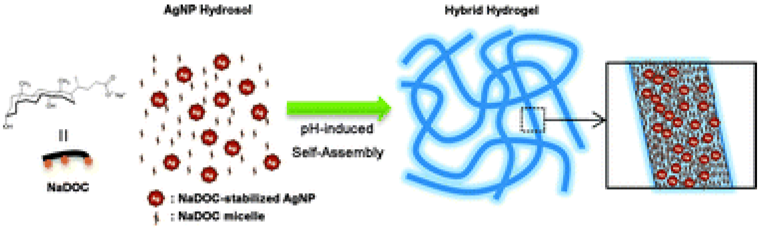
In the past decade, non-invasive and biocompatible mesoporous silica materials as efficient drug delivery systems have attracted special attention. Great progress in structure control and functionalization (magnetism and luminescence) design has been achieved for biotechnological and biomedical applications. This review highlights the most recent research progress on silica-based controlled drug delivery systems, including: (i) pure mesoporous silica sustained-release systems, (ii) magnetism and/or luminescence functionalized mesoporous silica systems which integrate targeting and tracking abilities of drug molecules, and (iii) stimuli-responsive controlled release systems which are able to respond to environmental changes, such as pH, redox potential, temperature, photoirradiation, and biomolecules. Although encouraging and potential developments have been achieved, design and mass production of novel multifunctional carriers, some practical biological application, such as biodistribution, the acute and chronic toxicities, long-term stability, circulation properties and targeting efficacy *in vivo* are still challenging.

- A vapoluminescent Eu-based metallo-supramolecular polymer
  Sato, T.; Higuchi, M. *Chem. Commun.* **2012**, *48*, 4947-4949.
  Abstract:



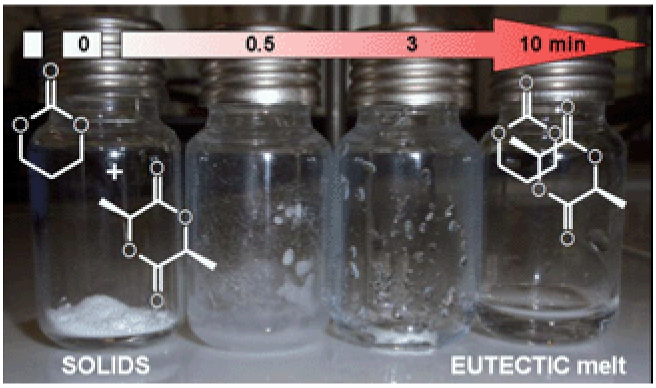
An Eu-based metallo-supramolecular polymer (polyEu) was prepared by self-assembly coordination polymerization. Unique vapoluminescence property of polyEu triggered by acid–base vapor was found and a photoluminescence display in switchable imaging by acid–base vapor was fabricated.

- A novel method for preparing silver nanoparticle–hydrogel nanocomposites via pH-induced self-assembly
  Yook, J. Y.; Choi, G.; Suh, D. H. *Chem. Commun.* **2012**, *48*, 5001-5003.
  Abstract:



The silver nanoparticles (AgNPs)-immobilized hydrogel fabricated by the simultaneous pH-induced self-assembly of sodium deoxycholate (NaDOC)-stablized AgNPs and NaDOC micelles provides the three-dimensional continuous-phase hybrid nanocomposite.

- Synthesis of poly(L-lactide) and gradient copolymers from a L-lactide/trimethylene carbonate eutectic melt
  Coulembier, O.; Lemaur, V.; Josse, T.; Minoia, A. ; Cornil, J. ; Dubois, P. *Chem. Sci.* **2012**, *3*, 723-726.
  Abstract:



A 50 : 50 wt% mixture of L-lactide and trimethylene carbonate yields a eutectic at 21.3 °C.

- Inhibition of metal-induced amyloid aggregation using light-responsive magnetic nanoparticle prochelator conjugates
  Li, M.; Liu, Z.; Ren, J.; Qu, X. *Chem. Sci.* **2012**, *3*, 868-873.
  Abstract:

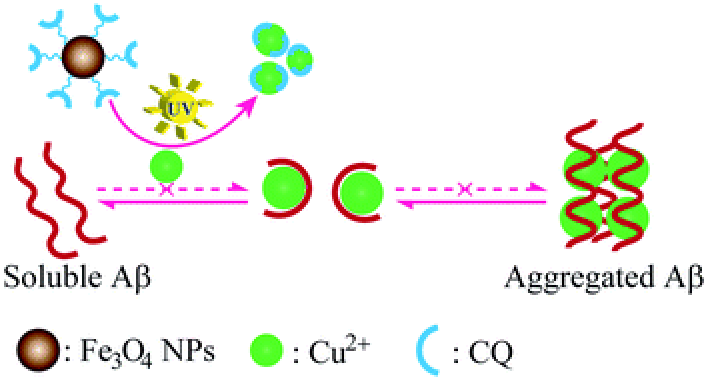
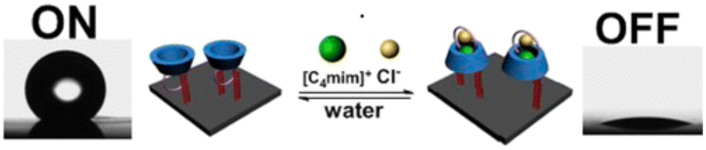


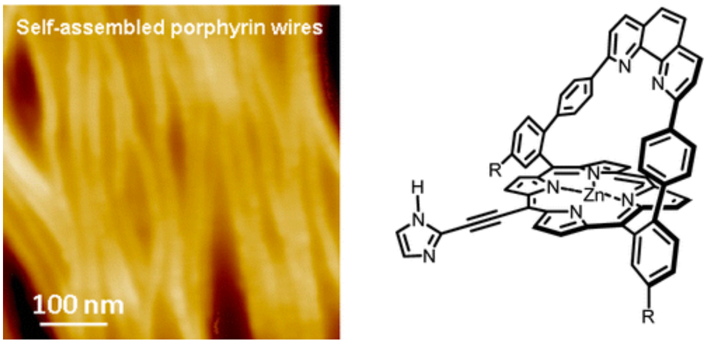
Photo-activitation triggers prochelator conjugates to inhibit metal-induced Aβ aggregation and protect cells from Aβ-related toxicity.

- Switchable Wettability Sensor for Ion Pairs Based on Calix[4]azacrown Clicking
  Feng, N.; Zhao, H.; Zhan, J.; Tian, D.; Li, H. *Org. Lett.* **2012**, *14*, 1958-1961.
  Abstract:



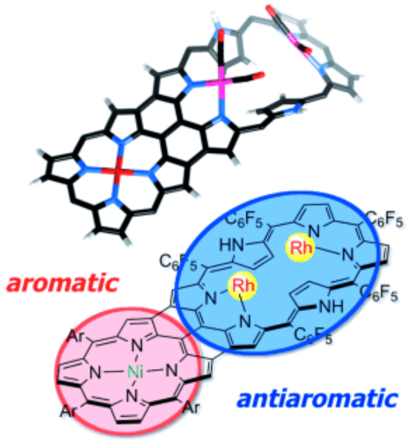
A new calix[4]azacrown is synthesized from 1,3-dipropynyloxycalix[4]arene in a good yield of 85% and was modified on a silicon surface via click chemistry to be a switchable wettability sensor for ion pairs ($[C_4mim]Cl$). A cooperative mechanism involving supramolecular interactions is proposed.

- Dynamic Assembly of Porphyrin Wires Trapped on a Highly Oriented Pyrolitic Graphite Surface
  Rauch, V.; Wytko, J. A.; Takahashi, M.; Kikkawa, Y.; Kanesato, M.; Weiss, J. *Org. Lett.* **2012**, *14*, 1998-2001.
  Abstract:



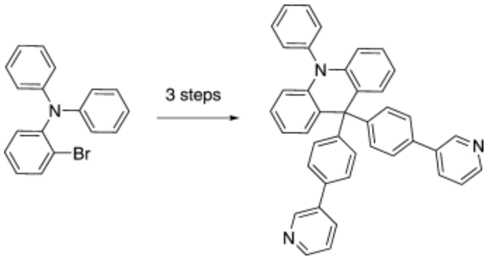
Carefully designed porphyrin building blocks assemble through selective imidazole binding in various solvents to form linear multiporphyrin objects. From a dynamic mixture of monomers, dimers, and oligomers, linear objects were observed on a highly oriented pyrolitic graphite (HOPG) surface. On the surface, the objects' morphology clearly depended on the solvent used for deposition and was modified upon heating.

- Aromatic-to-Antiaromatic Switching in Triply Linked Porphyrin Bis(rhodium(I)) Hexaphyrin Hybrids
  Tanaka, T.; Aratani, N.; Osuka, A. *Chem. Asian J.* **2012**, *7*, 889–893.
  Abstract:



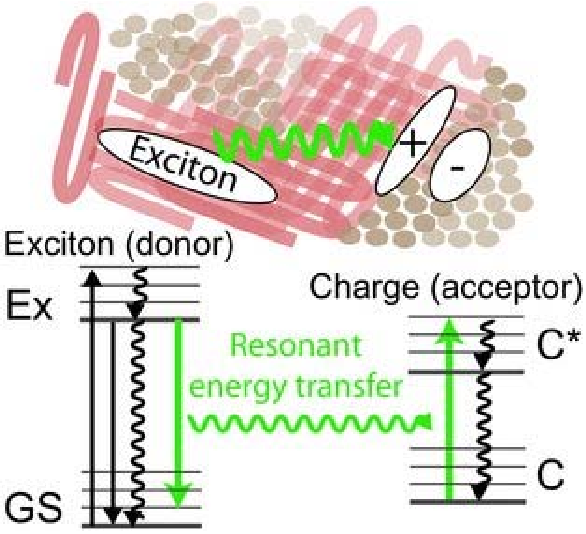
**Switch 'em up**: Two-electron oxidation and reduction switches the title complexes between aromatic and antiaromatic character (see picture). The switching is confirmed by $^1$H NMR and UV/Vis/NIR absorption spectroscopy and by cyclic voltammetry. The structure of the porphyrin–[26]hexaphyrin hybrid tape was elucidated by X-ray diffraction analysis.

- Pyridine-Modified Acridine-Based Bipolar Host Material for Green Phosphorescent Organic Light-Emitting Diodes
  Kim, M.; Lee, J. Y. *Chem. Asian J.* **2012**, *7*, 899–902.
  Abstract:



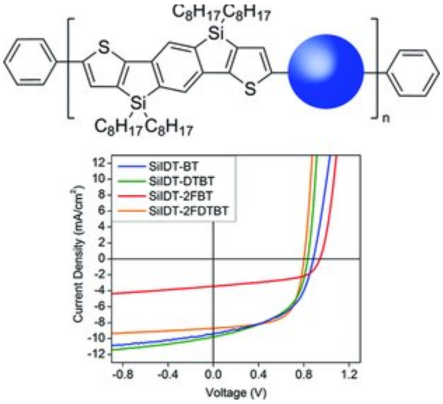
**A bipolar host material** with a phenyl-modified acridine core and a pyridine unit in the molecular structure was synthesized as the host material for green phosphorescent organic light-emitting diodes (PHOLEDs). A high triplet energy of 2.76 eV was obtained from the host and a high quantum efficiency of 13.5 % was achieved in green PHOLEDs using the acridine-based host material.

- Exciton-Charge Annihilation in Organic Semiconductor Films
  Hodgkiss, J. M.; Albert-Seifried, S.; Rao, A.; Barker, A. J.; Campbell, A. R.; Marsh, R. A.; Friend, R. H. *Adv. Funct. Mater.* **2012**, *22*, 1567–1577.
  Abstract:



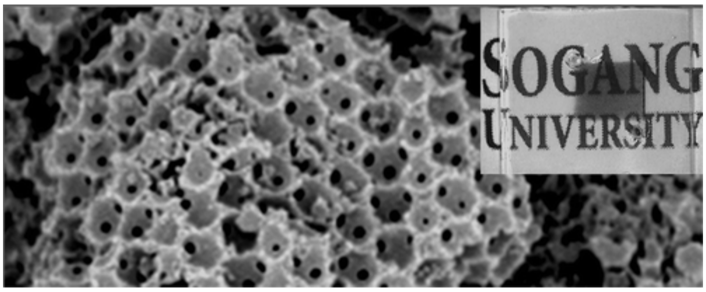
Time-resolved optical spectroscopy is used to investigate exciton-charge annihilation reactions in blended films of organic semiconductors. In donor–acceptor blends where charges are photogenerated via excitons, pulsed optical excitation can deliver a sufficient density of temporally overlapping excitons and charges for them to interact. Transient absorption spectroscopy measurements demonstrate clear signatures of exciton-charge annihilation reactions at excitation densities of ≈$10^{18}$ $cm^{-3}$. The strength of exciton-charge annihilation is consistent with a resonant energy transfer mechanism between fluorescent excitons and resonantly absorbing charges, which is shown to generally be strong in organic semiconductors. The extent of exciton-charge annihilation is very sensitive not only to fluence but also to blend morphology, becoming notably strong in donor–acceptor blends with nanomorphologies optimized for photovoltaic operation. The results highlight both the value of transient optical spectroscopy to interrogate exciton-charge annihilation reactions and the need to recognize and account for annihilation reactions in other transient optical investigations of organic semiconductors.

- Silaindacenodithiophene-Based Low Band Gap Polymers – The Effect of Fluorine Substitution on Device Performances and Film Morphologies
  Schroeder, B. C.; Huang, Z.; Ashraf, R. S.; Smith, J.; D'Angelo, P.; Watkins, S. E.; Anthopoulos, T. D.; Durrant, J. R.; McCulloch, I. *Adv. Funct. Mater.* **2012**, *22*, 1663–1670.
  Abstract:



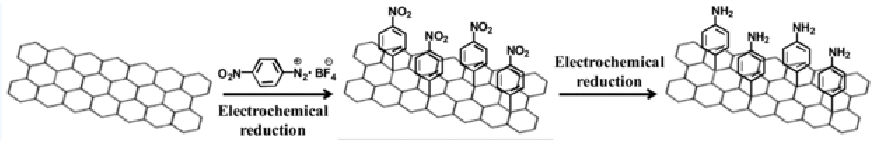
**Silaindacenodithiophene is copolymerized with** benzo[*c*][1,2,5]thiadiazole (**BT**) and 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**DTBT**), respectively their fluorinated counter parts 5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**2FBT**) and 5,6-difluoro-4,7-di(thiophen-2-yl) benzo[*c*][1,2,5]thiadiazole (**2FDTBT**). The influence of the thienyl spacers and fluorine atoms on molecular packing and active layer morphology is investigated with regard to device performances. bulk heterojunction (BHJ) solar cells based on **silaindacenodithiophene** donor-acceptor polymers achieved PCE's of 4.5% and hole mobilities of as high as 0.28 $cm^2/(V\ s)$ are achieved in an organic field-effect transistor (OFET).

- Inverse Opal Carbons for Counter Electrode of Dye-Sensitized Solar Cells
  Kang, D.-Y.; Lee, Y.; Cho, C.-Y.; Moon, J. H. *Langmuir* **2012**, *28*, 7033–7038.
  Abstract:



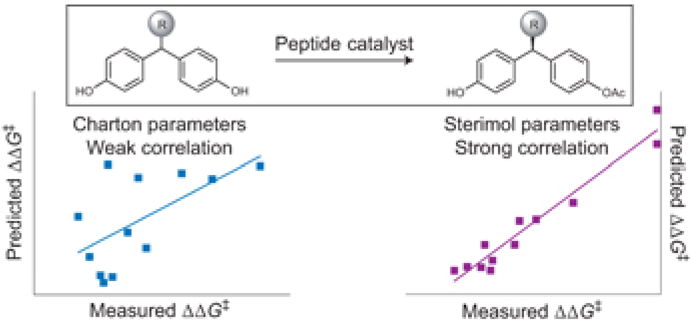
We investigated the fabrication of inverse opal carbon counter electrodes using a colloidal templating method for DSSCs. Specifically, bare inverse opal carbon, mesopore-incoporated inverse opal carbon, and graphitized inverse opal carbon were synthesized and stably dispersed in ethanol solution for spray coating on a FTO substrate. The thickness of the electrode was controlled by the number of coatings, and the average relative thickness was evaluated by measuring the transmittance spectrum. The effect of the counter electrode thickness on the photovoltaic performance of the DSSCs was investigated and analyzed by interfacial charge transfer resistance ($R_{CT}$) under EIS measurement. The effect of the surface area and conductivity of the inverse opal was also investigated by considering the increase in surface area due to the mesopore in the inverse opal carbon and conductivity by graphitization of the carbon matrix. The results showed that the FF and thereby the efficiency of DSSCs were increased as the electrode thickness increased. Consequently, the larger FF and thereby the greater efficiency of the DSSCs were achieved for mIOC and gIOC compared to IOC, which was attributed to the lower $R_{CT}$. Finally, compared to a conventional Pt counter electrode, the inverse opal-based carbon showed a comparable efficiency upon application to DSSCs.

- Electrochemistry: An Efficient Way to Chemically Modify Individual Monolayers of Graphene
  Gan, L.; Zhang, D.; Guo, X. *Small* **2012**, *8*, 1326–1330.
  Abstract:



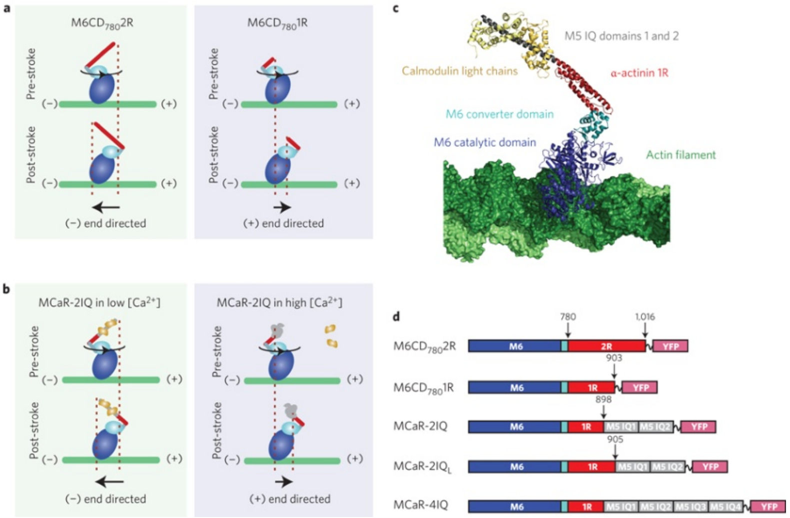
**Fast and efficient surface functionalization of graphene** is achieved by the electrochemical formation of aryl radicals from diazonium salts under mild conditions. Precise control of the ratio of electron-deficient nitro groups to electron-rich amino groups is also demostrated, potentially resulting in the controllable tuning of the electrical properties of graphenes.

- Multidimensional steric parameters in the analysis of asymmetric catalytic reactions
  Harper, K. C.; Bess, E. N.; Sigman, M. S. *Nature Chem.* **2012**, *4*, 366–374.
  Abstract:



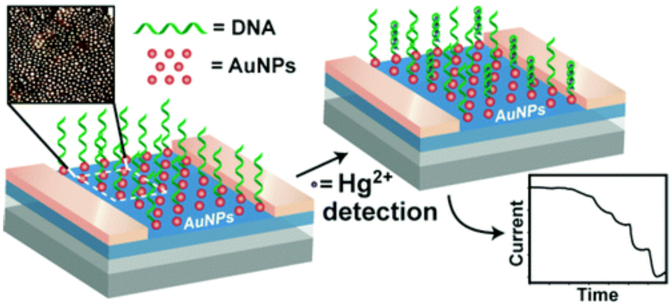
Although asymmetric catalysis is universally dependent on spatial interactions to impart specific chirality on a given substrate, examination of steric effects in these catalytic systems remains empirical. Previous efforts by our group and others have seen correlation between steric parameters developed by Charton and simple substituents in both substrate and ligand; however, more complex substituents were not found to be correlative. Here, we review and compare the steric parameters common in quantitative structure activity relationships (QSAR), a common method for pharmaceutical function optimization, and how they might be applied in asymmetric catalysis, as the two fields are undeniably similar. We re-evaluate steric/enantioselection relationships, which we previously analysed with Charton steric parameters, using the more sophisticated Sterimol parameters developed by Verloop and co-workers in a QSAR context. Use of these Sterimol parameters led to strong correlations in numerous processes where Charton parameters had previously failed. Sterimol parameterization also allows for greater mechanistic insight into the key elements of asymmetric induction within these systems.

- Engineering controllable bidirectional molecular motors based on myosin
  Chen, L.; Nakamura, M.; Schindler, T. D.; Parker, D.; Bryant, Z. *Nature Nanotech.* **2012**, *7*, 252–256.
  Abstract:



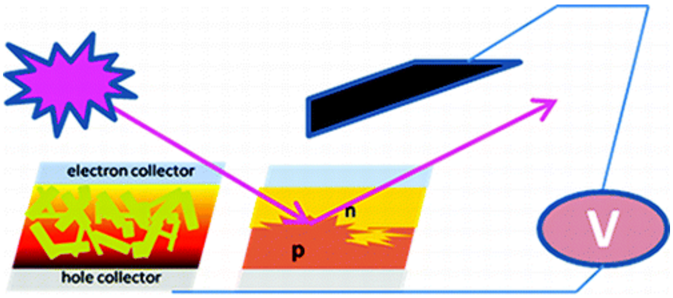
Cytoskeletal motors drive the transport of organelles and molecular cargoes within cells and have potential applications in molecular detection and diagnostic devices. Engineering molecular motors with controllable properties will allow selective perturbation of mechanical processes in living cells and provide optimized device components for tasks such as molecular sorting and directed assembly. Biological motors have previously been modified by introducing activation/deactivation switches that respond to metal ions and other signals. Here, we show that myosin motors can be engineered to reversibly change their direction of motion in response to a calcium signal. Building on previous protein engineering studies and guided by a structural model for the redirected power stroke of myosin VI, we have constructed bidirectional myosins through the rigid recombination of structural modules. The performance of the motors was confirmed using gliding filament assays and single fluorophore tracking. Our strategy, in which external signals trigger changes in the geometry and mechanics of myosin lever arms, should make it possible to achieve spatiotemporal control over a range of motor properties including processivity, stride size and branchpoint turning.

- Organic Transistors with Ordered Nanoparticle Arrays as a Tailorable Platform for Selective, In Situ Detection
  Hammock, M. L.; Sokolov, A. N.; Stoltenberg, R. M.; Naab, B. D.; Bao, Z. *ACS Nano* **2012**, *6*, 3100-3108.
  Abstract:



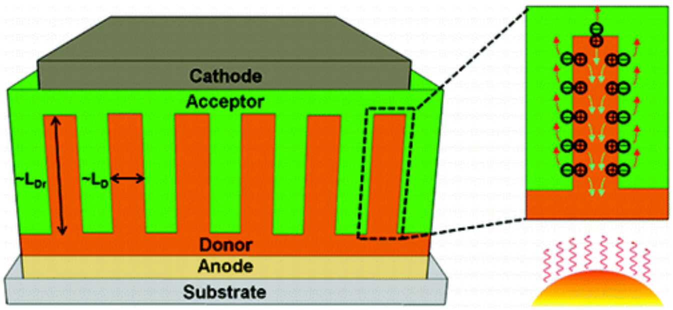
The use of organic transistors as sensing platforms provides a number of distinct advantages over conventional detection technologies, including their tunability, portability, and ability to directly transduce binding events without tedious and expensive labeling procedures. However, detection efforts using organic transistors lack a general method to uniquely specify and detect a target of interest. While highly sensitive liquid- and vapor-phase sensors have been previously reported, detection has been restricted either to the serendipitous interaction of the analyte molecules with the organic semiconductor or to the covalent functionalization of the semiconductor with receptor groups to enhance specificity. However, the former technique cannot be regularly relied upon for tailorable sensing while the latter may result in unpredictable decreases in electronic performance. Thus, a method to provide modular receptor sites on the surface of an organic transistor without damaging the device will significantly advance the field, especially regarding biological species detection. In this work, we utilized a block copolymer to template ordered, large-area arrays of gold nanoparticles, with sub-100 nm center-to-center spacing onto the surface of an organic transistor. This highly modular platform is designed for orthogonal modification with a number of available chemical and biological functional groups by taking advantage of the well-studied gold–thiol linkage. Herein, we demonstrate the functionalization of gold nanoparticles with a mercury-binding oligonucleotide sequence. Finally, we demonstrate the highly selective and robust detection of mercury(II) using this platform in an underwater environment.

- Next-Generation Polymer Solar Cell Materials: Designed Control of Interfacial Variables
  Lecover, R.; Williams, N.; Markovic, N.; Reich, D. H.; Naiman, D. Q.; Katz, H. E. *ACS Nano* **2012**, *6*, 2865-2870.
  Abstract:



Organic bulk heterojunction solar cells (BHJSCs) are the focus of a burgeoning research effort. While extensive characterization is performed in the course of many reported experimental studies, correlation of performance and physical parameters among studies done in different laboratories is low, pointing out the need to address some aspects of BHJSC active materials that have received relatively little attention. This Perspective describes how a new polymer additive series described by Lobez *et al.* in this issue of *ACS Nano*, along with some emerging morphological tools and scanning electronic nanoprobes, can help fill in some of this needed insight. A brief statistical discussion of interstudy correlations and a summary of past work on additives and interfacial studies are presented.

- Nanoimprinted Polymer Solar Cell
  Yang, Y.; Mielczarek, K.; Aryal, M.; Zakhidov, A.; Hu, W. *ACS Nano* **2012**, *6*, 2877-2892.
  Abstract:



Among the various organic photovoltaic devices, the conjugated polymer/fullerene approach has drawn the most research interest. The performance of these types of solar cells is greatly determined by the nanoscale morphology of the two components (donor/acceptor) and the molecular orientation/crystallinity in the photoactive layer. A vertically bicontinuous and interdigitized heterojunction between donor and acceptor has been regarded as one of the ideal structures to enable both efficient charge separation and transport. Synergistic control of polymer orientation in the nanostructured heterojunction is also critical to improve the performance of polymer solar cells. Nanoimprint lithography has emerged as a new approach to simultaneously control both the heterojunction morphology and polymer chains in organic photovoltaics. Currently, in the area of nanoimprinted polymer solar cells, much progress has been achieved in the fabrication of nanostructured morphology, control of molecular orientation/crystallinity, deposition of acceptor materials, patterned electrodes, understanding of structure–property correlations, and device performance. This review article summarizes the recent studies on nanoimprinted polymer solar cells and discusses the outstanding challenges and opportunities for future work.