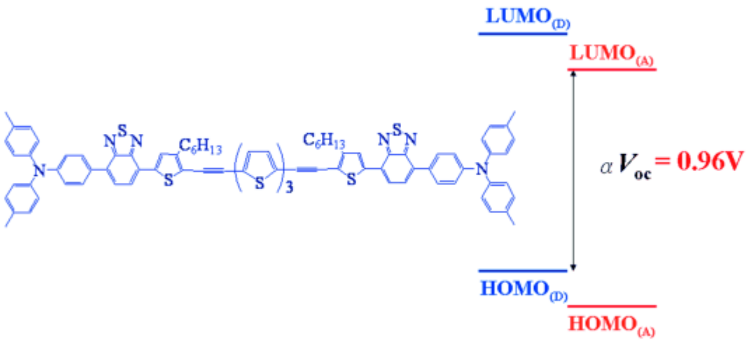
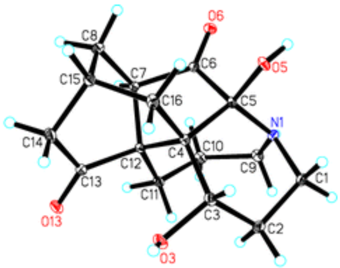
- Oligothiophene-Bridged Bis(arylene ethynylene) Small Molecules for Solution-Processible Organic Solar Cells with High Open-Circuit Voltage
  Liu, Q.; Zhan, H.; Ho, C.-L.; Dai, F.-R.; Fu, Y.; Xie, Z.; Wang, L.; Li, J.-H.; Yan, F.; Huang, S.-P.; Wong, W.-Y. *Chem. Asian J.* **2013**, *8,* 1892-1900.
  Abstract:



A new series of conjugated oligothiophene-bridged bis(arylene ethynylene) small molecules have been designed, synthesized, and characterized by photophysical, electrochemical and computational methods. These compounds were found to have optimal LUMO levels that ensure effective charge transfer from these compounds to [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{70}BM$). They were utilized as good electron-donor materials that can be blended with electron-acceptor $PC_{70}BM$ in the fabrication of solution-processed molecular bulk heterojunction (BHJ) solar cells. All of these BHJ devices showed very high open-circuit voltage (V_{oc}) of 0.90–0.97 V, and the best power conversion efficiency achieved was 3.68 %. The high V_{oc} is consistent with the deeper low-lying HOMO level and is relatively insensitive to the donor : acceptor blend ratio. The spin-coated thin films of these small molecules showed p-channel field-effect charge transport with the hole mobilities of up to 2.04×10^{-4} $cm^2\,V^{-1}\,s^{-1}$. These compounds illuminate the potential of solution-processible small-molecular aryl acetylide compounds for efficient power generation in photovoltaic implementation.

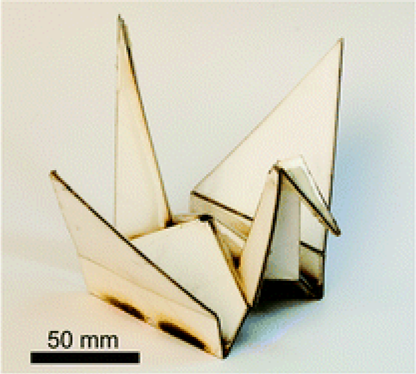
- Isopalhinine A, a Unique Pentacyclic *Lycopodium* Alkaloid from *Palhinhaea cernua*
  Dong, L.-B.; Gao, X.; Liu, F.; He, J.; Wu, X.-D.; Li,Y.; Zhao, Q.-S. *Org. Lett.* **2013**, *15,* 3570-3573.
  Abstract:

isopalhinine A (**1**)



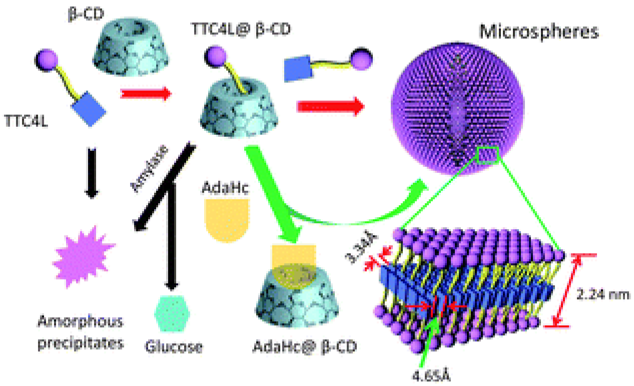
A new pentacyclic (5/6/6/6/7) Lycopodium alkaloid named isopalhinine A (1), which possesses a sterically congested architecture built with a tricyclo[4.3.1.$0^{3,7}$]decane (isotwistane) moiety and a 1-azabicyclo[4.3.1]decane moiety, and palhinines B (2) and C (3) were isolated from Palhinhaea cernua. The structure and absolute configuration of 1 were elucidated by a combination of NMR spectra, optical rotation calculation, and X-ray diffraction experiment. A possible biogenetic pathway was also proposed.

- Self-folding with shape memory composites
  Felton, S. M.; Tolley, M. T.; Shin, B.; Onal, C. D.; Demaine, E. D.; Rus, D.; Wood, R. J. *Soft Matter* **2013,** *9*, 7688-7694.
  Abstract:



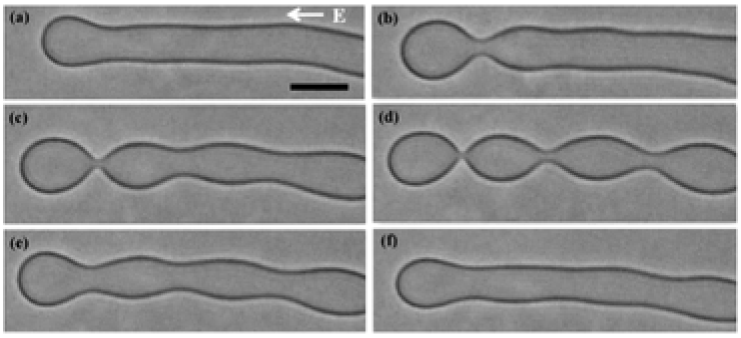
Origami-inspired manufacturing can produce complex structures and machines by folding two-dimensional composites into three-dimensional structures. This fabrication technique is potentially less expensive, faster, and easier to transport than more traditional machining methods, including 3-D printing. Self-folding enhances this method by minimizing the manual labor involved in folding, allowing for complex geometries and enabling remote or automated assembly. This paper demonstrates a novel method of self-folding hinges using shape memory polymers (SMPs), paper, and resistive circuits to achieve localized and individually addressable folding at low cost. A model for the torque exerted by these composites was developed and validated against experimental data, in order to determine design rules for selecting materials and designing hinges. Torque was shown to increase with SMP thickness, resistive circuit width, and supplied electrical current. This technique was shown to be capable of complex geometries, as well as locking assemblies with sequential folds. Its functionality and low cost make it an ideal basis for a new type of printable manufacturing based on two-dimensional fabrication techniques.

- A case of cyclodextrin-catalyzed self-assembly of an amphiphile into microspheres
  Zhao, L.; Jiang, L.; Han, Y.; Xian, Z.; Huang, J.; Yan, Y. *Soft Matter* **2013,** *9*, 7710-7717.
  Abstract:



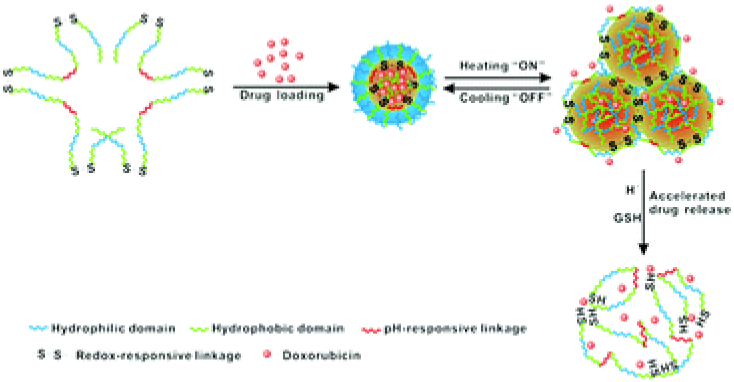
One of the recent challenges in nanotechnology is the development of 'catalyzed self-assembly'. So far successful cases are still scarce. In this work we report the delicate case of a cyclodextrin (CD) catalyzed self-assembly of the terthiophene-containing amphiphile TTC4L into microspheres. TT4CL can form precipitates when CDs are not present, whereas it self-assembles into microspheres in the presence of CDs. The CDs were not involved into the microspheres, but they stayed in the supernate in the form of the TTC4L@CD inclusion complex. This complex may further transform into microspheres in the presence of a competitive guest. ITC and ^{1}H NMR measurements suggest that part of the terthiophene group binds weakly with CDs. We expect that this weak binding interferes with the quick stacking of TTC4L, so that a 'slow' arrangement of the terthiophene moiety becomes possible which finally leads to the formation of microspheres. Our results not only provide a new solid example of a catalyzed molecular self-assembly, but also envisage a new paradigm for the possible role of CDs in supramolecular chemistry.

- Electric field induced pearling instability in cylindrical vesicles
  Sinha, K. P.; Gadkari, S.; Thaokar, R. M., *Soft Matter* **2013,** *9*, 7274-7293.
  Abstract:



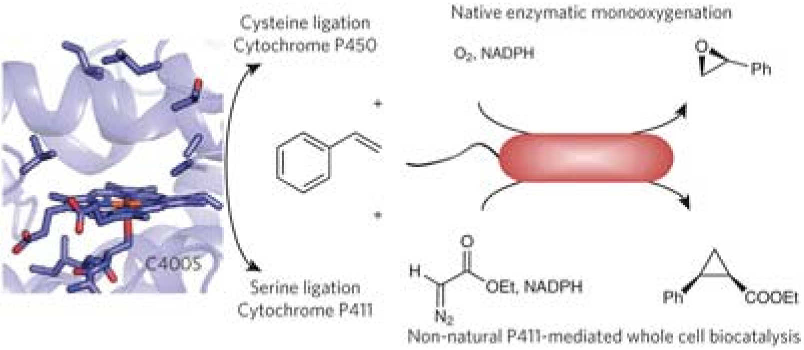
A theoretical and experimental study on the effect of an electric field on a cylindrical vesicle is presented. Experiments show that a cylindrical vesicle when subjected to an axial electric field, displays an axisymmetric pearling instability (the Rayleigh–Plateau instability) beyond a threshold electric field. Unlike fluid jets, in which electric fields are known to stabilize the Rayleigh–Plateau instability, cylindrical vesicles exhibit dual effects of electric field. The tension required to induce the instability is produced by the electric field. At higher values of field strength however, a stabilizing action of the electric field is seen. This renders the fastest growing wavenumber, k_m, independent of the electric field at high electric field strength. Theoretical results predict, albeit qualitatively, a weak dependence of k_m on the electric field. It also explains the substantially higher experimental values of k_m (around 0.64–1.0) observed in vesicles as compared to k_m = 0.56 for fluid cylinders. Theory and experiments show that the instability is induced using a much lower value of pulsed DC field as compared to an AC field. At long times, a pearled state is observed, with the pearls separated by short cylindrical nanotubules. The pearled structure is converted into crowded, taut spherical globules, which are connected by very thin short bilayer cylinders when the field is switched off, before they eventually disappear and the original cylindrical vesicle is recovered. All of the morphological changes in cylindrical vesicles in electric fields are completely reversible. This study demonstrates the dominance of tension and stretching at short and long timescales respectively.

- On–off switchable drug release from multi-responsive degradable poly(ether urethane) nanoparticles
  Wang, Y.; Wu, G.; Li, X.; Wang, Y.; Gao, H.; Ma, J. *Biomater. Sci.* **2013**, *1*, 614-624.
  Abstract:



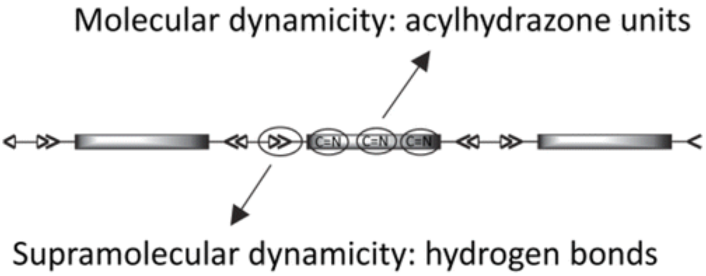
A novel on–off switchable drug-release system was developed based on a series of multi-responsive degradable poly(ether urethane)s. The multi-segmented poly(ether urethane)s were synthesized through a simple one-pot condensation polymerization of poly(ethylene glycol), 2,2′-dithiodiethanol, *N*-methyldiethanolamine and hexamethylene diisocyanate. The obtained amphiphilic copolymers could self-assemble into nanoparticles in aqueous solution, which were responsive to temperature, pH and redox potential with tailored phase-transition temperature. The whole process for the responsive behaviours of the poly(ether urethane) nanoparticles was confirmed by light transmission, dynamic light scattering, nuclear magnetic resonance and transmission electron microscopy. The nanoparticles could encapsulate hydrophobic drugs and showed a temperature-triggered accelerated and complete drug-release profile. The mechanism of the temperature-triggered multi-responsive accelerated drug release was also elucidated. These results presented the polymeric nanoparticles as an effective multi-responsive degradable nanocarrier to achieve on–off drug release.

- A serine-substituted P450 catalyzes highly efficient carbene transfer to olefins in vivo
  Coelho, P. S.; Wang, Z. J.; Ener, M. E.; Baril, S. A.; Kannan, A.; Arnold, F. H.; Brustad, E. M. *Nature Chem. Biol.* **2013**, *9*, 485–487.
  Abstract:



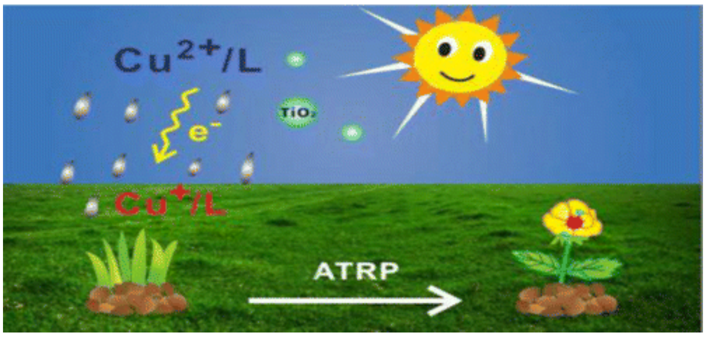
Whole-cell catalysts for non-natural chemical reactions will open new routes to sustainable production of chemicals. We designed a cytochrome 'P411' with unique serine-heme ligation that catalyzes efficient and selective olefin cyclopropanation in intact *Escherichia coli* cells. The mutation C400S in cytochrome $P450_{BM3}$ gives a signature ferrous CO Soret peak at 411 nm, abolishes monooxygenation activity, raises the resting-state Fe^{III}-to-Fe^{II} reduction potential and substantially improves NAD(P)H-driven activity.

- Double Dynamic Supramolecular Polymers of Covalent Oligo-Dynamers
  Schaeffer, G.; Buhler, E.; Candau, S. J.; Lehn, J.-M. *Macromolecules* **2013**, *46*, 5664-5671.
  Abstract:



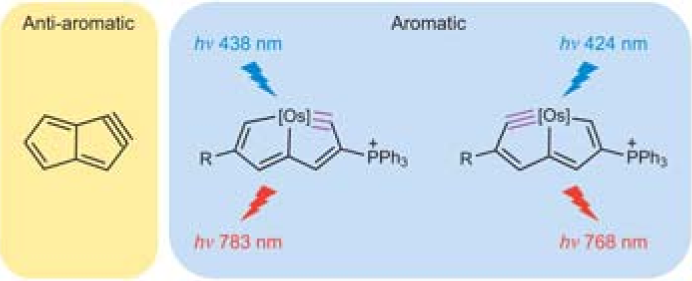
Double-dynamic polymers, incorporating both molecular and supramolecular dynamic features ("double dynamers") have been generated, where these functions are present in a nonstoichiometric ratio in the main chain of the polymer. It has been achieved by (1) the formation of covalent oligo-dynamers in which the monomers are connected by reversible covalent interactions and (2) the association of these oligomers through supramolecular interactions (hydrogen bonding). This procedure leads to the formation of an entity that can be seen as a supramolecular polymer of molecular oligo-dynamers. It thus combines two types of dynamic processes that do not simply alternate in the polymeric chain but may be incorporated in various ratios. These non-alternating double dynamic polymers have been generated by sequential construction and the different steps have been characterized by NMR spectroscopy, mass spectrometry and light scattering.

- Ultraviolet Light-Induced Surface-Initiated Atom-Transfer Radical Polymerization
  Yan, J.; Li, B.; Zhou, F.; Liu, W. *ACS Macro Lett.* **2013**, *2*, 592-596.
  Abstract:



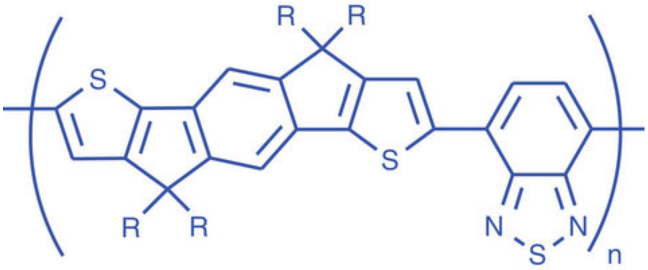
UV light-induced surface-initiated atom-transfer radical polymerization (ATRP) was reported. This method uses TiO_2 nanoparticles as photoactive materials to reduce Cu(II)/L to a Cu(I)/L complex under UV irradiation by a one-electron transfer process for ATRP with multiple usage of monomer solutions. The growth of polymer brushes can be manipulated by either varying the content of photoactive materials or regulating the irradiation intensity, thereby yielding polymer brushes with controllable thickness, composition, and architecture.

- Stabilization of anti-aromatic and strained five-membered rings with a transition metal
  Zhu, C.; Li, S.; Luo, M.; Zhou, X.; Niu, Y.; Lin, M.; Zhu, J.; Cao, Z.; Lu, X.; Wen, T.; Xie, Z.; Schleyer, P. v R.; Xia, H. *Nature Chem.* **2013**, *5*, 698–703.
  Abstract:



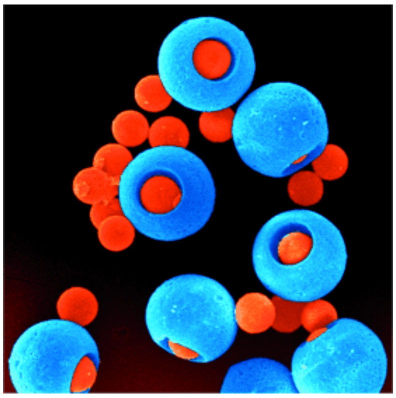
Anti-aromatic compounds, as well as small cyclic alkynes or carbynes, are particularly challenging synthetic goals. The combination of their destabilizing features hinders attempts to prepare molecules such as pentalyne, an 8π-electron anti-aromatic bicycle with extremely high ring strain. Here we describe the facile synthesis of osmapentalyne derivatives that are thermally viable, despite containing the smallest angles observed so far at a carbyne carbon. The compounds are characterized using X-ray crystallography, and their computed energies and magnetic properties reveal aromatic character. Hence, the incorporation of the osmium centre not only reduces the ring strain of the parent pentalyne, but also converts its Hückel anti-aromaticity into Craig-type Möbius aromaticity in the metallapentalynes. The concept of aromaticity is thus extended to five-membered rings containing a metal–carbon triple bond. Moreover, these metal–aromatic compounds exhibit unusual optical effects such as near-infrared photoluminescence with particularly large Stokes shifts, long lifetimes and aggregation enhancement.

- Molecular origin of high field-effect mobility in an indacenodithiophene–benzothiadiazole copolymer
  Zhang, X.; Bronstein, H.; Kronemeijer, A. J.; Smith, J.; Kim, Y.; Kline, R. J.; Richter, L. J.; Anthopoulos, T. D.; Sirringhaus, H.; Song, K.; Heeney, M.; Zhang, W.; McCulloch, I.; DeLongchamp, D. M. *Nature Commun.* **2013**, *4*, 2238.
  Abstract:



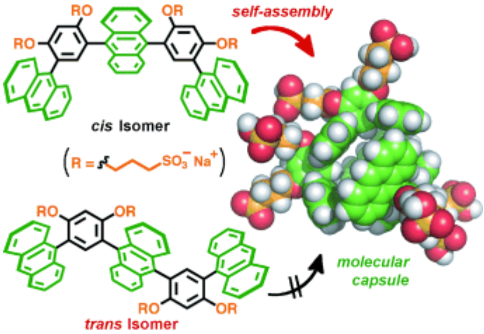
One of the most inspiring and puzzling developments in the organic electronics community in the last few years has been the emergence of solution-processable semiconducting polymers that lack significant long-range order but outperform the best, high-mobility, ordered semiconducting polymers to date. Here we provide new insights into the charge-transport mechanism in semiconducting polymers and offer new molecular design guidelines by examining a state-of-the-art indacenodithiophene–benzothiadiazole copolymer having field-effect mobility of up to 3.6 $cm^2\,V^{-1}\,s^{-1}$ with a combination of diffraction and polarizing spectroscopic techniques. Our results reveal that its conjugated planes exhibit a common, comprehensive orientation in both the non-crystalline regions and the ordered crystallites, which is likely to originate from its superior backbone rigidity. We argue that charge transport in high-mobility semiconducting polymers is quasi one-dimensional, that is, predominantly occurring along the backbone, and requires only occasional intermolecular hopping through short π-stacking bridges.

- Hole–Shell Microparticles from Controllably Evolved Double Emulsions
  Wang, W.; Zhang, M.-J.; Xie, R.; Ju, X.-J.; Yang, C.; Mou, C.-L.; Weitz, D. A.; Chu, L.-Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 8084–8087.
  Abstract:



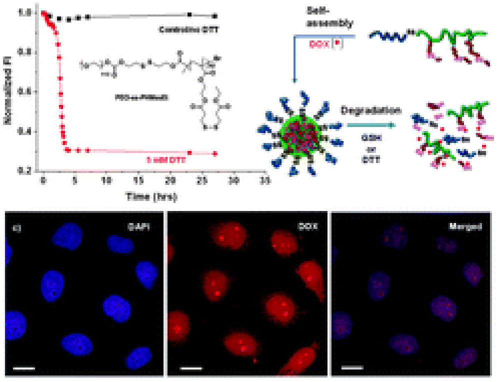
Hole in one! Hole–shell microparticles (blue, see picture) with controllable structures and flexible internal surfaces have been fabricated from W/O/W emulsions. These microparticles could be used as microcontainers for the controlled capture/release of molecules, microsphere classification/separation, confined cell culture, or as microreactors for catalysis.

- Atroposelective Self-Assembly of a Molecular Capsule from Amphiphilic Anthracene Trimers
  Suzuki, A.; Kondo, K.; Akita, M.; Yoshizawa, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 8120–8123.
  Abstract:



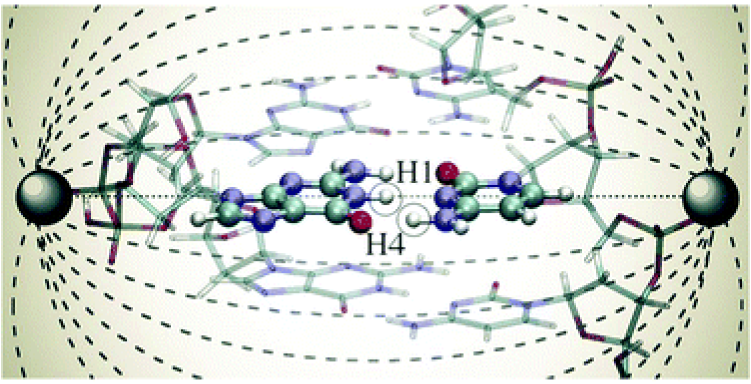
Atroposelective formation: Selective formation of a molecular capsule was demonstrated from an amphiphilic *cis*-atropisomer bearing three anthracene rings and four sulfonate groups through hydrophobic and aromatic–aromatic interactions. The dimeric capsule binds small guest molecules; the resultant host–guest complexes exhibit ground-state charge-transfer interactions accompanied by changes in host emission.

- A dual location stimuli-responsive degradation strategy of block copolymer nanocarriers for accelerated release
  Chan, N.; Khorsand, B.; Aleksaniana, S.; Oh, J. K. *Chem. Commun*. **2013**, *49*, 7534-7536.
  Abstract:



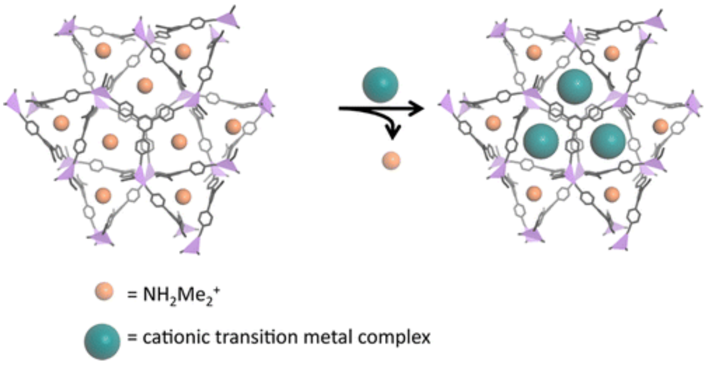
A new strategy that centers on the incorporation of stimuli-responsive cleavable linkages in dual or multiple locations as in both micellar cores and at polymer/solution interfaces leading to synergistically enhanced release of encapsulated anticancer drugs in cancer cells.

- Electric field induced DNA damage: an open door for selective mutations
  Cerón-Carrasco, J. P.; Jacquemin, D. *Chem. Commun*. **2013**, *49*, 7578-7580.
  Abstract:



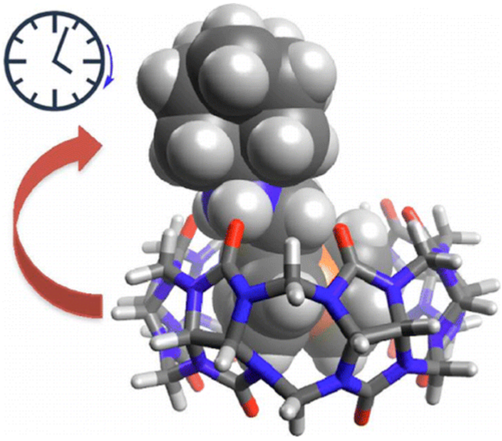
Intense electric fields activate the mutagenic mechanism of a single guanine–cytosine base pair. Would they be able to induce a permanent mutation in real DNA? This question is addressed here by modeling a DNA-embedded fragment with state-of-the-art theoretical tools. We show how DNA can, in principle, be mutated if an appropriate electric field is applied.

- Heterogenization of Homogeneous Catalysts in Metal–Organic Frameworks via Cation Exchange
  Genna, D. T.; Wong-Foy, A. G.; Matzger, A. J.; Sanford, M. S. *J. Am. Chem. Soc.* **2013***, 135,* 10586–10589.
  Abstract:



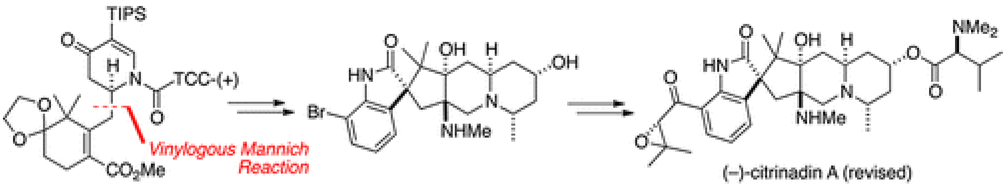
This paper describes the heterogenization of single-site transition-metal catalysts in metal–organic frameworks (MOFs) via cation exchange. A variety of cationic complexes of Pd, Fe, Ir, Rh, and Ru have been incorporated into ZJU-28, and the new materials have been characterized by optical microscopy, inductively coupled plasma optical emission spectroscopy, and powder X-ray diffraction. MOF-supported [Rh(dppe)(COD)]BF_4 catalyzes the hydrogenation of 1-octene to n-octane. The activity of this supported catalyst compares favorably to its homogeneous counterpart, and it can be recycled at least four times. Overall, this work provides a new and general approach for supporting transition-metal catalysts in MOFs.

- Detection of Isomeric Microscopic Host–Guest Complexes. A Time-Evolving Cucurbit[7]uril Complex
  Tootoonchi, M. H.; Yi, S.; Kaifer, A. E. *J. Am. Chem. Soc.* **2013***, 135,* 10804–10809.
  <u>Abstract:</u>



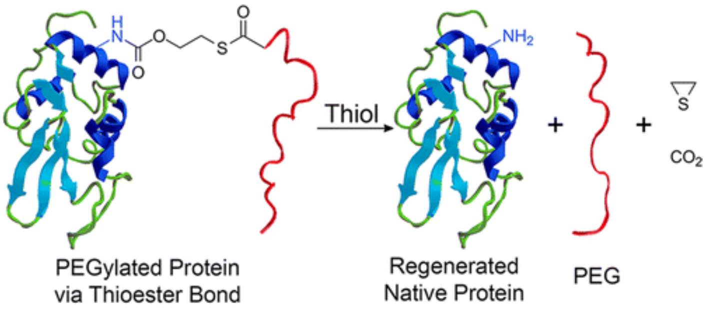
The formation of inclusion complexes between the cucurbit[7]uril host and a cationic guest containing ferrocenylmethyl and adamantyl residues connected to an ammonium nitrogen initially leads to an 1:1 mixture of two isomeric microscopic complexes, which evolves as a function of time toward the thermodynamically stable mixture, dominated by the adamantyl-included complex.

- Enantioselective Total Synthesis of (−)-Citrinadin A and Revision of Its Stereochemical Structure
  Bian, Z.; Marvin, C. C.; Martin, S. F. *J. Am. Chem. Soc.* **2013**, *135,* 10886–10889.
  <u>Abstract:</u>



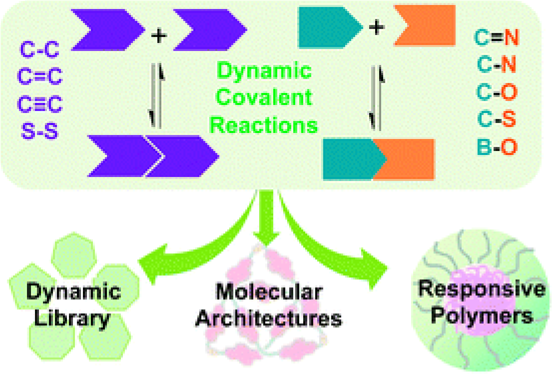
The first enantioselective total synthesis of (−)-citrinadin A has been accomplished in 20 steps from commercially available materials via an approach that minimizes refunctionalization and protection/deprotection operations. The cornerstone of this synthesis features an asymmetric vinylogous Mannich addition of a dienolate to a chiral pyridinium salt to set the initial chiral center. A sequence of substrate-controlled reactions, including a highly stereoselective epoxidation/ring-opening sequence and an oxidative rearrangement of an indole to furnish a spirooxindole, are then used to establish the remaining stereocenters in the pentacyclic core of (−)-citrinadin A. The successful synthesis of citrinadin A led to a revision of the stereochemical structure of the core substructure of the citrinadins.

- Tunable Thioesters as “Reduction” Responsive Functionality for Traceless Reversible Protein PEGylation
  Chen, J.; Zhao, M.; Feng, F.; Sizovs, A.; Wang, J. *J. Am. Chem. Soc.* **2013**, *135*, 10938–10941.
  <u>Abstract:</u>



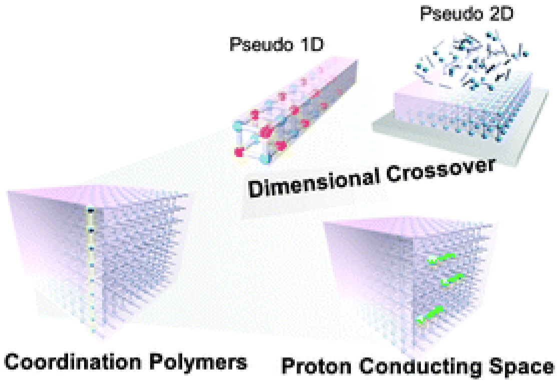
Disulfide has been the only widely used functionality to serve as a reduction responsive trigger in drug delivery. We introduce thioester as a novel thiol responsive chemistry for drug delivery, whose reactivity can be conveniently modulated by choosing the appropriate steric environment around the thioester. Compared with disulfides, thioesters are facile to synthesize and have an order of magnitude broader kinetic tunability. A novel traceless reversible protein PEGylation reagent is developed based on thioester chemistry.

- Recent advances in dynamic covalent chemistry
  Jin, Y.; Yu, C.; Denmana, R. J.; Zhang, W. *Chem. Soc. Rev.* **2013**, *42*, 6634-6654.
  <u>Abstract:</u>



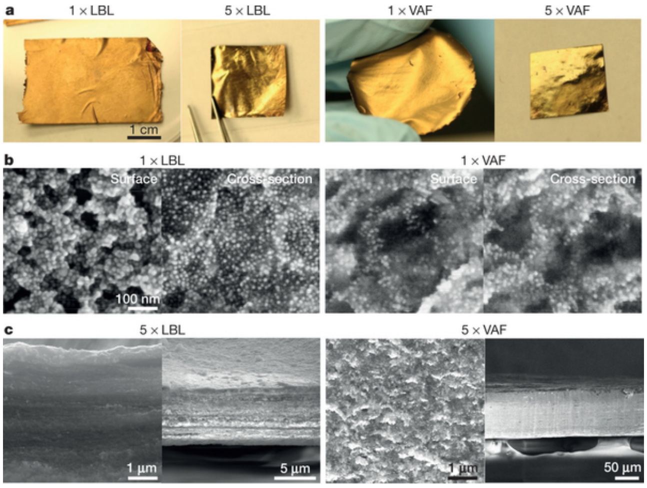
Dynamic covalent chemistry (DCvC) has been strongly integrated into diverse research fields, and has enabled easy access to a variety of combinatorial libraries, 2-D macrocycles, and 3-D molecular cages that target many important applications, such as drug discovery, biotechnology, molecular separation, light harvesting, *etc.* DCvC relies on the reversible formation and breaking of rather strong covalent bonding within molecules. Therefore it combines the error-correction capability of supramolecular chemistry and the robustness of covalent bonding. Compared to those supramolecular interactions, dynamic covalent reactions usually have slower kinetics and require the assistance of catalysts to achieve rapid equilibrium. Although the scope of dynamic covalent reactions is rapidly expanding, the reversible reactions suitable for DCvC are still very limited. The identification and development of new dynamic reactions and catalysts would be critical for the further advancement of DCvC. This review covers the recent development of dynamic covalent reactions as well as their applications.

- Designer coordination polymers: dimensional crossover architectures and proton conduction
  Yamada, T.; Otsubo,K.; Makiurac, R.; Kitagawa, H. *Chem. Soc. Rev.* **2013**, *42*, 6655-6669.
  Abstract:



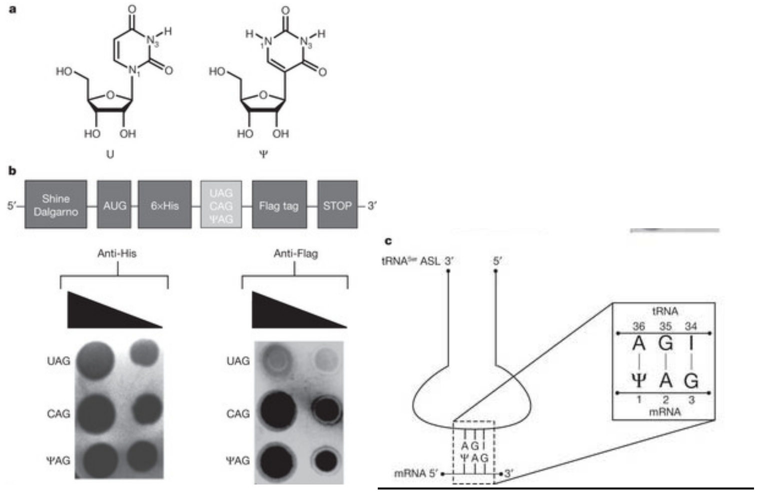
Coordination polymers (CPs) have large degrees of freedom in framework compositions and in the structures and environment of the inner pores. This review focuses on the recent significant progress achieved by controlling these degrees of freedom. Two breakthroughs are reviewed for constructing sophisticated structures of CP frameworks, especially in dimensional crossover regions. The first is the synthesis of quasi one-dimensional halogen-bridged coordinative tubes by applying state-of-the-art techniques of coordination chemistry. The electronic state of the coordinative tube was studied by structural, spectroscopic and theoretical methods and found to be distinct from conventional one-dimensional systems. The second breakthrough is the achievement of a quasi-two-dimensional architecture by combining Langmuir–Blodgett and layer-by-layer methods. Two-dimensional LB CP films were prepared on liquid; the films were stacked layer by layer, and a crystalline quasi-two-dimensional structure was constructed. This review also covers the design of the environment of the inner pore, where hydrogen bond networks with various acidic sites were modified. By appropriate design of the hydrogen bond network, proton-conductive CPs are invented, which are summarized in this review. Types of proton donor sites are discussed and classified, and superprotonic conductive CPs were achieved in these investigations. These results will provide new strategies for constructing functional materials for smart devices.

- Stretchable nanoparticle conductors with self-organized conductive pathways
  Kim, Y.; Zhu, J.; Yeom, B.; Di Prima, M.; Su, X.; Kim, J.-G.; Jo Yoo, S.; Uher, C.; Kotov, N. A. *Nature* **2013**, *500*, 59–63.
  Abstract:



Research in stretchable conductors is fuelled by diverse technological needs. Flexible electronics, neuroprosthetic and cardiostimulating implants, soft robotics and other curvilinear systems require materials with high conductivity over a tensile strain of 100 per cent. Furthermore, implantable devices or stretchable displays need materials with conductivities a thousand times higher while retaining a strain of 100 per cent. However, the molecular mechanisms that operate during material deformation and stiffening make stretchability and conductivity fundamentally difficult properties to combine. The macroscale stretching of solids elongates chemical bonds, leading to the reduced overlap and delocalization of electronic orbitals. This conductivity–stretchability dilemma can be exemplified by liquid metals, in which conduction pathways are retained on large deformation but weak interatomic bonds lead to compromised strength. The best-known stretchable conductors use polymer matrices containing percolated networks of high-aspect-ratio nanometre-scale tubes or nanowires to address this dilemma to some extent. Further improvements have been achieved by using fillers (the conductive component) with increased aspect ratio, of all-metallic composition, or with specific alignment (the way the fillers are arranged in the matrix). However, the synthesis and separation of high-aspect-ratio fillers is challenging, stiffness increases with the volume content of metallic filler, and anisotropy increases with alignment. Pre-strained substrates, buckled microwires and three-dimensional microfluidic polymer networks have also been explored. Here we demonstrate stretchable conductors of polyurethane containing spherical nanoparticles deposited by either layer-by-layer assembly or vacuum-assisted flocculation. High conductivity and stretchability were observed in both composites despite the minimal aspect ratio of the nanoparticles. These materials also demonstrate the electronic tunability of mechanical properties, which arise from the dynamic self-organization of the nanoparticles under stress. A modified percolation theory incorporating the self-assembly behaviour of nanoparticles gave an excellent match with the experimental data.

- Unusual base pairing during the decoding of a stop codon by the ribosome
  Fernández, I. S.; Leong Ng, C.; Kelley, A. C.; Wu, G.; Yu, Y.-T.; Ramakrishnan, V. *Nature* **2013**, *500*, 107–110.
  Abstract:



During normal translation, the binding of a release factor to one of the three stop codons (UGA, UAA or UAG) results in the termination of protein synthesis. However, modification of the initial uridine to a pseudouridine (Ψ) allows efficient recognition and read-through of these stop codons by a transfer RNA (tRNA), although it requires the formation of two normally forbidden purine–purine base pairs. Here we determined the crystal structure at 3.1 Å resolution of the 30S ribosomal subunit in complex

with the anticodon stem loop of $tRNA^{Ser}$ bound to the ΨAG stop codon in the A site. The ΨA base pair at the first position is accompanied by the formation of purine–purine base pairs at the second and third positions of the codon, which show an unusual Watson–Crick/Hoogsteen geometry. The structure shows a previously unsuspected ability of the ribosomal decoding centre to accommodate non-canonical base pairs.