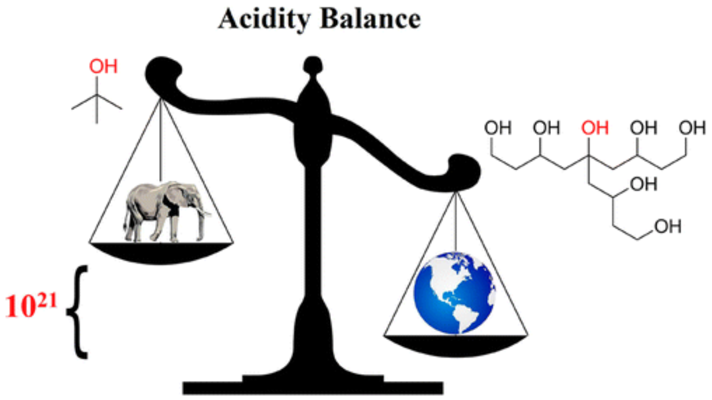
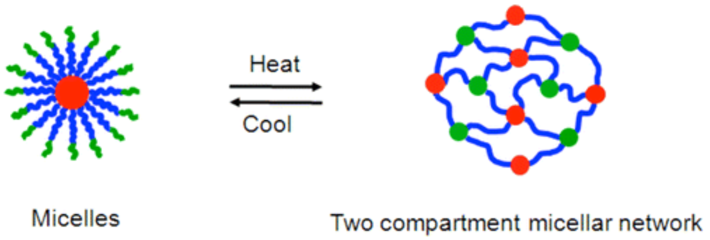
- Effect of Hydrogen Bonds on pKa Values: Importance of Networking
  Shokri, A.; Abedin, A.; Fattahi, A. ; Kass, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 10646–10650.
  Abstract:



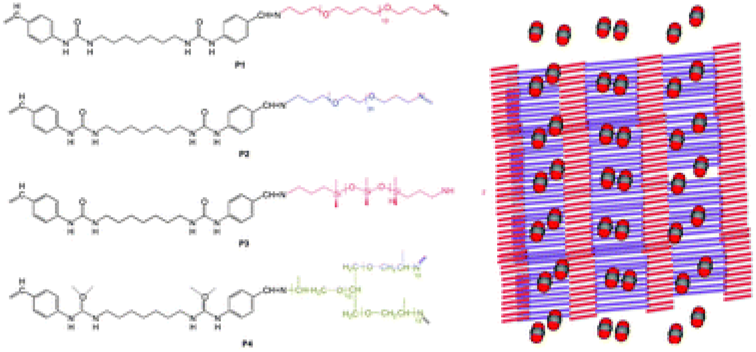
The pK_a of an acyclic aliphatic heptaol ($(HOCH_2CH_2CH(OH)CH_2)_3COH$) was measured in DMSO, and its gas-phase acidity is reported as well. This tertiary alcohol was found to be 10^{21} times more acidic than *tert*-butyl alcohol in DMSO and an order of magnitude more acidic than acetic acid (i.e., pK_a = 11.4 vs 12.3). This can be attributed to a 21.9 kcal mol^{-1} stabilization of the charged oxygen center in the conjugate base by three hydrogen bonds and another 6.3 kcal mol^{-1} stabilization resulting from an additional three hydrogen bonds between the uncharged primary and secondary hydroxyl groups. Charge delocalization by both the first and second solvation shells may be used to facilitate enzymatic reactions. Acidity constants of a series of polyols were also computed, and the combination of hydrogen-bonding and electron-withdrawing substituents was found to afford acids that are predicted to be extremely acidic in DMSO (i.e., pK_a < 0). These hydrogen bond enhanced acids represent an attractive class of Brønsted acid catalysts.

- Efficient Formation of Multicompartment Hydrogels by Stepwise Self-Assembly of Thermoresponsive ABC Triblock Terpolymers
  Zhou, C.; Hillmyer, M. A.; Lodge, T. P. *J. Am. Chem. Soc.* **2012**, *134*, 10365–10368.
  Abstract:



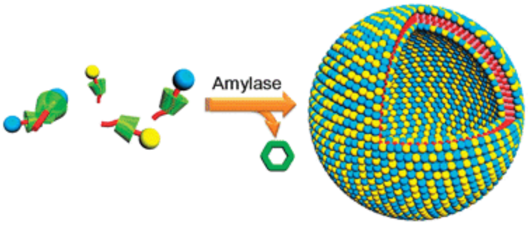
The gelation behavior of a poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide)-*b*-poly(*N*-isopropylacrylamide) (PON) triblock terpolymer and a poly(*N*-isopropylacrylamide)-*b*-poly(ethylene oxide)-*b*-poly(*N*-isopropylacrylamide) (NON) triblock copolymer was studied by rheology over the concentration range 1–5 wt %. In comparison to the NON copolymer, gelation of the PON terpolymer was achieved at a much lower concentration, with a much sharper sol–gel transition. This is due to a stepwise gelation of PON terpolymers involving micellization at room temperature and gelation at elevated temperatures. The separation of micellization and gelation leads to the formation of a two-compartment network as observed by cryoTEM. The results highlight the intricate and tunable nanostructures and new properties accessible from ABC terpolymer hydrogels.

- Systems membranes – combining the supramolecular and dynamic covalent polymers for gas-selective dynameric membranes
  Nasr, G.; Macron, T.; Gilles, A.; Petit, E.; Barboiu, M. *Chem. Commun.* **2012**, *48*, 7398-7400.
  Abstract:



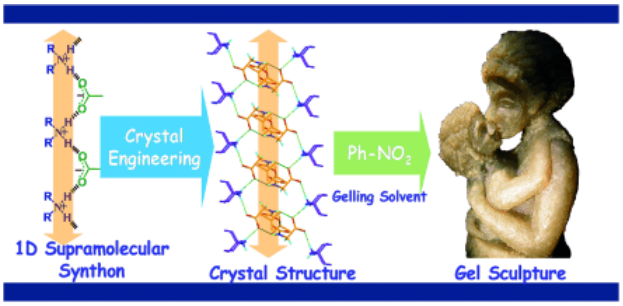
Constitutional modulation of double dynameric supramolecular and dynamic covalent membranes controls the gas transport performances at the molecular level.

- Enzyme-triggered model self-assembly in surfactant–cyclodextrin systems
  Jiang, L.; Yan, Y.; Drechsler, M.; Huang, J. *Chem. Commun.* **2012**, *48*, 7347-7349.
  Abstract:



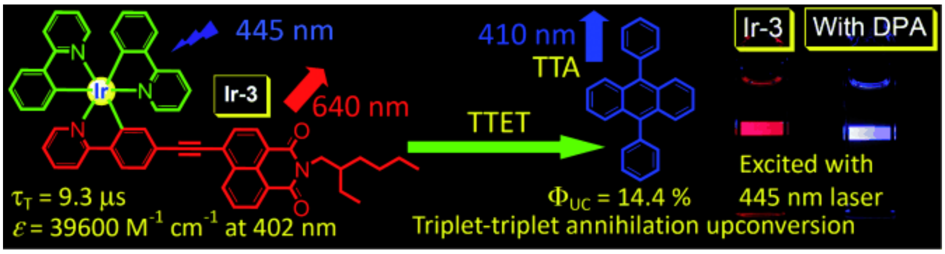
We present here a host–guest approach to construct enzyme-triggered assembly systems on the basis of surfactant–cyclodextrin complexes and α-amylase.

- Gel Sculpture: Moldable, Load-Bearing and Self-Healing Non-Polymeric Supramolecular Gel Derived from a Simple Organic Salt
  Sahoo, P.; Sankolli, R.; Lee, H.-Y.; Raghavan, S. R.; Dastidar, P. *Chem. Eur. J.* **2012**, *18*, 8057–8063.
  Abstract:



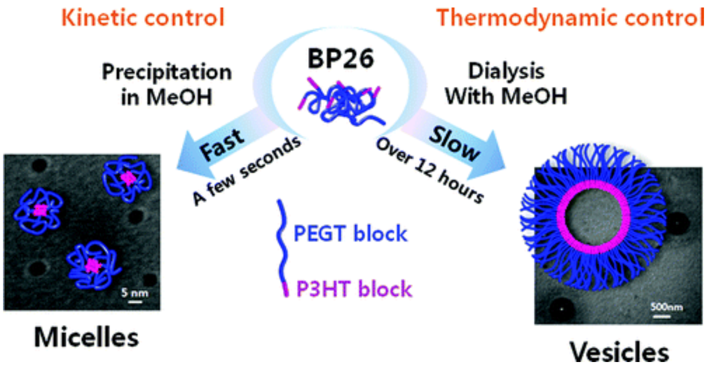
An easy access to a library of simple organic salts derived from *tert*-butoxycarbonyl (Boc)-protected L-amino acids and two secondary amines (dicyclohexyl- and dibenzyl amine) are synthesized following a supramolecular synthon rationale to generate a new series of low molecular weight gelators (LMWGs). Out of the 12 salts that we prepared, the nitrobenzene gel of dicyclohexylammonium Boc-glycinate (**GLY.1**) displayed remarkable load-bearing, moldable and self-healing properties. These remarkable properties displayed by **GLY.1** and the inability to display such properties by its dibenzylammonium counterpart (**GLY.2**) were explained using microscopic and rheological data. Single crystal structures of eight salts displayed the presence of a 1D hydrogen-bonded network (HBN) that is believed to be important in gelation. Powder X-ray diffraction in combination with the single crystal X-ray structure of **GLY.1** clearly established the presence of a 1D hydrogen-bonded network in the xerogel of the nitrobenzene gel of **GLY.1**. The fact that such remarkable properties arising from an easily accessible (salt formation) small molecule are due to supramolecular (non-covalent) interactions is quite intriguing and such easily synthesizable materials may be useful in stress-bearing and other applications.

- Long-Lived Room-Temperature Deep-Red-Emissive Intraligand Triplet Excited State of Naphthalimide in Cyclometalated IrIII Complexes and its Application in Triplet-Triplet Annihilation-Based Upconversion
  Sun, J.; Wu, W.; Zhao, J. *Chem. Eur. J.* **2012**, *18*, 8100–8112.
  Abstract:



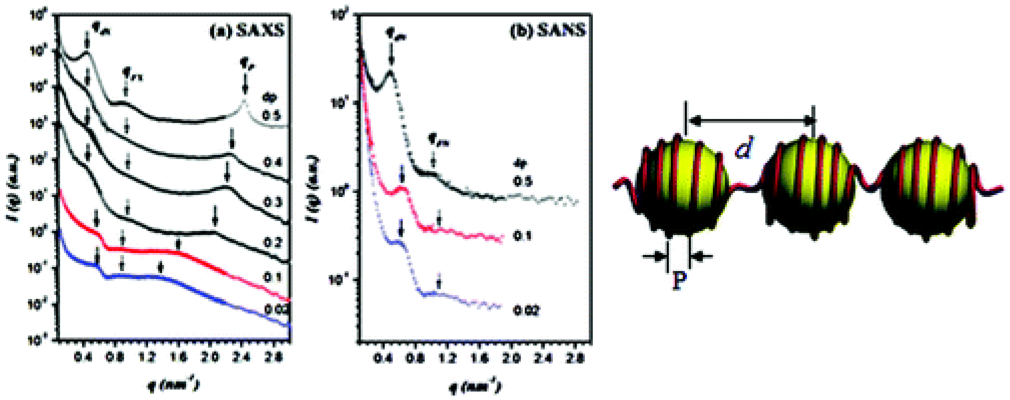
Cyclometalated Ir^{III} complexes with acetylide ppy and bpy ligands were prepared (ppy=2-phenylpyridine, bpy=2,2′-bipyridine) in which naphthal (**Ir-2**) and naphthalimide (NI) were attached onto the ppy (**Ir-3**) and bpy ligands (**Ir-4**) through acetylide bonds. $[Ir(ppy)_3]$ (**Ir-1**) was also prepared as a model complex. Room-temperature phosphorescence was observed for the complexes; both neutral and cationic complexes **Ir-3** and **Ir-4** showed strong absorption in the visible range (ε=39600 M^{-1} cm^{-1} at 402 nm and ε=25100 M^{-1} cm^{-1} at 404 nm, respectively), long-lived triplet excited states (τ_T=9.30 μs and 16.45 μs) and room-temperature red emission (λ_{em}=640 nm, Φ_p=1.4 % and λ_{em}=627 nm, Φ_p=0.3 %; cf. **Ir-1**: ε=16600 M^{-1} cm^{-1} at 382 nm, τ_{em}=1.16 μs, Φ_p=72.6 %). **Ir-3** was strongly phosphorescent in non-polar solvent (i.e., toluene), but the emission was completely quenched in polar solvents (MeCN). **Ir-4** gave an opposite response to the solvent polarity, that is, stronger phosphorescence in polar solvents than in non-polar solvents. Emission of **Ir-1** and **Ir-2** was not solvent-polarity-dependent. The T_1 excited states of **Ir-2**, **Ir-3**, and **Ir-4** were identified as mainly intraligand triplet excited states (^{3}IL) by their small thermally induced Stokes shifts (ΔE_s), nanosecond time-resolved transient difference absorption spectroscopy, and spin-density analysis. The complexes were used as triplet photosensitizers for triplet-triplet annihilation (TTA) upconversion and quantum yields of 7.1 % and 14.4 % were observed for **Ir-2** and **Ir-3**, respectively, whereas the upconversion was negligible for **Ir-1** and **Ir-4**. These results will be useful for designing visible-light-harvesting transition-metal complexes and for their applications as triplet photosensitizers for photocatalysis, photovoltaics, TTA upconversion, etc.

- Synthesis and Self-Assembly of Thiophene-Based All-Conjugated Amphiphilic Diblock Copolymers with a Narrow Molecular Weight Distribution
  Song, I. Y.; Kim, J.; Im, M. J.; Moon, B. J.; Park, T. *Macromolecules* **2012**, *45*, 5058–5068.
  Abstract:



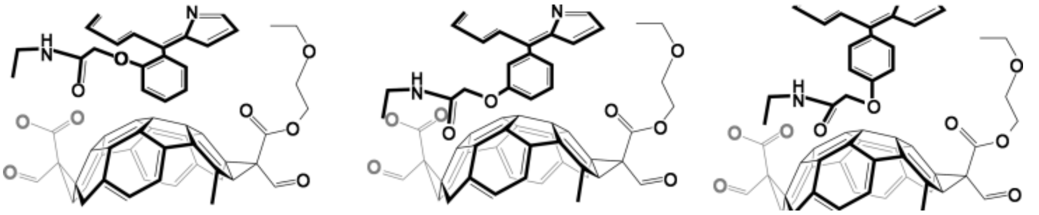
A series of amphiphilic poly(3-hexylthiophene-*b*-3-(2-(2-{2-[2-(2-methoxy–ethoxy)-ethoxy]-ethoxy}-ethyl))thiophene) (P(3HT-*b*-3EGT)) polymers was synthesized via a nickel-catalyzed quasi-living polymerization. Size exclusion chromatograms (SEC) revealed that the molecular weight distributions of the **P3HT** blocks in the block copolymers were comparable with those of the polystyrene standard (monodisperse). ^{1}H NMR spectra revealed that the **P3HT** and **PEGT** units in the block copolymers were well-defined and did not form compositionally mixed regions at the boundary between the blocks and the highly regioregular **P3HT** units. The correlations among the block ratio, the amphiphilicity, and the self-assembled nanostructures of the block copolymers in thin films and in solution were examined. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies revealed that the crystallinity of the **BP93** composed of 93 mol % **P3HT** blocks was higher than the crystallinity of the **P3HT** alone due to the packing effects caused by repulsion among the hydrophobic hexyl and hydrophilic ethylene glycol oligomer side chains. A long relaxation time was required to observe the ordering among **P3HT** blocks in the **BP26** composed of 26 mol % P3HT blocks, suggesting that self-assembly could occur if induced on the molecular level. We demonstrated that the molecular-level self-assembly of **BP26** (at dilute concentrations) via a slow dialysis method produced highly ordered polymer vesicles 200–250 nm in size under thermodynamic control. The size could be tuned via competitive hydrophobic interactions using polystyrene. In contrast, kinetic control via a rapid precipitation method yielded 5–20 nm micelles.

- Nucleosome-like Structure from Dendrimer-Induced DNA Compaction
  Su, C.-J.; Chen, C.-Y.; Lin, M.-C.; Chen, H.-L.; Iwase, H.; Koizumi, S.; Hashimoto, T. *Macromolecules* **2012**, *45*, 5208–5217.
  Abstract:



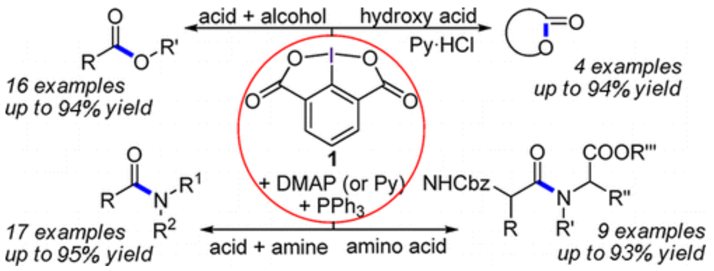
Genomic DNA in eukaryotes wraps around histone proteins to package into the limited space of cell nucleus. Since the precise structure of chromatin is not known in detail, attempts have been made to understand DNA–histone interaction and the associated self-organization behavior using synthetic model systems. Using small-angle X-ray and neutron scattering, here we show that the electrostatic attraction between DNA and polyamidoamine (PAMAM) dendrimer of generation nine (G9) led to the formation of beads-on-string structure, where DNA wrapped around the dendrimer tightly to yield the "chromatin-like fiber" composing of the interconnected "nucleosome-like particles". A "stiff chromatin-like fiber model" and a "wormlike chromatin-like fiber model" were introduced to obtain the theoretical scattering patterns closely resembling the experimentally observed ones, from which the pitch length (*P*) of the DNA superhelix wrapping around the dendrimer and the interparticle distance (*d*) of the nucleosome-like particles were deduced. Governed by the balance between the electrostatic interaction energy and DNA bending energy, *P* and *d* were found to decrease and increase with increasing charge density of dendrimer, respectively. The chromatin-like fibers formed at lower dendrimer charge densities exhibited certain conformational flexibility characterized by the orientation fluctuations of the nucleosome-like particles. The fiber however stiffened when the dendrimer charge density was increased to the extent that all the primary amine groups at the surface of the dendrimer were protonated. The present study revealed not only the accessibility of the beads-on-string structure by a potential model system for histone protein but also the effect of macrocation charge density on the DNA wrapping mode and the conformational feature associated with the chromatin-like fiber formed by the dendriplex.

- Dendronized Fullerene–Porphyrin Conjugates in *ortho*, *meta*, and *para* Positions: A Charge-Transfer Assay
  Krokos, E.; Schubert, C.; Spänig, F.; Ruppert, M.; Hirsch, A.; Guldi, D. M. *Chem. Asian J.* **2012**, *7*, 1451–1459.
  <u>Abstract:</u>



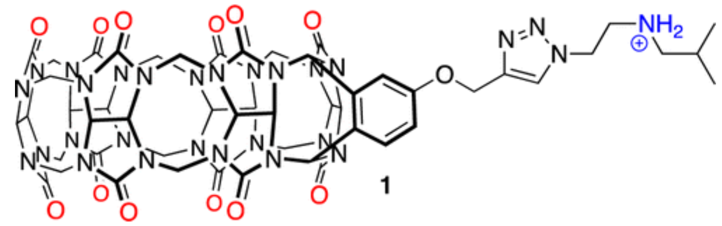
The physicochemical characterization, that is, ground and excited state, of a new series of dendronized porphyrin/fullerene electron donor–acceptor conjugates in nonaqueous and aqueous environments is reported. In contrast to previous work, we detail the charge-separation and charge-recombination dynamics in zinc and copper metalloporphyrins as a function of first- and second-generation dendrons as well as a function of *ortho*, *meta*, and *para* substitution. Both have an appreciable impact on the microenvironments of the redox-active constituents, namely the porphyrins and the fullerenes. As a matter of fact, the resulting charge-transfer dynamics were considerably impacted by the interplay between the associated forces that reach from dendron-induced shielding to dipole–charge interactions.

- Recyclable Hypervalent Iodine(III) Reagent Iodosodilactone as an Efficient Coupling Reagent for Direct Esterification, Amidation, and Peptide Coupling
  Tian, J.; Gao, W.-C.; Zhou, D.-M.; Zhang, C. *Org. Lett.* **2012**, *14*, 3020-3023.
  <u>Abstract:</u>



A hypervalent iodine(III) reagent plays a novel role as an efficient coupling reagent to promote the direct condensation between carboxylic acids and alcohols or amines to provide esters, macrocyclic lactones, amides, as well as peptides without racemization. The regeneration of iodosodilactone (**1**) can also be readily achieved. The intermediate acyloxyphosphonium ion C from the activation of a carboxylic acid is thought to be involved in the present esterification reaction.

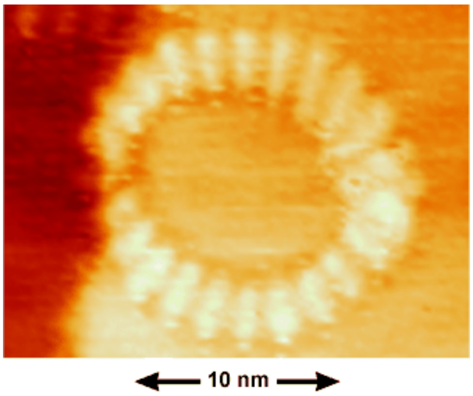
- Daisy Chain Assembly Formed from a Cucurbit[6]uril Derivative
  Cao, L.; Isaacs, L. *Org. Lett.* **2012**, *14*, 3072-3075.
  Abstract:



1

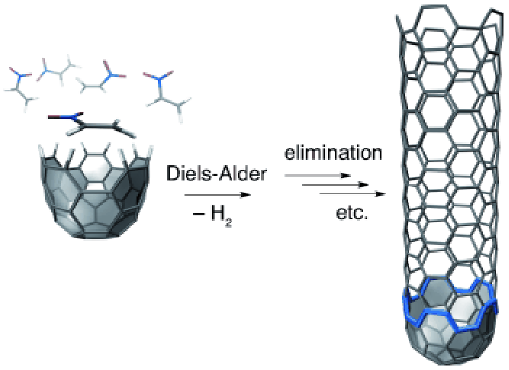
The building block synthesis of a derivative of CB[6] that bears a reactive propargyloxy group and its functionalization by click chemistry to yield **1** which contains a covalently attached isobutylammonium group is presented. Compound **1** undergoes self-assembly to yield a cyclic [c2] daisy chain assembly ($\mathbf{1}_2$) in water. The behavior of $\mathbf{1}_2$ in response to various stimuli (e.g., guests and CB[*n*] receptors) is described.

- Two Vernier-Templated Routes to a 24-Porphyrin Nanoring
  Kondratuk, D. V.; Perdigao, L. M. A.; O'Sullivan, M. C.; Svatek, S.; Smith, G.; O'Shea, J. N.; Beton, P. H.; Anderson, H. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 6696-6699.
  Abstract:



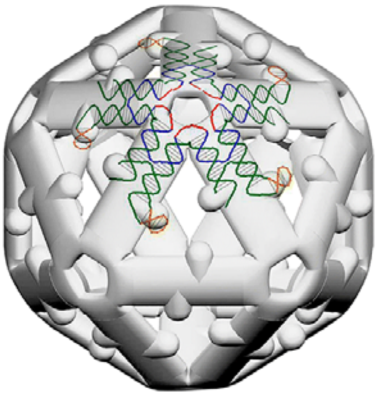
Many hands make light work: Small templates working together have directed the formation of a giant π-conjugated macrocycle with a diameter of 10 nm—larger than many enzymes. The 24 porphyrin subunits of the nanoring are well resolved in the STM image. The conformation of the nanoring can be controlled by self-assembly of a stable 2:24 double-strand sandwich complex with 1,4-diazabicyclo[2.2.2]octane (DABCO).

- Elements for a Rational Polymer Approach towards Carbon Nanostructures
  Schrettl, S.; Frauenrath, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 6569-6571.
  Abstract:



Growth spurt: A recent series of publications promises to pave the way for a polymer approach towards well-defined carbon nanostructures by combining the stepwise organic synthesis of carbon nanotube (CNT) end caps and their use as templates for CNT growth by Diels–Alder addition of nitroethylene as a masked acetylene derivative.

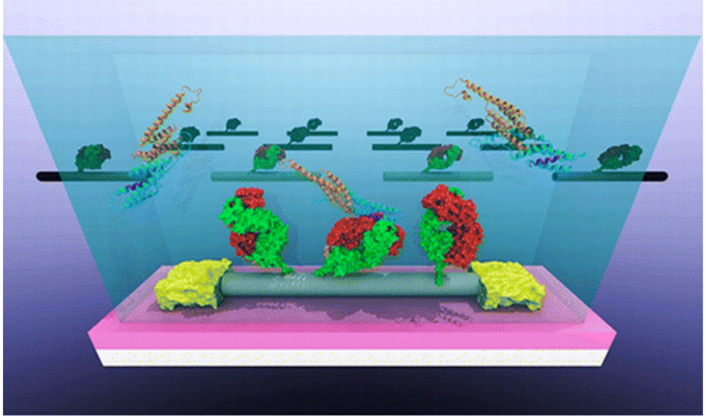
- DNA Polyhedra with T-Linkage
  Li, X.; Zhang, C.; Hao, C.; Tian, C.; Wang, G.; Mao, C. *ACS Nano* **2012**, *6*, 5138-5142.
  Abstract:



This paper reports a strategy for DNA self-assembly. Cross-over-based DNA nanomotifs are held together by T-junctions instead of commonly used sticky-end cohesion. We have demonstrated this strategy by assembling a DNA tetrahedron, an octahedron, and an icosahedron. The resulting DNA polyhedra contain out-pointing, short DNA hairpin spikes. These hairpins are well-structured relative to the polyhedra core and provide potential locations for introduction of functional chemicals such as proteins and gold nanoparticles. The T-linked DNA polyhedra have been characterized by polyacrylamide gel electrophoresis, atomic force microscopy, and dynamic light scattering.

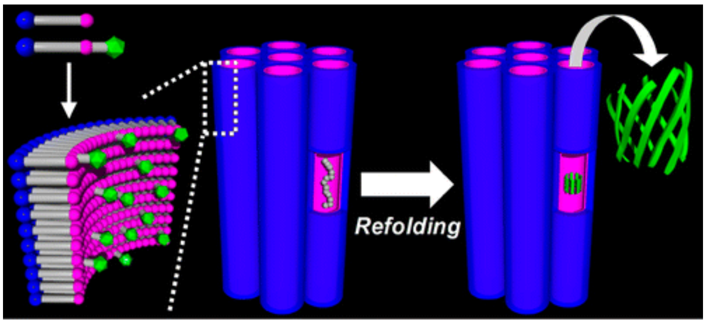
- Hybrids of a Genetically Engineered Antibody and a Carbon Nanotube Transistor for Detection of Prostate Cancer Biomarkers
  Lerner, M. B.; D'Souza, J.; Pazina, T.; Dailey, J.; Goldsmith, B. R.; Robinson, M. K.; Johnson, A. T. C. *ACS Nano* **2012**, *6*, 5143-5149.

Abstract:



We developed a novel detection method for osteopontin (OPN), a new biomarker for prostate cancer, by attaching a genetically engineered single-chain variable fragment (scFv) protein with high binding affinity for OPN to a carbon nanotube field-effect transistor (NT-FET). Chemical functionalization using diazonium salts is used to covalently attach scFv to NT-FETs, as confirmed by atomic force microscopy, while preserving the activity of the biological binding site for OPN. Electron transport measurements indicate that functionalized NT-FET may be used to detect the binding of OPN to the complementary scFv protein. A concentration-dependent increase in the source–drain current is observed in the regime of clinical significance, with a detection limit of approximately 30 fM. The scFv-NT hybrid devices exhibit selectivity for OPN over other control proteins. These devices respond to the presence of OPN in a background of concentrated bovine serum albumin, without loss of signal. On the basis of these observations, the detection mechanism is attributed to changes in scattering at scFv protein-occupied defect sites on the carbon nanotube sidewall. The functionalization procedure described here is expected to be generalizable to any antibody containing an accessible amine group and to result in biosensors appropriate for detection of corresponding complementary proteins at fM concentrations.

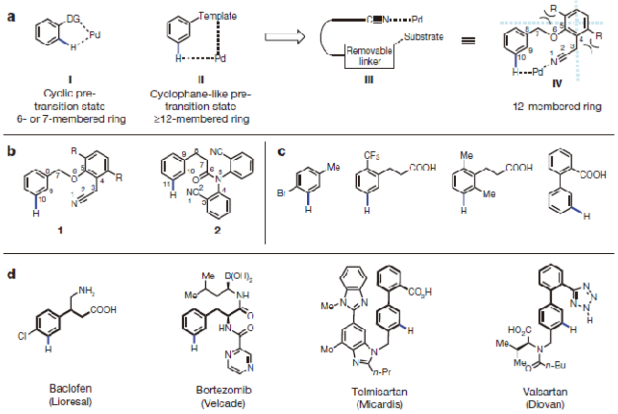
- Soft Nanotube Hydrogels Functioning As Artificial Chaperones
  Kameta, N.; Masuda, M.; Shimizu, T. *ACS Nano* **2012**, *6*, 5249-5258.
  Abstract:



Self-assembly of rationally designed asymmetric amphiphilic monomers in water produced nanotube hydrogels in the presence of chemically denatured proteins (green fluorescent protein, carbonic anhydrase, and citrate synthase) at room temperature, which were able to encapsulate the proteins in the one-dimensional channel of the nanotube consisting of a monolayer membrane. Decreasing the concentrations of the denaturants induced refolding of part of the encapsulated proteins in the nanotube channel. Changing the pH dramatically reduced electrostatic attraction between the inner surface mainly covered with amino groups of the nanotube channel and the encapsulated proteins.

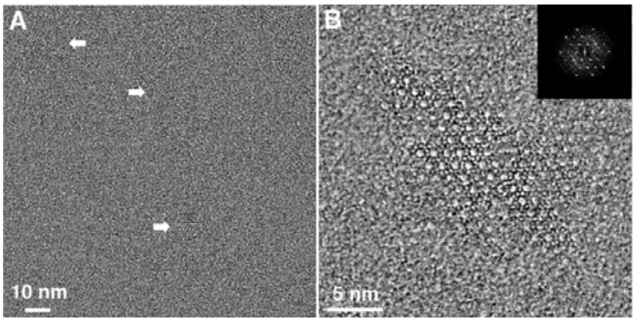
As a result, the refolded proteins were smoothly released into the bulk solution without specific additive agents. This recovery procedure also transformed the encapsulated proteins from an intermediately refolding state to a completely refolded state. Thus, the nanotube hydrogels assisted the refolding of the denatured proteins and acted as artificial chaperones. Introduction of hydrophobic sites such as a benzyloxycarbony group and a *tert*-butoxycarbonyl group onto the inner surface of the nanotube channels remarkably enhanced the encapsulation and refolding efficiencies based on the hydrophobic interactions between the groups and the surface-exposed hydrophobic amino acid residues of the intermediates in the refolding process. Refolding was strongly dependent on the inner diameters of the nanotube channels. Supramolecular nanotechnology allowed us to not only precisely control the diameters of the nanotube channels but also functionalize their surfaces, enabling us to fine-tune the biocompatibility. Hence, these nanotube hydrogel systems should be widely applicable to various target proteins of different molecular weights, charges, and conformations.

- Activation of remote meta-C–H bonds assisted by an end-on template.
  Leow, D.; Li, G.; Mei, T.-S..; Yu, J.-Q. *Nature* **2012**, *486*, 518-522.
  <u>Abstract:</u>



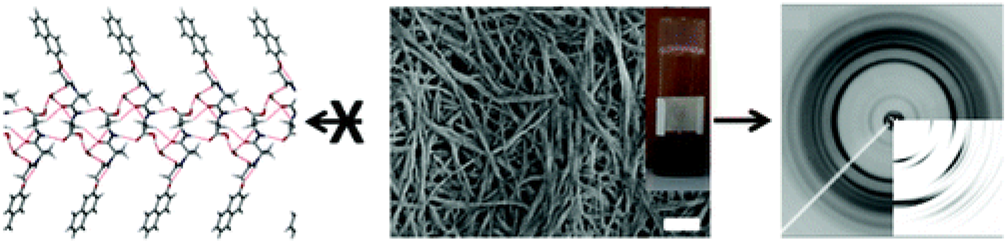
Functionalization of unactivated carbon–hydrogen (C–H) single bonds is an efficient strategy for rapid generation of complex molecules from simpler ones. However, it is difficult to achieve selectivity when multiple inequivalent C–H bonds are present in the target molecule. The usual approach is to use σ-chelating directing groups, which lead to *ortho*-selectivity through the formation of a conformationally rigid six- or seven-membered cyclic pre-transition state. Despite the broad utility of this approach, proximity-driven reactivity prevents the activation of remote C–H bonds. Here we report a class of easily removable nitrile-containing templates that direct the activation of distal *meta*-C–H bonds (more than ten bonds away) of a tethered arene. We attribute this new mode of C–H activation to a weak 'end-on' interaction between the linear nitrile group and the metal centre. The 'end-on' coordination geometry relieves the strain of the cyclophane-like pre-transition state of the meta-C–H activation event. In addition, this template overrides the intrinsic electronic and steric biases as well as *ortho*-directing effects with two broadly useful classes of arene substrates (toluene derivatives and hydrocinnamic acids).

- Synthesis of Self-Pillared Zeolite Nanosheets by Repetitive Branching
  Zhang, X.; Liu, D.; Xu, D.; Asahina, S.; Cychosz, K. A.; Agrawal, K. V.; Al Wahedi, Y.; Bhan, A.; Al Hashimi, S.; Terasaki, O.; Thommes, M.; Tsapatsis, M. *Science* **2012**, *336*, 1684-1687.
  <u>Abstract:</u>



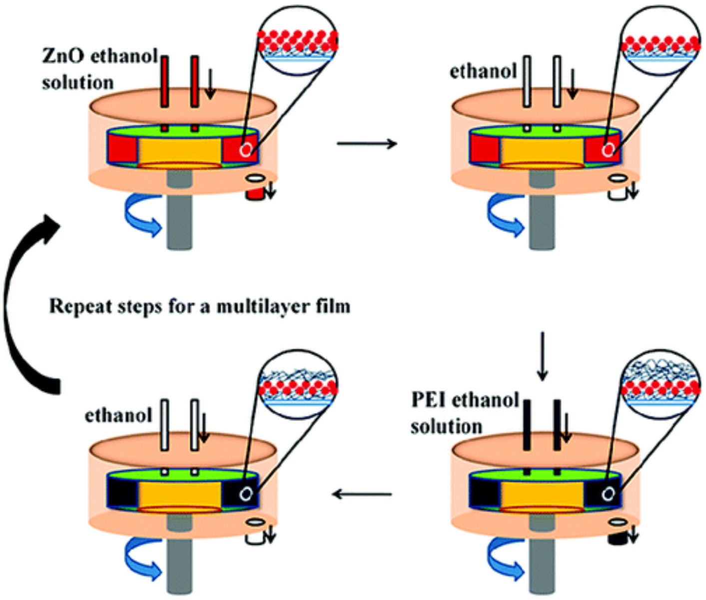
Hierarchical zeolites are a class of microporous catalysts and adsorbents that also contain mesopores, which allow for fast transport of bulky molecules and thereby enable improved performance in petrochemical and biomass processing. We used repetitive branching during one-step hydrothermal crystal growth to synthesize a new hierarchical zeolite made of orthogonally connected microporous nanosheets. The nanosheets are 2 nanometers thick and contain a network of 0.5-nanometer micropores. The house-of-cards arrangement of the nanosheets creates a permanent network of 2- to 7-nanometer mesopores, which, along with the high external surface area and reduced micropore diffusion length, account for higher reaction rates for bulky molecules relative to those of other mesoporous and conventional MFI zeolites.

- On Crystal versus Fiber Formation in Dipeptide Hydrogelator Systems
  Houton, K. A.; Morris, K. L.; Chen, L.; Schmidtmann, M.; Jones, J. T. A.; Serpell, L. C.; Lloyd, G. O.; Adams, D. J. *Langmuir* **2012**, *28*, 9797-9806.
  Abstract:



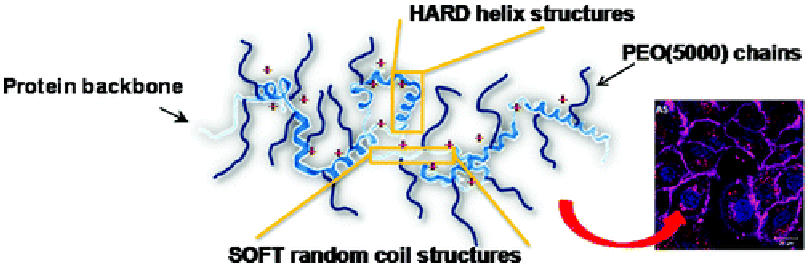
Naphthalene dipeptides have been shown to be useful low-molecular-weight gelators. Here we have used a library to explore the relationship between the dipeptide sequence and the hydrogelation efficiency. A number of the naphthalene dipeptides are crystallizable from water, enabling us to investigate the comparison between the gel/fiber phase and the crystal phase. We succeeded in crystallizing one example directly from the gel phase. Using X-ray crystallography, molecular modeling, and X-ray fiber diffraction, we show that the molecular packing of this crystal structure differs from the structure of the gel/fiber phase. Although the crystal structures may provide important insights into stabilizing interactions, our analysis indicates a rearrangement of structural packing within the fibers. These observations are consistent with the fibrillar interactions and interatomic separations promoting 1D assembly whereas in the crystals the peptides are aligned along multiple axes, allowing 3D growth. This observation has an impact on the use of crystal structures to determine supramolecular synthons for gelators.

- Layer-by-Layer Self-Assembly under High Gravity Field
  Ma, L.; Cheng, M.; Jia, G.; Wang, Y.; An, Q.; Zeng, X.; Shen, Z.; Zhang, Y.; Shi, F. *Langmuir* **2012**, *28*, 9849-9856.
  Abstract:



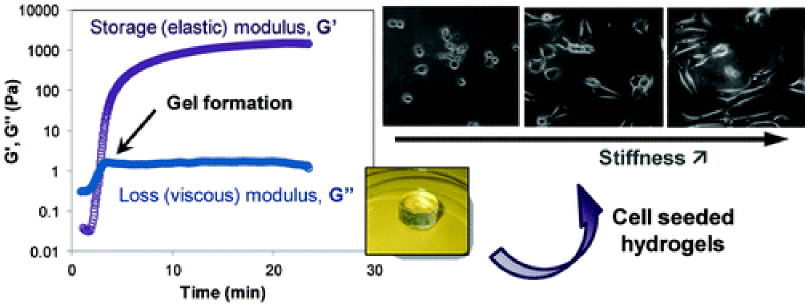
In the present article, we have developed a facile and rapid method to fabricate a polyelectrolyte multilayer under high gravity field and investigated the difference of mass transfer in the diffusing process between LbL self-assembled technique under high gravity field (HG-LbL) and dipping assembly. Herein, we have employed polyethyleneimine and zinc oxide nanoparticles, which is a well-known UV blocking material with typical absorption properties in the range of 300–400 nm, as building blocks and applied hydrogen bonding as the driving force to construct the multilayer under HG-LbL and dipping assembly. The results show that, compared with dipping assembly, HG-LbL can highly improve the utilization and adsorption efficiency of building blocks by hastening the diffusing process, and meanwhile the resulting multilayer films still achieve comparable quality as those prepared from dipping assembly.

- Convenient Approach to Polypeptide Copolymers Derived from Native Proteins
  Wu, Y.; Pramanik, G.; Eisele, K.; Weil, T. *Biomacromolecules* **2012**, *13*, 1890–1898.
  Abstract:



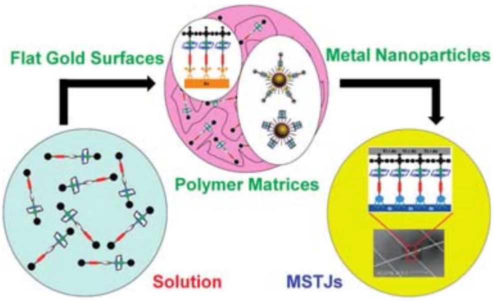
A convenient approach for the synthesis of narrowly dispersed polypeptide copolymers of defined compositions is presented. The controlled denaturation of the proteins serum albumin and lysozyme followed by an in situ stabilization with polyethylene(oxide) chains yields polypeptide side chain copolymers of precisely defined backbone lengths as well as the presence of secondary structure elements. Supramolecular architectures are formed in solution because of the presence of hydrophobic and hydrophilic amino acids along the polypeptide main chain. Polypeptide copolymers reported herein reveal excellent solubility and stability in aqueous media and no significant cytotoxicity at relevant concentrations, and they can be degraded via proteolysis, which is very attractive for biomedical applications. This “semi-synthetic chemistry” approach is based on a novel and convenient concept for producing synthetic polypeptides from native protein resources, which complements traditional polypeptide synthesis and expression approaches and offers great opportunities for the preparation of diverse polypeptides with unique architectures.

- Design of Biomimetic Cell-Interactive Substrates Using Hyaluronic Acid Hydrogels with Tunable Mechanical Properties
  Hachet, E.; Van Den Berghe, H.; Bayma, E.; Block, M. R.; Auzély-Velty, R. *Biomacromolecules* **2012**, *13*, 1818–1827.
  Abstract:



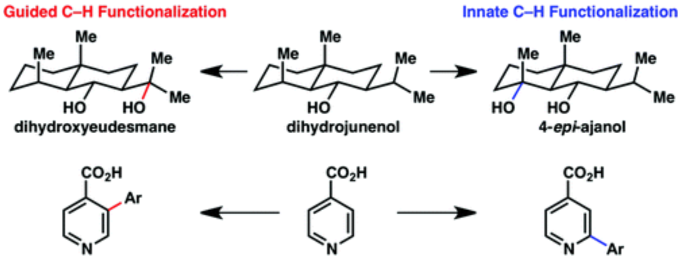
Hyaluronic acid (HA) is a natural polysaccharide abundant in biological tissues with excellent potential for constructing synthetic extracellular matrix analogues. In this work, we established a simple and dependable approach to prepare hyaluronic acid-based hydrogels with controlled stiffness and cell recognition properties for use as cell-interactive substrates. This approach relied on a new procedure for the synthesis of methacrylate-modified HA macromers (HA–MA) and, on photorheometry allowing real time monitoring of gelation during photopolymerization. We showed in this way the ability to obtain gels that encompass the range of physiologically relevant elastic moduli while still maintaining the recognition properties of HA by specific cell surface receptors. These hydrogels were prepared from HA macromers having a degree of methacrylation <0.5, which allows to minimize compromising effects on the binding affinity of HA to its cell receptors due to high substitution on the one hand, and to achieve nearly 100% conversion of the methacrylate groups on the other. When the HA hydrogels were immobilized on glass substrates, it was observed that the attachment and the spreading of a variety of mammalian cells rely on CD44 and its coreceptor RHAMM. The attachment and spreading were also shown to be modulated by the elastic properties of the HA matrix. All together, these results highlight the biological potential of these HA hydrogel systems and the needs of controlling their chemical and physical properties for applications in cell culture and tissue engineering.

- High hopes: can molecular electronics realise its potential?
  Coskun, A.; Spruell, J. M.; Barin, G.; Dichtel, W. R.; Flood, A. H.; Botros, Y. Y.; Stoddart, J. F. *Chem. Soc. Rev.* **2012**, *41*, 4827-4859.
  Abstract:



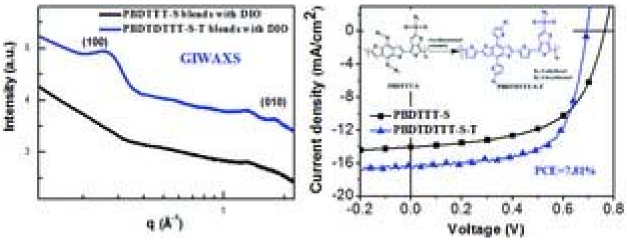
Manipulating and controlling the self-organisation of small collections of molecules, as an alternative to investigating individual molecules, has motivated researchers bent on processing and storing information in molecular electronic devices (MEDs). Although numerous ingenious examples of single-molecule devices have provided fundamental insights into their molecular electronic properties, MEDs incorporating hundreds to thousands of molecules trapped between wires in two-dimensional arrays within crossbar architectures offer a glimmer of hope for molecular memory applications. In this critical review, we focus attention on the collective behaviour of switchable mechanically interlocked molecules (MIMs)—specifically, bistable rotaxanes and catenanes—which exhibit reset lifetimes between their ON and OFF states ranging from seconds in solution to hours in crossbar devices.

- Innate and Guided C–H Functionalization Logic
  Brückl, T.; Baxter, R. D.; Ishihara, Y.; Baran, P. S. *Acc. Chem. Res.* **2012**, *45*, 826–839.
  <u>Abstract:</u>



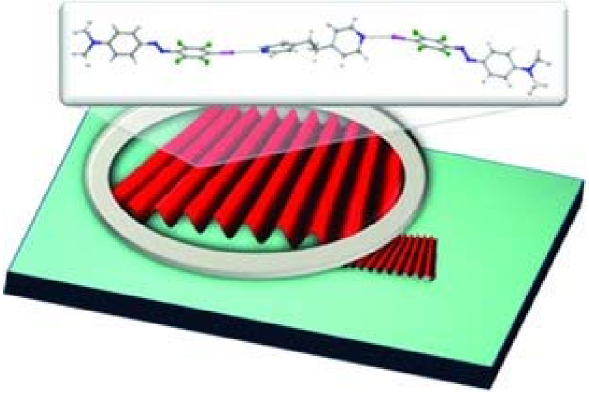
In this Account, we trace our own studies in the area of C–H functionalization in synthesis through the lens of “guided” and “innate” descriptors. We show how harnessing innate reactivity can be beneficial for achieving unique bond constructions between heterocycles and carbonyl compounds, enabling rapid and scalable total syntheses. Guided and innate functionalizations were used synergistically to create an entire family of terpenes in a controlled fashion. We continue with a discussion of the synthesis of complex alkaloids with high nitrogen content, which required the invention of a uniquely chemoselective innate C–H functionalization protocol. These findings led us to develop a series of innate C–H functionalization reactions for forging C–C bonds of interest to the largest body of practicing organic chemists: medicinal chemists. Strategic use of C–H functionalization logic can have a dramatically positive effect on the efficiency of synthesis, whether guided or innate.

- Improving the Ordering and Photovoltaic Properties by Extending π–Conjugated Area of Electron-Donating Units in Polymers with D-A Structure
  Huang, Y.; Guo, X.; Liu, F.; Huo, L.; Chen, Y.; Russell, T. P.; Han, C. C.; Li, Y.; Hou, J. *Adv. Mater.* **2012**, *24*, 3383–3389.
  <u>Abstract:</u>



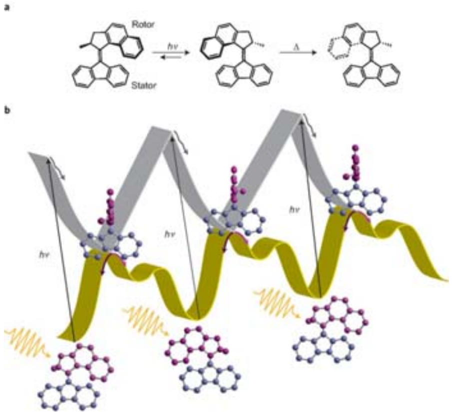
A systematic molecular design process from PBDTTT-S to PBDTDTTT-S-T, a high-performance semiconducting polymer for organic photovoltaics, has been achieved by enhancing structural order, self-assembly and carrier mobility. Solar cells made from **PBDTDTTT-S-T** blended with $PC_{70}BM$ show a power conversion efficiency (PCE) of 7.81%, which is 25% higher than that of the parent **PBDTTT-S**.

- Halogen Bonding versus Hydrogen Bonding in Driving Self-Assembly and Performance of Light-Responsive Supramolecular Polymers
  Priimagi, A.; Cavallo, G.; Forni, A.; Gorynsztejn–Leben, M.; Kaivola, M.; Metrangolo, P.; Milani, R.; Shishido, A.; Pilati, T.; Resnati, G.; Terraneo, G. *Adv. Funct. Mater.* **2012**, *22*, 2572–2579.
  Abstract:



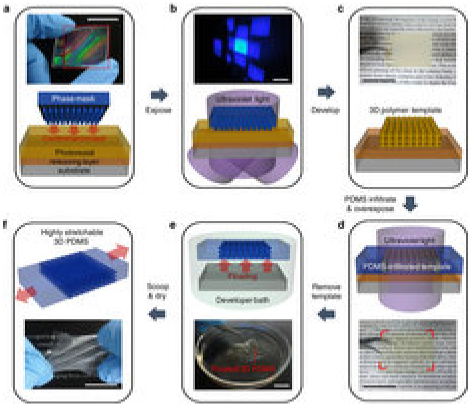
Halogen bonding is arguably the least exploited among the many non-covalent interactions used in dictating molecular self-assembly. However, its directionality renders it unique compared to ubiquitous hydrogen bonding. Here, the role of this directionality in controlling the performance of light-responsive supramolecular polymers is highlighted. In particular, it is shown that light-induced surface patterning, a unique phenomenon occurring in azobenzene-containing polymers, is more efficient in halogen-bonded polymer–azobenzene complexes than in the analogous hydrogen-bonded complexes. A systematic study is performed on a series of azo dyes containing different halogen or hydrogen bonding donor moieties, complexed to poly(4-vinylpyridine) backbone. Through single-atom substitution of the bond-donor, control of both the strength and the nature of the noncovalent interaction between the azobenzene units and the polymer backbone is achieved. Importantly, such substitution does not significantly alter the electronic properties of the azobenzene units, hence providing us with unique tools in studying the structure–performance relationships in the light-induced surface deformation process. The results represent the first demonstration of light-responsive halogen-bonded polymer systems and also highlight the remarkable potential of halogen bonding in fundamental studies of photoresponsive azobenzene-containing polymers.

- Photochemistry: Molecular motor speed limits
  Miller, R. J. D. *Nature Chemistry* **2012***, 4,* 523–525.
  Abstract:



To improve the efficiency of molecular motors, a better understanding of the dynamics of their functional motions is required. Now, ultrafast fluorescence spectroscopy has been used to monitor the excited-state evolution of a light-driven molecular motor.

- Three-dimensional nanonetworks for giant stretchability in dielectrics and conductors
  Park, J.; Wang, S.; Li, M.; Ahn, C.; Hyun, J. K.; Kim, D. S.; Kim, D. K.; Rogers, J. A.; Huang, Y.; Jeon, S. *Nature Communications* **2012**, *3*, 916.
  <ins>Abstract:</ins>



The realization of levels of stretchability that extend beyond intrinsic limits of bulk materials is of great importance to stretchable electronics. Here we report large-area, three-dimensional nano-architectures that achieve this outcome in materials that offer both insulating and conductive properties. For the elastomer poly(dimethylsiloxane), such geometries enhance the stretchability and fracture strain by ~62% and ~225% over the bulk, unstructured case. The underlying physics involves local rotations of narrow structural elements in the three-dimensional network, as identified by mechanical modelling. To demonstrate the applications of three-dimensional poly(dimethylsiloxane), we create a stretchable conductor obtained by filling the interstitial regions with liquid metal. This stretchable composite shows extremely high electrical conductivity (~24,100 S cm−1) even at strains >200%, with good cyclic properties and with current-carrying capacities that are sufficient for interconnects in light-emitting diode systems. Collectively, these concepts provide new design opportunities for stretchable electronics.