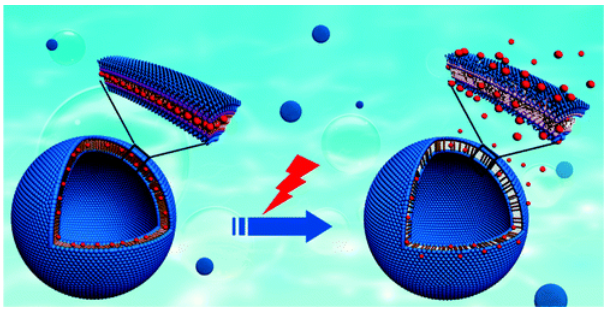
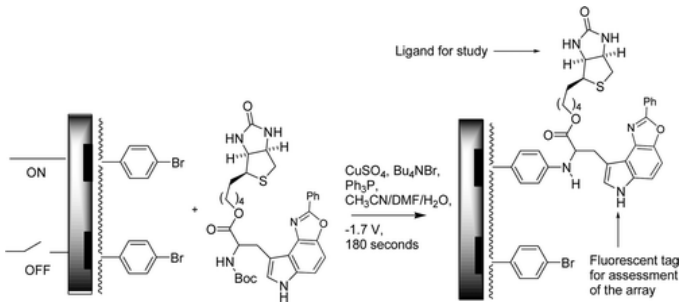
- Stabilized Vesicles Consisting of Small Amphiphiles for Stepwise Photorelease via UV Light
  Dong, J.; Zeng, Y.; Xun, Z.; Han, Y.; Chen, J.; Li, Y.-Y.; Li, Y. *Langmuir* **2012**, *28*, 1733-1737.
  Abstract:



A small amphiphile consisting of hydrophilic tetraethylene glycol monoacrylate and hydrophobic alkyl chain which were connected by an *o*-nitrobenzyl unit, a photolabile group, was designed and synthesized. The critical aggregate concentration of the synthesized amphiphile was determined to be about 3×10^{-5} M by the fluorescence probe technique. Nanosized vesicles were prepared and stabilized by in-situ radical polymerization without altering the morphology. The polymeric vesicle was highly stable which retained vesicular shape under dilution or UV irradiation. Hydrophobic guests can be encapsulated within the vesicle membrane and released out of the vesicle by UV stimulus through splitting the amphiphilic structure of the amphiphile. Distinguished dose-controlled photorelease of the polymeric vesicle is achieved due to the maintenance of the vesicular shape integrity which makes the guest release depend on the cleavage amount of amphiphilic structure during UV irradiation. This study provides a promising strategy to develop stable drug delivery systems for sustained and phototriggered release.

- Building Addressable Libraries: Amino Acid Derived Fluorescent Linkers
  Tanabe, T.; Bi, B.; Hu, L.; Maurer, K.; Moeller, K. D. *Langmuir* **2012**, *28*, 1689-1693.
  Abstract:

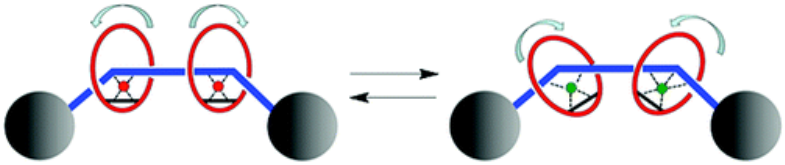


A new amino acid derived fluorescent linker for attaching molecules to the surface of a microelectrode array has been developed. Molecules to be monitored on an array are attached to the C-terminus of the linker, the N-terminus is then used to attach the linker to the array, and the side chain is used to synthesize a fluorescent tag. The fluorescent group is made with a one-step oxidative cycloaddition reaction starting from a hydroxyindole group. The linker is compatible with site-selective Cu(I)-chemistry on the array, it allows for quality control assessment of the array itself, and it is compatible with the electrochemical impedance experiments used to monitor binding events on the surface of the array.

- Copper(I)-Assembled [3]Rotaxane Whose Two Rings Act as Flapping Wings

Joosten, A.; Trolez, Y.; Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2012**, *134*, 1802–1809.

Abstract:

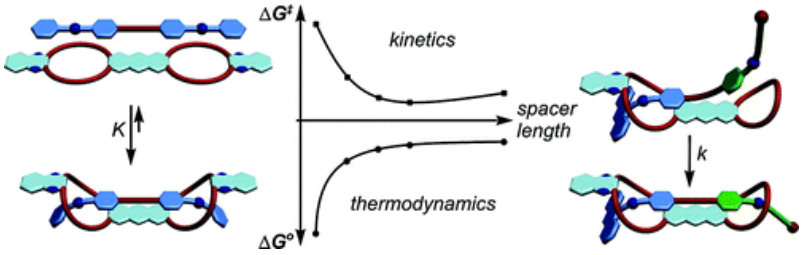


A new copper-complexed [3]rotaxane consisting of two coordinating 30-membered rings threaded by a two-binding-site axis has been prepared in good yieldfromrelatively simple organic fragments. The main specificity of the system originates from the stoppe ring reaction, based on “click” chemistry, and thus from the presence of two triazole groups at positions next to the bidentate chelates of the axis central part. The geometry of the coordinating atoms belonging to the axis is such that the triazole groups can either be part of the coordinating fragments when the metal center is 5-coordinate or be not at all involved in coordination to the metal when the latter is 4-coordinate. To be more specific, when the two complexed metal centers are monovalent copper(I) centers, the triazoles are not included in the metal coordination sphere, where as when the metal centers are Cu(II) or Zn^{2+}, the triazole groups are bound to the metals. This is easily explained by the fact that Cu(I) is preferably 4-coordinate and Cu(II) and Zn^{2+} are 5-coordinate. The inter conversion between both situations (4- or 5-coordinate) can be quantitatively induced by metal exchange (Cu(I)/Zn^{2+}) or by a redox process (Cu(II)/Cu(I)). It leads to important geometrical changes and in particular to a strong modification of the angle between the two rings. As a consequence, the two threaded rings undergo a motion which is reminiscent of awing-flapping movement similar to that of birds. This flapping motion is fast and quantitative. It should lead to new functional molecular machines in the future.

- Chelate Cooperativity and Spacer Length Effects on the Assembly Thermodynamics and Kinetics of Divalent Pseudo rotaxanes

  Jiang, W.; Nowosinski, K.; Löw, N. L.; Dzyuba, E. V.; Klautzsch,F.; Schäfer, A.; Huuskonen, J.; Rissanen, K.; Schalley, C. A. *J. Am. Chem. Soc.* **2012**, *134*, 1860–1868.

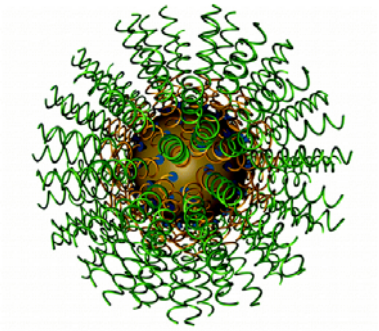
  Abstract:



Homo- and heterodivalent crown-ammonium pseudo rotaxanes with different spacers connecting the two axle ammonium binding sites have been synthesized and characterized by NMR spectroscopy and ESI mass spectrometry. The homo divalent pseudo rotaxanes are investigated with respect to the thermodynamics of divalent binding and to chelate cooperativity. The shortest spacer exhibits achelate cooperativity much stronger than that of the longer spacers. On the basis of crystal structure, this can be explained by a non innocent spacer, which contributes to the binding strength in addition to the two binding sites. Already very subtle changes in the spacer length, i.e., the introduction of an additional methylene group, cause substantial changes in the magnitude of cooperative binding as expressed in the large differences in effective molarity. With a similar series of

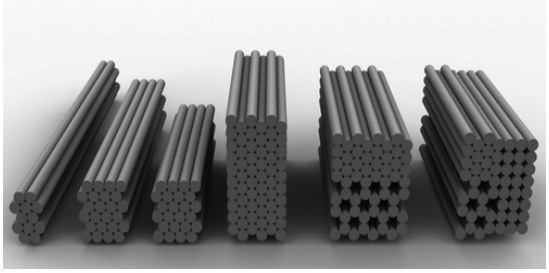
heterodivalent pseudo rotaxanes, the spacer effects on the barrier for the intra molecular threading step has been examined with the result that the shortest spacer causes a strained transition structure and thus the second binding event occurs slower than that of the longer spacers. The activation enthalpies and entropies show clear trends. While the longer spacers reduce the enthalpic strain that is present in the transition state for the shortest member of the series, the longer spacers become entropically slightly more unfavorable because of conformational fixation of the spacer chain during the second binding event. These results clearly show the non innocent spacers to complicate the analysis of multivalent binding. An approximate description which considers the binding sites to be connected just by a flexible chain turns out to be more a rough approximation than a good model. The second conclusion from the results presented here is that multi valency is expressed in both the thermodynamics and the kinetics in different ways. A spacer optimized for strong binding is suboptimal for fast pseudo rotaxane formation.

- Spherical Nucleic Acids
  Cutler, J. I.; Auyeung, E.; Mirkin, C. A. *J. Am. Chem. Soc.* **2012**, *134*, 1376-1391.
  Abstract :



A historical perspective of the development of spherical nucleic acid (SNA) conjugates and other three-dimensional nucleic acid nanostructures is provided. This Perspective details the synthetic methods for preparing them, followed by a discussion of their unique properties and theoretical and experimental models for understanding them. Important examples of technological advances made possible by their fundamental properties spanning the fields of chemistry, molecular diagnostics, gene regulation, medicine, and materials science are also presented.

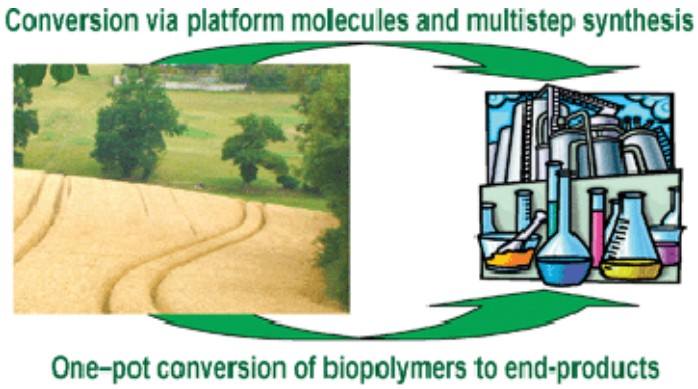
- Multilayer DNA Origami Packed on Hexagonal and Hybrid Lattices
  Ke, Y.; Voigt, N. V.; Gothelf, K. V.; Shih, W. M. *J. Am. Chem. Soc.* **2012**, *134*, 1770-1774.
  Abstract :



"Scaffolded DNA origami" has been proven to be a powerful and efficient approach to construct two-dimensional or three-dimensional objects with great complexity. Multilayer DNA origami has been demonstrated with helices packing along either honeycomb-lattice geometry or square-lattice geometry. Here we report successful folding of multilayer DNA origami with helices arranged on a

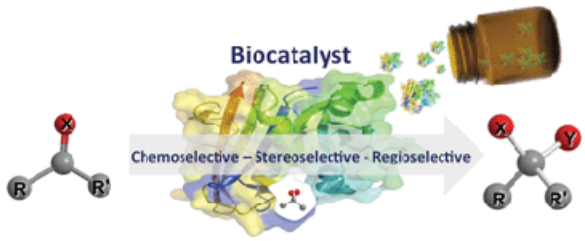
close-packed hexagonal lattice. This arrangement yields a higher density of helical packing and therefore higher resolution of spatial addressing than has been shown previously. We also demonstrate hybrid multilayer DNA origami with honeycomb-lattice, square-lattice, and hexagonal-lattice packing of helices all in one design. The availability of hexagonal close-packing of helices extends our ability to build complex structures using DNA nanotechnology.

- Conversion of biomass to selected chemical products
  Gallezot, P. *Chem. Soc. Rev.* **2012,** *41*, 1538-1558.
  Abstract :



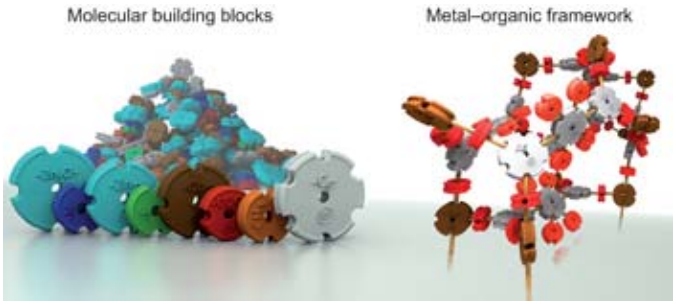
This *critical review* provides a survey illustrated by recent references of different strategies to achieve a sustainable conversion of biomass to bioproducts. Because of the huge number of chemical products that can be potentially manufactured, a selection of starting materials and targeted chemicals has been done. Also, thermochemical conversion processes such as biomass pyrolysis or gasification as well as the synthesis of biofuels were not considered. The synthesis of chemicals by conversion of platform molecules obtained by depolymerisation and fermentation of biopolymers is presently the most widely envisioned approach. Successful catalytic conversion of these building blocks into intermediates, specialties and fine chemicals will be examined. However, the platform molecule value chain is in competition with well-optimised, cost-effective synthesis routes from fossil resources to produce chemicals that have already a market. The literature covering alternative value chains whereby biopolymers are converted in one or few steps to functional materials will be analysed. This approach which does not require the use of isolated, pure chemicals is well adapted to produce high tonnage products, such as paper additives, paints, resins, foams, surfactants, lubricants, and plasticisers. Another objective of the review was to examine critically the green character of conversion processes because using renewables as raw materials does not exempt from abiding by green chemistry principles (368 references).

- Expanding the organic toolbox: a guide to integrating biocatalysis in synthesis
  Clouthier, C. M.; Pelletier, J. N. *Chem. Soc. Rev.* **2012**, *41*, 1585-1605
  Abstract :



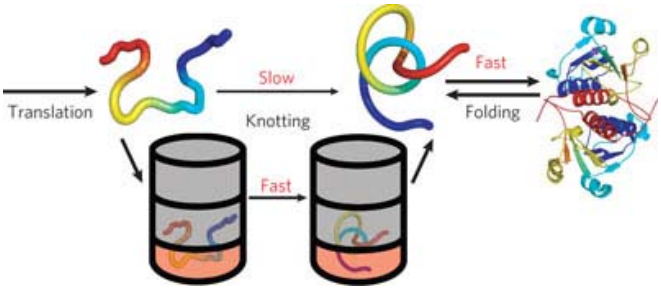
This *critical review* presents an introduction to biocatalysis for synthetic chemists. Advances in biocatalysis of the past 5 years illustrate the breadth of applications for these powerful and selective catalysts in conducting key reaction steps. Asymmetric synthesis of value-added targets and other reaction types are covered, with an emphasis on pharmaceutical intermediates and bulk chemicals. Resources of interest for the non-initiated are provided, including specialized websites and service providers to facilitate identification of suitable biocatalysts, as well as references to recent volumes and reviews for more detailed biocatalytic procedures. Challenges related to the application of biocatalysts are discussed, including how 'green' a biocatalytic reaction may be, and trends in biocatalyst improvement through enzyme engineering are presented (152 references).

- Large-scale screening of hypothetical metal–organic frameworks
  Wilmer,C. E.; Leaf,M.; Lee,C. Y.; Farha,O. K.; Hauser,B. G.; Hupp,J. T.; Snurr,R. Q. *Nature Chem.* **2012**, *4*, 83-89.
  Abstract :



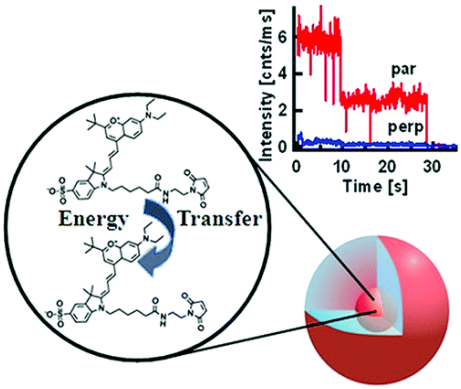
Metal–organic frameworks (MOFs) are porous materials constructed from modular molecular building blocks, typically metal clusters and organic linkers. These can, in principle, be assembled to form an almost unlimited number of MOFs, yet materials reported to date represent only a tiny fraction of the possible combinations. Here, we demonstrate a computational approach to generate all conceivable MOFs from a given chemical library of building blocks (based on the structures of known MOFs) and rapidly screen them to find the best candidates for a specific application. From a library of 102 building blocks we generated 137,953 hypothetical MOFs and for each one calculated the pore-size distribution, surface area and methane-storage capacity. We identified over 300 MOFs with a predicted methane-storage capacity better than that of any known material, and this approach also revealed structure–property relationships. Methyl-functionalized MOFs were frequently top performers, so we selected one such promising MOF and experimentally confirmed its predicted capacity.

- Knot formation in newly translated proteins is spontaneous and accelerated by chaperonins
  Mallam, A. L.; Jackson,S. E. *Nat.Chem. Biol.* **2012**, *8*, 147-153.
  Abstract :



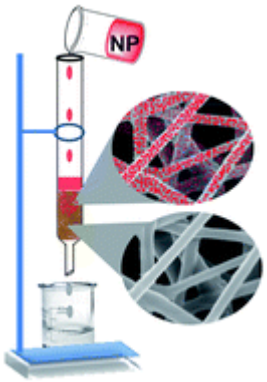
Topological knots are found in a considerable number of protein structures, but it is not clear how they knot and fold within the cellular environment. We investigated the behavior of knotted protein molecules as they are first synthesized by the ribosome using a cell-free translation system. We found that newly translated knotted proteins can spontaneously self-tie and do not require the assistance of molecular chaperones to fold correctly to their trefoil-knotted structures. This process is slow but efficient, and we found no evidence of misfolded species. A kinetic analysis indicates that the knotting process is rate limiting, occurs post-translationally, and is specifically and significantly ($P < 0.001$) accelerated by the GroEL–GroESchaperonin complex. This demonstrates a new active mechanism for this molecular chaperone and suggests that chaperonin-catalyzed knotting probably dominates in vivo. These results explain how knotted protein structures have withstood evolutionary pressures despite their topological complexity.

- Single Dye Molecule Behavior in Fluorescent Core-Shell Silica Nanoparticles.
  Cohen, B.; Martin, C.; Iyer, S. K.; Wiesner, U.; Douhal, A. *Chem. Mater.* **2012**, *24*, 361-372.
  Abstract:



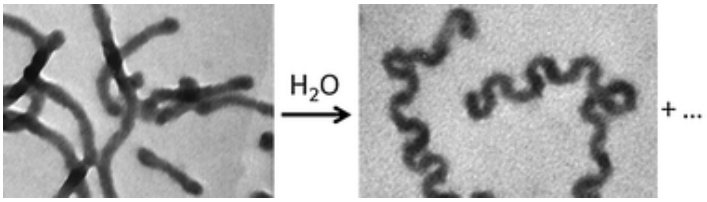
Understanding the parameters that control the intermolecular interactions of chromophores encapsulated within nanoparticles is of fundamental importance to various fields of nanoscience. Employing single-molecule time and spectral domains, we studied a red-absorbing hemicyanine analogue (DY-630) covalently encapsulated in the core of ~20 and ~30 nm core-shell silica nanoparticles. We find that on average 4 and 7 dyes are encapsulated within these particles, respectively. Steady state and fluorescence correlation spectroscopy show unusually strong enhancements (up to 16 times) in the relative fluorescence efficiency of the nanoparticles as compared to the free dye in aqueous solution. This increase is explained in terms of restriction of the trans-cis isomerization process due to the more rigid local environment provided by the silica, and protection from the solute-solvent interaction, while preserving the spectral characteristics of the constituent dye. Single molecule measurements reveal that the majority of the nanoparticles behave as systems of independently emitting chromophores. Two subpopulations of molecules are identified and assigned to molecules embedded within and on the surface of the core, respectively. Fluorescence lifetime and polarization trajectories of single molecules provide evidence that under certain conditions intermolecular interactions between several encapsulated molecules, such as energy hopping and singlet–singlet annihilation, can occur within single nanoparticles. We find that the energy transfer processes are more efficient in the smaller nanoparticles (~11%), probably due to the limited space provided by the core and the shorter distance between the trapped molecules (4 nm). In the bigger nanoparticles energy hopping is present only in 5% of the studied cases.

- Isolation and characterization of cellulose-based nanofibers for nanoparticle extraction from an aqueous environment.
  Mahanta, N.; Leong, W. Y.; Valiyaveettil, S. *J. Mater. Chem.* **2012,** *22*, 1985-1993.
  Abstract:



The increased use of nanoparticles in various commercial products enhances the contamination of nanomaterials in the environment which may cause serious health concern in the near future. To address this problem, new methods need to be developed for removal of nanomaterials from the environment. In this report, we explored the removal of nanoparticles from water using cellulosic nanofibers extracted from a renewable source such as sugarcane bagasse. The nanofibers were coated with chitosan to introduce additional functional groups on the surface. The designed cellulosic nanofibers showed high extraction efficiency (80-90%) towards silver (Ag) and gold (Au) nanoparticles. The maximum adsorption efficiency (Q_t) towards citrate and polyvinylpyrrolidone (PVP) capped Ag-nanoparticles using chitosan coated cellulose nanofibers was 13.1 mg g^{-1}. Similarly, Q_t values for citrate and PVP capped Au-nanoparticles were 17.9 mg g^{-1} and 17.4 mg g^{-1}, respectively. The adsorption of nanoparticles onto the nanofibers was confirmed using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). Even though we used spiked solutions for the current study, it is expected that such low cost, highly abundant nanofibers may be used for setting up a large-scale nanoparticle removal system for water purification.

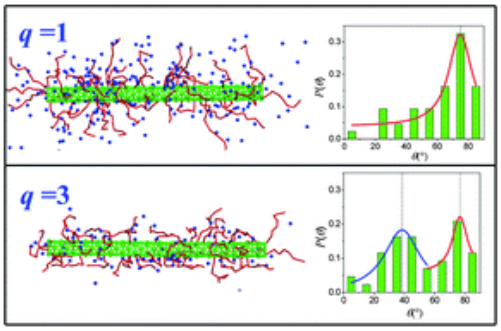
- Morphological transition of triblock copolymer cylindrical micelles responding to solvent change
  Han, D.; Li, X.; Hong, S.; Jinnai H.; Liu, G. *Soft Matter* **2012**, *8*, 2144-2151.
  Abstract:



Reported is the morphological transition of micelles of a BCA triblock copolymer after the solvation medium was changed from one that was selective for B and A to one that was selective for A only. Here B, C, and A denote poly(*tert*-butyl acrylate), poly(2-cinnamoyloxyethyl methacrylate), and the amine-bearing poly(*N*,*N*-dimethylaminoethyl methacrylate) blocks respectively. In methanol, BCA formed cylindrical micelles with the insoluble C block as the core and the soluble A and B blocks as the corona. Adding water reduced the solubility of the B coronal chains. The micellar morphological evolution was followed using transmission electron microscopy (TEM) by analyzing samples, which were taken at different times after water addition to the water volume fractions (f_w) of 2.7% and

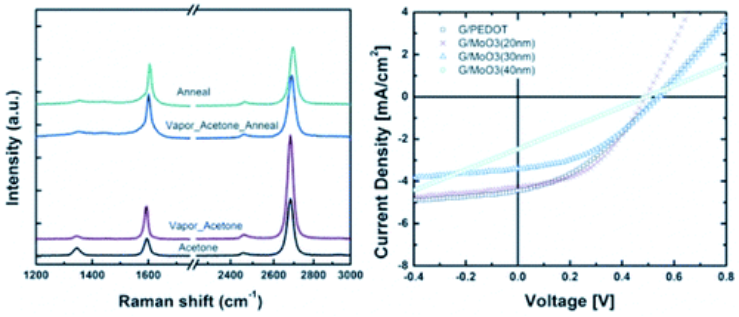
10.7%, respectively. Also reported are the stabilized morphologies of the micelles formed in methanol/water mixtures with f_w ranging from 2.9% to 23%.

- Effects of multivalent counterions on the morphology and interactions of polyelectrolyte chains grafted on carbon nanotubes
  Yan L. T.; Guo, R. *Soft Matter* **2012**, *8*, 660-666.
  Abstract:



The morphology of polymer chains grafted on nanotubes plays an important role in the effective interaction between these functionalized nanotubes. Herein we perform mesoscopic simulations to investigate the precise morphology of polyelectrolyte (PE) chains grafted on a single-walled carbon nanotube (SWNT) in the presence of added salts. We find that there are two peaks in the probability density distribution for the orientation angle of the grafted PE chains. Increasing counterion valency leads to the height of each peak changing, reflecting the morphology transition of the grafted chains. Our simulations indicate that the counterions with a higher valency induce a stronger collapse of the grafted PE chains wrapping around the SWNT, which strengthens the interaction between the SWNT and the grafted PE chains, and consequently modifies the orientation of these PE chains. The influence of the counterion valency from added salts on the interaction between two functionalized SWNTs is also investigated through examining the potential of mean force (PMF). The results reveal that the PMF between functionalized nanotubes can be effectively tuned through changing the counterion valency. The findings could provide guidelines for fine control over the SWNT aggregation status and may have implications in designing supramolecular nanohybrids composed of functionalized nanotubes and other charged components.

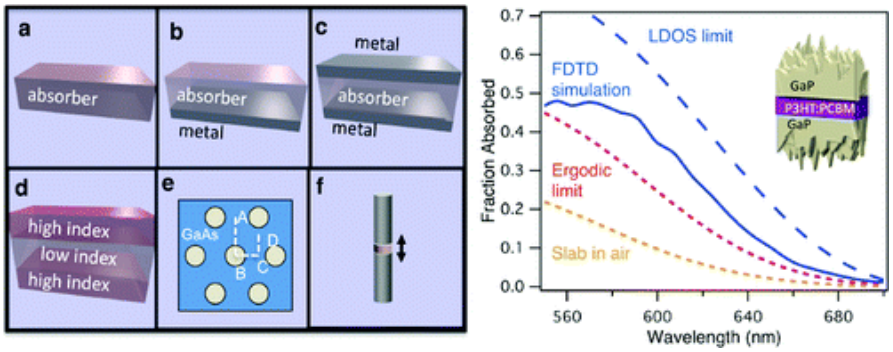
- Graphene As Transparent Conducting Electrodes in Organic Photovoltaics: Studies in Graphene Morphology, Hole Transporting Layers, and Counter Electrodes
  Park, H.; Brown, P. R.; Bulović, V.; Kong, J. *Nano Lett.* **2012**, *12*, 133–140.
  Abstract :



In this work, organic photovoltaics (OPV) with graphene electrodes are constructed where the effect of graphene morphology, hole transporting layers (HTL), and counter electrodes are presented.

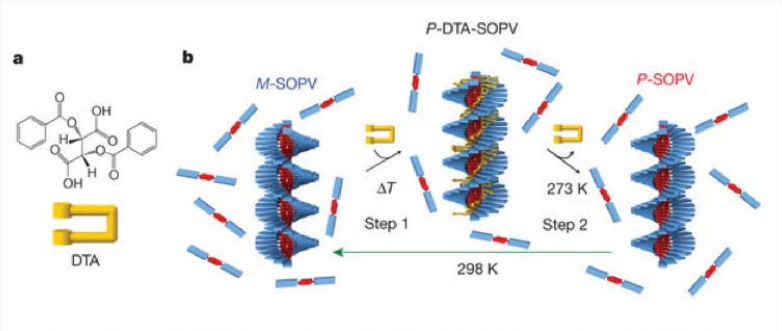
Instead of the conventional poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) PEDOT:PSS HTL, an alternative transition metal oxide HTL (molybdenum oxide (MoO_3)) is investigated to address the issue of surface immiscibility between graphene and PEDOT:PSS. Graphene films considered here are synthesized via low-pressure chemical vapor deposition (LPCVD) using a copper catalyst and experimental issues concerning the transfer of synthesized graphene onto the substrates of OPV are discussed. The morphology of the graphene electrode and HTL wettability on the graphene surface are shown to play important roles in the successful integration of graphene films into the OPV devices. The effect of various cathodes on the device performance is also studied. These factors (i.e., suitable HTL, graphene surface morphology and residues, and the choice of well-matching counter electrodes) will provide better understanding in utilizing graphene films as transparent conducting electrodes in future solar cell applications.

- Solar Cell Light Trapping beyond the Ray Optic Limit
  Callahan, D. M.; Munday, J. N.; Atwater, H. A. *Nano Lett.* **2012**, *12*, 214–218.
  Abstract :



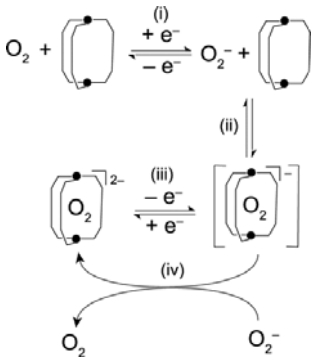
In 1982, Yablonovitch proposed a thermodynamic limit on light trapping within homogeneous semiconductor slabs, which implied a minimum thickness needed to fully absorb the solar spectrum. However, this limit is valid for geometrical optics but not for a new generation of subwavelength solar absorbers such as ultrathin or inhomogeneously structured cells, wire-based cells, photonic crystal-based cells, and plasmonic cells. Here we show that the key to exceeding the conventional ray optic or so-called ergodic light trapping limit is in designing an elevated local density of optical states (LDOS) for the absorber. Moreover, for any semiconductor we show that it is always possible to exceed the ray optic light trapping limit and use these principles to design a number of new solar absorbers with the key feature of having an elevated LDOS within the absorbing region of the device, opening new avenues for solar cell design and cost reduction.

- Pathway complexity in supramolecular polymerization
  Korevaar, P. A.; George, S. J.; Markvoort, A. J.; Smulders, M. M. J.; Hilbers, P. A. J.; Schenning, A. P. H. J.; De Greef, T. F. A.; Meijer, E. W. *Nature* **2012,** *481*, 492-496.
  Abstract :



Self-assembly provides an attractive route to functional organic materials, with properties and hence performance depending sensitively on the organization of the molecular building blocks. Molecular organization is a direct consequence of the pathways involved in the supramolecular assembly process, which is more amenable to detailed study when using one-dimensional systems. In the case of protein fibrils, formation and growth have been attributed to complex aggregation pathways that go beyond traditional concepts of homogeneous and secondary nucleation events. The self-assembly of synthetic supramolecular polymers has also been studied and even modulated, but our quantitative understanding of the processes involved remains limited. Here we report time-resolved observations of the formation of supramolecular polymers from π-conjugated oligomers. Our kinetic experiments show the presence of a kinetically favoured metastable assembly that forms quickly but then transforms into the thermodynamically favoured form. Quantitative insight into the kinetic experiments was obtained from kinetic model calculations, which revealed two parallel and competing pathways leading to assemblies with opposite helicity. These insights prompt us to use a chiral tartaric acid as an auxiliary to change the thermodynamic preference of the assembly process. We find that we can force aggregation completely down the kinetically favoured pathway so that, on removal of the auxiliary, we obtain only metastable assemblies.

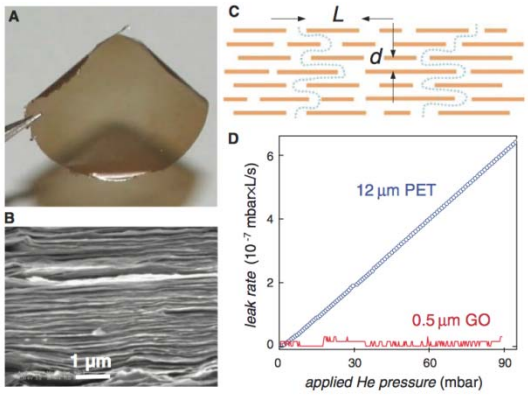
- Reversible Reduction of Oxygen to Peroxide Facilitated by Molecular Recognition
  Lopez, N.; Graham, D. J.; McGuire, R.; Alliger, G. E.; Shao-Horn, Y.; Cummins, C. C.; Nocera, D. G. *Science* **2012**, *335*, 450-453.
  Abstract :



Generation of soluble sources of peroxide dianion (O_2^{2-}) is a challenge in dioxygen chemistry. The oxidizing nature of this anion renders its stabilization in organic media difficult. This Report describes the chemically reversible reduction of oxygen (O_2) to cryptand-encapsulated O_2^{2-}. The dianion is stabilized by strong hydrogen bonds to N-H groups from the hexacarboxamide cryptand. Analogous stabilization of peroxide by hydrogen bonding has been invoked recently in crystalline saccharide and protein systems. The present peroxide adducts are stable at room temperature in dimethyl sulfoxide (DMSO) and *N*,*N*′-dimethylformamide (DMF). These adducts can be obtained in gram quantities from

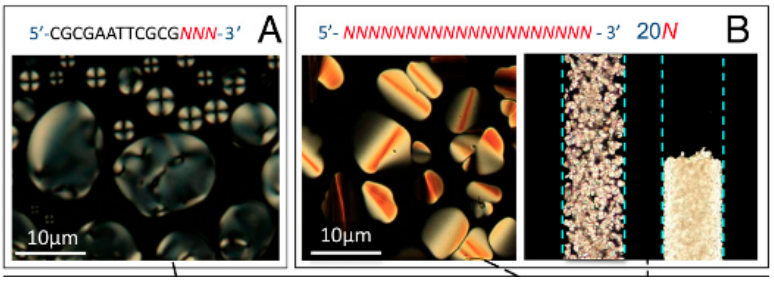
the cryptand-driven disproportionation reaction of potassium superoxide (KO_2) at room temperature.

- Unimpeded Permeation of Water Through Helium-Leak–Tight Graphene-Based Membranes
  Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K. *Science* **2012,** *335*, 442-444.
  Abstract :



Permeation through nanometer pores is important in the design of materials for filtration and separation techniques and because of unusual fundamental behavior arising at the molecular scale. We found that submicrometer-thick membranes made from graphene oxide can be completely impermeable to liquids, vapors, and gases, including helium, but these membranes allow unimpeded permeation of water (H_2O permeates through the membranes at least 10^{10} times faster than He). We attribute these seemingly incompatible observations to a low-friction flow of a monolayer of water through two-dimensional capillaries formed by closely spaced graphene sheets. Diffusion of other molecules is blocked by reversible narrowing of the capillaries in low humidity and/or by their clogging with water.

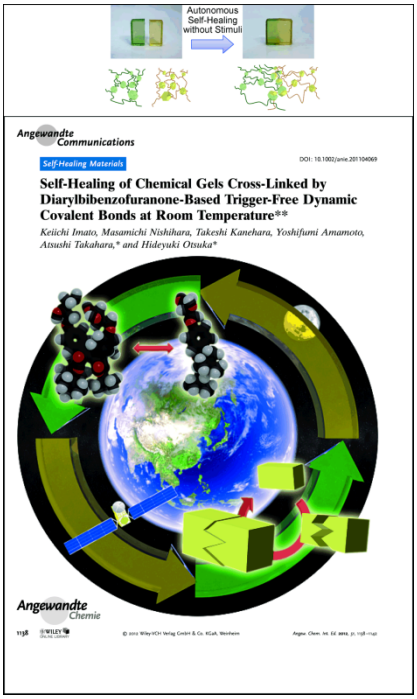
- Liquid crystal self-assembly of random-sequence DNA oligomers
  Bellini, T.; Zanchetta, G.; Fraccia, T. P.; Cerbino, R.; Tsai, E.; Smith, G. P.; Moran, M. J.; Walba, D. M.; Clark, N. A. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 1110-1115.
  Abstract :



In biological systems and nanoscale assemblies, the self-association of DNA is typically studied and applied in the context of the evolved or directed design of base sequences that give complementary pairing, duplex formation, and specific structural motifs. Here we consider the collective behavior of DNA solutions in the distinctly different regime where DNA base sequences are chosen at random or with varying degrees of randomness. We show that in solutions of completely random sequences, corresponding to a remarkably large number of different molecules, e.g., approximately 10^{12} for random 20-mers, complementary still emerges and, for a narrow range of oligomer lengths, produces a subtle hierarchical sequence of structured self-assembly and organization into liquid

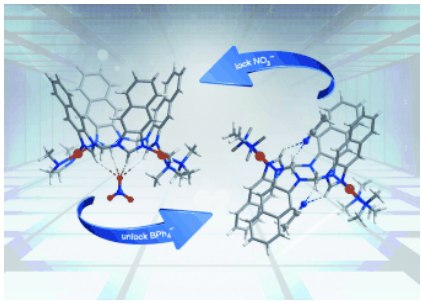
crystal (LC) phases. This ordering follows from the kinetic arrest of oligomer association into long-lived partially paired double helices, followed by reversible association of these pairs into linear aggregates that in turn condense into LC domains.

- Self-Healing of Chemical Gels Cross-Linked by Diarylbibenzofuranone-Based Trigger-Free Dynamic Covalent Bonds at Room Temperature
  Imato, K.; Nishihara, M.; Kanehara, T.; Amamoto, Y.; Takahara, A.; Otsuka, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 1138-1142.
  Abstract:



Linked: Polymers cross-linked with diary lbiben zofuranone units have been prepared by polyaddition. The exchange of bonds of the gels and their macroscopic self-healing were accomplished under air at room temperature in the dark. The macroscopic fusion of completely separated parts was successful (see picture).

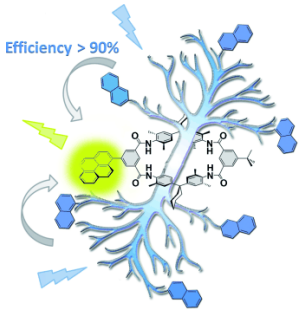
- Fine-Tuning Conformational Motion of a Self-Assembled Metal–Organic Macrocycle by Multiple CH…Anion Hydrogen Bonds
  Xie, T. Z.; Guo, C.; Yu, S. Y.; Pan, Y. J. *Angew. Chem. Int. Ed.* **2012**, *51,* 1177-1181.
  Abstract :



Anion switches: A bistable self-assembled metal–organic macrocycle undergoes intramolecular conformational motion that is switched reversibly with anions by multiple hydrogen-bonding

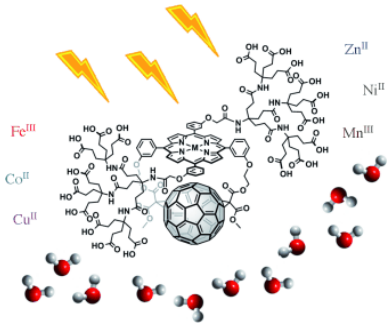
interactions (see picture; Pd orange, N blue, O red). The molecular bowl fixed with a nitrate anion could be freed to a partial chair by adding a tetraphenylborate anion.

- Light-Harvesting in Multichromophoric Rotaxanes
  Gallina, M. E.; Baytekin, B.; Schalley, C.; Ceroni, P. *Chem. Eur. J.***2012**, *18*, 1528-1535.
  Abstract:



Two rotaxanes with benzyl ether axles and tetralactam wheels were synthesized through an anion template effect. They carry naphthalene chromophores attached to the stopper groups and a pyrenechromophore attached to the wheel. The difference between the two rotaxanes is represented by the connecting unit of the naphthylchromophore to the rotaxane axle: a triazole or an alkynyl group. Both rotaxanes exhibit excellent light-harvesting properties: excitation of the naphthalene chromophores is followed by energy transfer to the pyrene unit with efficiency higher than 90□% in both cases. This represents an example of light-harvesting function among chromophores belonging to mechanically interlocked components, that is, the axle and the wheel of the rotaxanes.

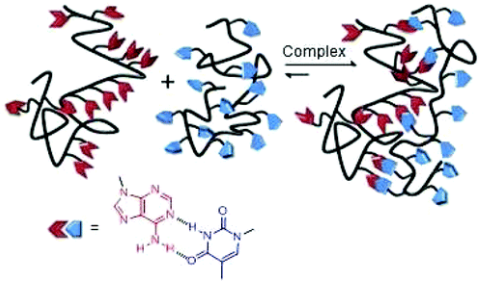
- A Charge-Transfer Challenge: Combining Fullerenes and Metalloporphyrins in Aqueous Environments
  Krokos, E.; Spänig, F.; Ruppert, M.; Hirsch, A.; Guldi, D. M. *Chem. Eur. J.***2012**, *18*, 1328-1341.
  Abstract:



A series of truly water-soluble C60/porphyrin electron donor–acceptor conjugates has been synthesized to serve as powerful mimics of photosynthetic reaction centers. To this end, the overall water-solubility of the conjugates was achieved by adding hydrophilic dendrimers of different generations to the porphyrin moiety. An important variable is the metal center of the porphyrin; we examined zinc(II), copper(II), cobalt(II), nickel(II), iron(III), and manganese(III). The first insights into electronic communication between the electron donors and the electron acceptors came from electrochemical assays, which clearly indicate that the redox processes centered either on C60 or the porphyrins are mutually affected. Absorption measurements, however, revealed that the electronic communication in terms of, for example, charge-transfer features, remains spectroscopically invisible. The polar environment that water provides is likely to be a cause of the lack of detection.

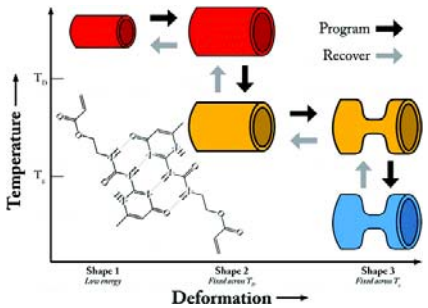
Despite this, transient absorption measurements confirm that intramolecular charge separation processes in the excited state lead to rapid deactivation of the excited states and, in turn, afford the formation of radical ion pair states in all of the investigated cases. Most importantly, the lifetimes of the radical ion pairs were found to depend strongly on several aspects. The nature of the coordinated metal center and the type of dendrimer have a profound impact on the lifetime. It has been revealed that the nature/electronic configuration of the metal centers is decisive in powering a charge recombination that either reinstates the ground state or any given multiplet excited state. Conversely, the equilibrium of two opposing forces in the dendrimers, that is, the interactions between their hydrophilic regions and the solvent and the electronic communication between their hydrophobic regions and the porphyrin and/or fullerene, is the key to tuning the lifetimes.

- Nucleobase Self-Assembly in Supramolecular Adhesives
  Cheng, S.; Zhang, M.; Dixit, N.; Moore, R. B.; Long, T. E. *Macromolecules* **2012,** *45*, 805–812.
  Abstract:



Novel acrylic monomers functionalized with nucleobase-containing units (adenine and thymine) were prepared upon aza-Michael addition and successfully copolymerized with n-butyl acrylate. At a content of 7 mol %, adenine-containing units self-assembled into needle-like microstructures within amorphous polymer matrices as shown with atomic force microscopy (AFM), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD); thymine-containing units did not aggregate into distinct morphologies even to 30 mol %. Upon blending, thymine- and adenine-containing statistical copolymers associated into a thermodynamically stable complex, which was physically cross-linked through adenine–thymine base pairing. The molar fractions of the nucleobase monomer, nucleobase stacking interactions, and complementary hydrogen bonding principally influenced self-assembly. Additionally, the nucleobase-functionalized polyacrylates exhibited tunable adhesive and cohesive strength.

- Triple-Shape Memory Polymers Based on Self-Complementary Hydrogen Bonding
  Ware, T.; Hearon, K.; Lonnecker, A.; Wooley, K. L.; Maitland, D. J.; Voit, W. *Macromolecules* **2012,** *45*, 1062–1069.
  Abstract:



Triple shape memory polymers (TSMPs) are a growing subset of a class of smart materials known as shape memory polymers, which are capable of changing shape and stiffness in response to a stimulus. A TSMP can change shapes twice and can fix two metastable shapes in addition to its permanent shape. In this work, a novel TSMP system comprised of both permanent covalent cross-links and supramolecular hydrogen bonding cross-links has been synthesized via a one-pot method. Triple shape properties arise from the combination of the glass transition of (meth)acrylate copolymers and the dissociation of self-complementary hydrogen bonding moieties, enabling broad and independent control of both glass transition temperature (Tg) and cross-link density. Specifically, ureidopyrimidone methacrylate and a novel monomer, ureidopyrimidone acrylate, were copolymerized with various alkyl acrylates and bisphenolAethoxylatediacrylate. Control of Tg from 0 to 60 °C is demonstrated: concentration of hydrogen bonding moieties is varied from 0 to 40 wt %; concentration of the diacrylate is varied from 0 to 30 wt %. Toughness ranges from 0.06 to 0.14 MPa and is found to peak near 20 wt % of the supramolecular cross-linker. A widely tunable class of amorphous triple-shape memory polymers has been developed and characterized through dynamic and quasi-static thermomechanical testing to gain insights into the dynamics of supramolecular networks.