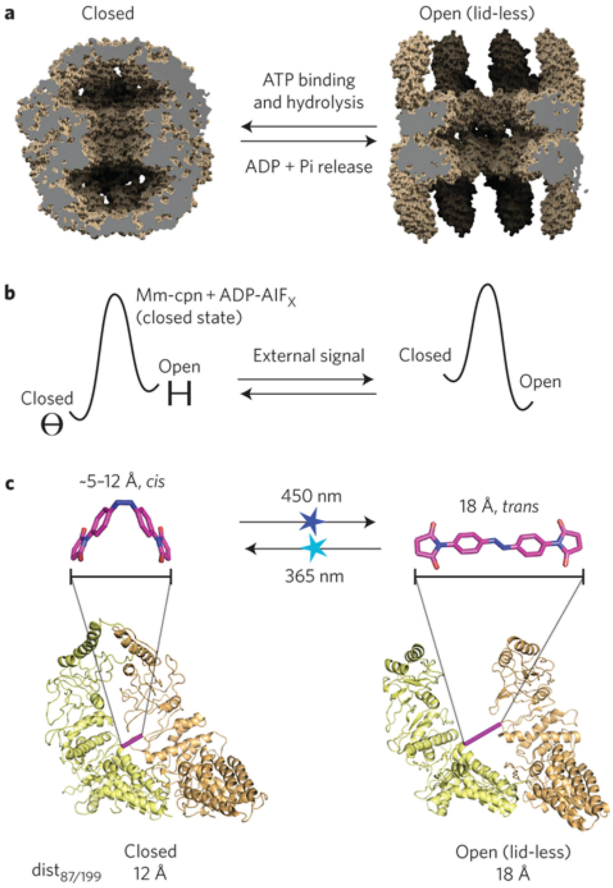
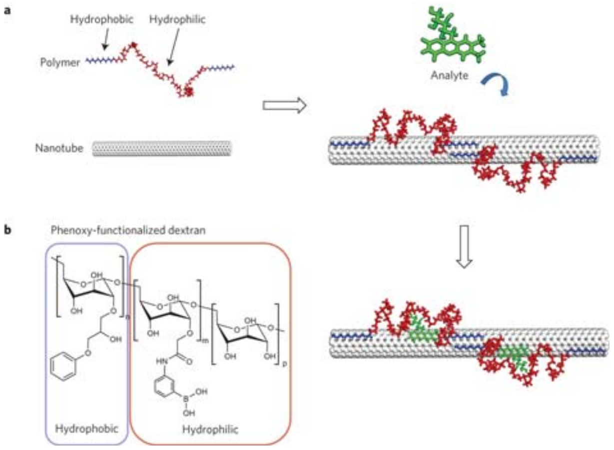
- Reprogramming an ATP-driven protein machine into a light-gated nanocage
  Hoersch, D.; Roh, S.-H.; Chiu, W.; Kortemme, T. *Nature Nanotech.* **2013**, *8*, 928–932.
  Abstract:



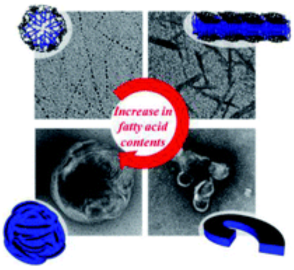
Natural protein assemblies have many sophisticated architectures and functions, creating nanoscale storage containers, motors and pumps. Inspired by these systems, protein monomers have been engineered to self-assemble into supramolecular architectures including symmetrical, metal-templated and cage-like structures. The complexity of protein machines, however, has made it difficult to create assemblies with both defined structures and controllable functions. Here we report protein assemblies that have been engineered to function as light-controlled nanocontainers. We show that an adenosine-5′-triphosphate-driven group II chaperonin, which resembles a barrel with a built-in lid, can be reprogrammed to open and close on illumination with different wavelengths of light. By engineering photoswitchable azobenzene-based molecules into the structure, light-triggered changes in interatomic distances in the azobenzene moiety are able to drive large-scale conformational changes of the protein assembly. The different states of the assembly can be visualized with single-particle cryo-electron microscopy, and the nanocages can be used to capture and release non-native cargos. Similar strategies that switch atomic distances with light could be used to build other controllable nanoscale machines.

- Molecular recognition using corona phase complexes made of synthetic polymers adsorbed on carbon nanotubes
  Zhang, J.; Landry, M. P.; Barone, P. W.; Kim, J.-H. *et al. Nature Nanotech.* **2013**, *8*, 959–968.
  Abstract:



Understanding molecular recognition is of fundamental importance in applications such as therapeutics, chemical catalysis and sensor design. The most common recognition motifs involve biological macromolecules such as antibodies and aptamers. The key to biorecognition consists of a unique three-dimensional structure formed by a folded and constrained bioheteropolymer that creates a binding pocket, or an interface, able to recognize a specific molecule. Here, we show that synthetic heteropolymers, once constrained onto a single-walled carbon nanotube by chemical adsorption, also form a new corona phase that exhibits highly selective recognition for specific molecules. To prove the generality of this phenomenon, we report three examples of heteropolymer–nanotube recognition complexes for riboflavin, L-thyroxine and oestradiol. In each case, the recognition was predicted using a two-dimensional thermodynamic model of surface interactions in which the dissociation constants can be tuned by perturbing the chemical structure of the heteropolymer. Moreover, these complexes can be used as new types of spatiotemporal sensors based on modulation of the carbon nanotube photoemission in the near-infrared, as we show by tracking riboflavin diffusion in murine macrophages.

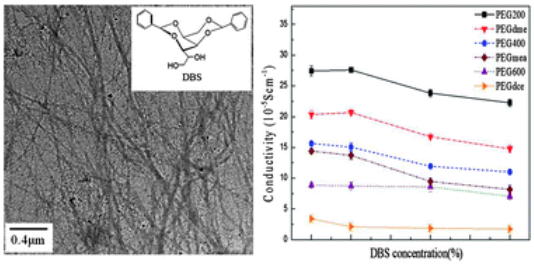
- Self-assembly modulation in ionic PAMAM derivatives
  Hernández-Ainsa, S.; Fedeli, E.; Barberá, J.; Marcos, M.; Sierra, T.; Serrano, J. L. *Soft Matter* **2014**, *10,* 281-289.
  Abstract:



The self-assembly behaviour both in the bulk and water of a series of amphiphilic dendrimers constituted by second generation PAMAM ionically functionalized with different amounts of myristic acid is shown here. The number of acids in the dendrimer determines the liquid-crystal properties and the structural parameters of their supramolecular organization. Most of them present mesomorphism, organizing in a smectic A mesophase, with a layer spacing decreasing when increasing the number of acids. All these dendrimers form well-defined nanoobjects in water. Micelles and broken lamellae have been found for compounds with low acid contents. In contrast, dendrimers with higher fatty acid contents self-assemble forming nanospheres with a lamellar

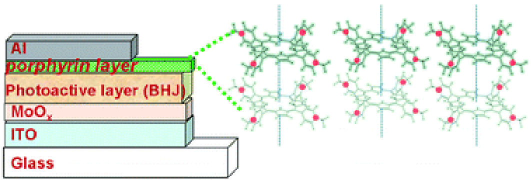
nanostructure. All compounds are able to trap the hydrophobic molecule 9,10-diphenylanthracene independent of the acid contents. Interestingly, the trapped hydrophobic molecule dominates the self-assembly trend of the dendrimers with low acid contents and thus different nanoobjects are found after the encapsulation.

- Novel poly(ethylene glycol) gel electrolytes prepared using self-assembled 1,3:2, 4-dibenzylidene-D-sorbitol
  Lai, W.-C.; Chen, C.-C. *Soft Matter* **2014**, *10,* 312-319.
  Abstract:



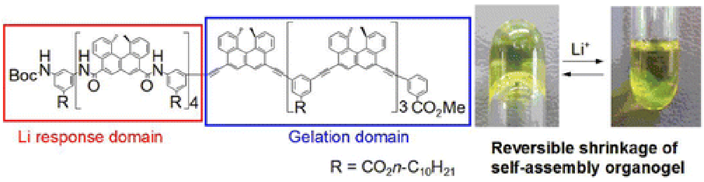
Gel electrolytes have usually been prepared by adding gelators or polymers to the liquid organic solventbased electrolytes. In this study, we proposed a method to prepare gel electrolytes using gelators in liquid (low molecular weight) polymer-based electrolytes. Inexpensive 1,3:2,4-dibenzylidene-D-sorbitol (DBS) was chosen as a gelator for poly(ethylene glycol) (PEG)-based electrolytes at relatively low DBS concentrations. A series of gel electrolytes was produced by varying the DBS amounts, PEG molecular weights and PEG end groups. First, we found that DBS molecules self-assembled into 3-D networks consisting of nanofibrils that were approximately 10 nm in diameter, as measured by transmission electron microscopy; they exhibited spherulite-like morphologies under polarizing optical microscopy. Second, the dynamic rheological measurements demonstrated that the elastic modulus and the dissolution temperature of DBS–PEG gels increased with the increasing DBS content. The thermal degradation temperature of these gels also increased when the DBS concentration increased, as determined by thermogravimetric analysis. In addition, adding DBS may help to facilitate the dissolution of iodide and iodine in PEG due to its ether groups. Furthermore, the conductivity of the prepared DBS–PEG gel electrolytes was similar to that of the liquid PEG electrolytes (without DBS). When used in dyesensitized solar cells (DSSC), the PEG-based electrolytes having inactive methyl end groups achieved the highest energy conversion efficiency among the tested cells. The efficiency of DSSC filled with our gel electrolytes remained basically the same over a one-month period, implying that the materials were relatively stable.

- Porphyrin oriented self-assembled nanostructures for efficient exciton dissociation in high-performing organic photovoltaics
  Vasilopoulou, M.; Georgiadou, D. G.; Douvas, A. M.; Soultati, A.; Constantoudis, V.; Davazoglou, D.; Gardelis, S.; Palilis, L. C.; Fakis, M.; Kennou, S.; Lazarides, T.; Coutsolelos, A. G.; Argitisa, P. *J. Mater. Chem. A* **2014**, *2*, 182–192.
  Abstract:



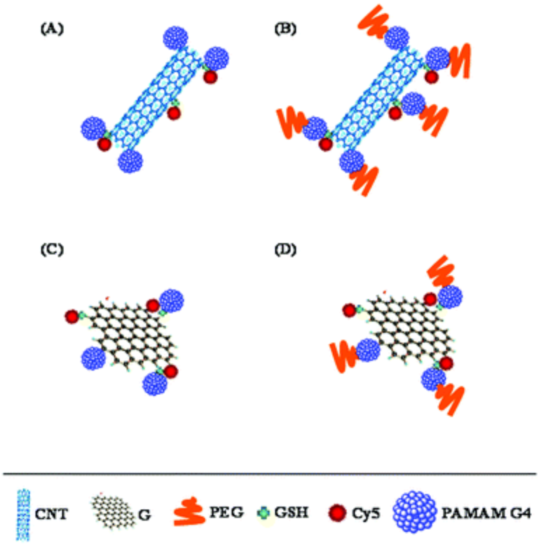
Herein we report on enhanced organic solar cell performance through the incorporation of cathode interfacial layers consisting of self-organized porphyrin nanostructures with a face-on configuration. In particular, a water/methanol-soluble porphyrin molecule, the free base meso-tetrakis(1-methylpyridinium-4-yl)porphyrin chloride, is employed as a novel cathode interlayer in bulk heterojunction organic photovoltaics. It is demonstrated that the self-organization of this porphyrin compound into aggregates in which molecules adopt a face-to-face orientation parallel to the organic semiconducting substrate induces a large local interfacial electric field that results in a significant enhancement of exciton dissociation. Consequently, enhanced photocurrent and open circuit voltage were obtained resulting in overall device efficiency improvement in organic photovoltaics based on bulk heterojunction mixtures of different polymeric donors and fullerene acceptors, regardless of the specific combination of donor–acceptor employed. To highlight the impact of molecular orientation a second porphyrin compound, the Zn-metallated meso-tetrakis(1-methylpyridinium-4-yl)porphyrin chloride, was also studied and it was found that it forms aggregates with an edge-to-edge molecular configuration inducing a smaller increase in the device performance.

- Reversible Shrinkage of Self-Assembled Two-Component Organogels by Lithium Salts: Synthesis of Gelation Property and Lithium Salt Response Using Bidomain Helicene Oligomer
  Ichinose, W.; Miyagawa, M.; Yamaguchi, M. *Chem. Mater.* **2013***, 25,* 4036–4043.
  Abstract:



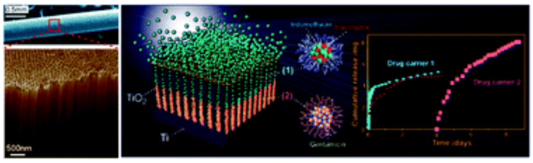
A bidomain oligomer containing a (P)-amidohelicene tetramer domain and a (P)-ethynylhelicene tetramer domain formed self-assembled organogels in the presence of an (M)-ethynylhelicene pentamer. Strong Cotton effects were observed for gels in pyridine, piperidine, cyclohexanone, and 1,2-dimethoxybenzene (Type A solvents), and weak Cotton effects in anisole, ethyl benzoate, and toluene gels (Type B solvents). The amido domain was in the random-coil state in the gels of the Type A solvents, and in the helix-dimer state in the gels of the type B solvents. The pyridine gels shrank upon the addition of lithium perchlorate to 25% of their original volume, and the volume recovered when the supernatant was removed, the solvent was added, and the mixture was briefly heated and cooled. The shrinkage process could be reproducibly repeated five times. In contrast, the gels of anisole and toluene did not shrink in the presence of lithium perchlorate. The gelation property and lithium salt response were induced using the bidomain oligomer to achieve the reversible shrinkage property of self-assembly organogels.

- Structure effect of carbon nanovectors in regulation of cellular responses
  Banerjee, S. S.; Jalota-Badhwar, A.; Wate, P.; Asai, S.; Zope, K. R.; Mascarenhas, R.; Bhatia, D.; Khandare, J. *Biomater. Sci.* **2013**, *2*, 57-66.
  Abstract:



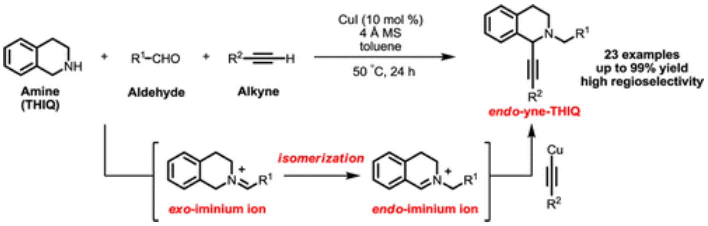
Carbon nanostructures such as multiwalled carbon nanotubes (CNT) and graphene (G) are potential candidates in a large number of biomedical applications. However, there is limited understanding and connection between the physicochemical properties of diverse carbon nanostructures and biological systems, particularly with regard to cellular responses. It is also crucial to understand how the structure and surface composition of carbon nanostructuresaffect the cellular internalization process. Here, through *in vitro* cellular entry kinetics and cytotoxicity studies using MCF-7 breast cancer cells and H460 human lung cancer cells, we show that the structure and surface composition of CNT and G conjugates with various molecules such as PAMAM dendrimers (G4) and G4-poly(ethylene glycol) (PEG) are directly related to their cellular internalization ability and toxicity. Interestingly, the cellular association of CNT and G nanoconjugates was observed to be structure and surface composition dependent. We found that CNT conjugates internalized more compared to G conjugates. Furthermore, G4 conjugated CNT internalized more compared to G4-PEG conjugated CNT, whereas, higher internalization was found for G4-PEG conjugated G than G4 conjugated G. We have also correlated the cytotoxicity and cellular uptake mechanisms of CNT, G, and their conjugates through zeta potential measurements, fluorescence quenching studies and by fluorescence-activated cell sorting. Altogether these studies suggest different biological activities of thecarbon nanostructures, with the shape and surface composition playing a primary role.

- Non-eroding drug-releasing implants with ordered nanoporous and nanotubular structures: concepts for controlling drug release
  Aw, M. S.; Kurian, M.; Losic, D. *Biomater. Sci.* **2014**, *2*, 10-34.
  Abstract:



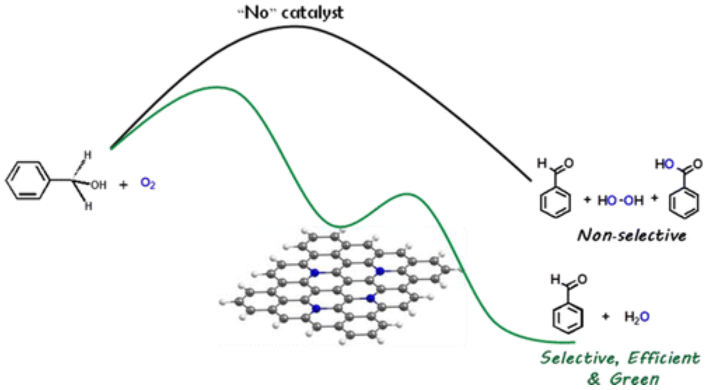
To address the limitations of systemic drug delivery, localized drug delivery systems (LDDS) based on nano-engineered drug-releasing implants are recognized as a promising alternative. Nanoporous anodic alumina (NAA) and nanotubular titania (TNT) fabricated by a simple, self-ordering electrochemical process, with regard to their outstanding properties, have emerged as one of the most reliable contenders for these applications. This review highlights the development of new LDDS based on NAA and TNT, focusing on a series of strategies for controlling their drug release characteristics that are based on: modification of their nanopore/nanotube structures, altering internal chemical functionalities, controlling pore openings by biopolymer coatings and using polymeric micelles as drug nano-carriers loaded within the implants. Several new strategies on externally triggered stimuli-responsive drug release for LDDS are also reviewed, and their significance toward the development of advanced smart implants for localized therapy is discussed. Finally, the review is summarized with conclusions and future prospects in this research field.

- CuI-Catalyzed C1-Alkynylation of Tetrahydroisoquinolines (THIQs) by A^3 Reaction with Tunable Iminium Ions
  Zheng, Q.-H.; Meng, W.; Jiang, G.-J.; Yu, Z.-X. *Org. Lett.* **2013,** *15*, 5928-5931.
  Abstract:



A CuI-catalyzed A^3 (amines, aldehydes and alkynes) reaction of tetrahydroisoquinolines (THIQs), aldehydes, and alkynes to give C1-alkynylated THIQ products (*endo*-yne-THIQs) was developed. This redox neutral C1-alkynylation of THIQs, which was conducted under mild conditions, has abroad scope for the used aldehydes and alkynes. It was proposed that the A^3 reaction first generates in situ exo-iminium ions, which then isomerize to endo-iminium ions and react with copper acetylides to give the *endo* alkynylated THIQs(*endo*-yne-THIQs).

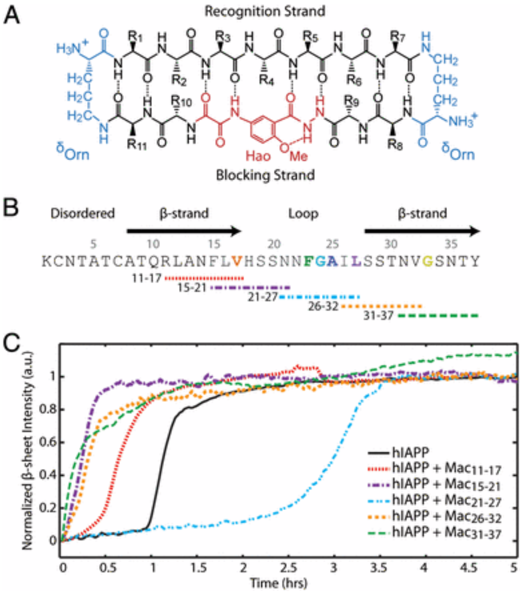
- Novel Chemistry for the Selective Oxidation of Benzyl Alcohol by Graphene Oxide and N-Doped Graphene
  Vijaya Sundar, J.; Subramanian, V. *Org. Lett.* **2013,** *15*, 5920-5923.
  Abstract:



A novel mechanism for the selective activation of benzyl alcohol by graphene oxide and N-doped graphene has been proposed using density functional theory based calculations. Interestingly, the proposed mechanism opens new avenues for graphene and its derivative-based catalysis.

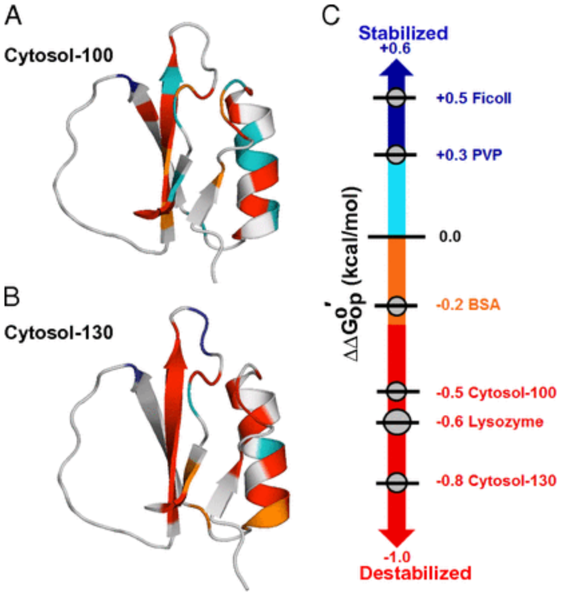
- Mechanism of IAPP amyloid fibril formation involves an intermediate with a transient β-sheet
  Buchanan, L. E.; Dunkelberger, E. B.; Tran, H. Q.; Cheng, P.-N.; Chiu, C.-C.; Cao, P.; Raleigh, D. P.; de Pablo, J. J.; Nowick, J. S.; Zanni, M. T. *Proc. Natl. Acad. Sci. U. S. A.* **2013,** *110*, 19285-19290.

Abstract:



There is an enormous interest in the mechanism by which proteins misfold and aggregate into amyloid fibrils. Amyloid has been implicated in many human diseases, but the mechanism of aggregation is not understood. Intermediates have been postulated to play an important role in the process, but there have been very few direct measurements that provide specific structural details. The use of isotope labeling and 2D IR methods has allowed the characterization of a critical intermediate generated during amyloid formation by islet amyloid polypeptide, the peptide responsible for amyloid formation in type 2 diabetes. Identification of this intermediate provides a structural explanation for the lag phase and may explain why some species develop amyloid deposits of hIAPP while others do not.

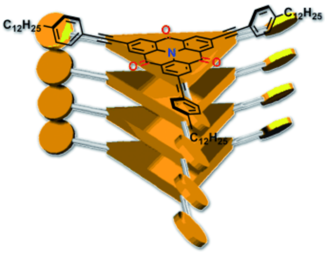
- Impact of reconstituted cytosol on protein stability
  Sarkar, M.; Smith, A. E.; Pielak, G. J. *Proc. Natl. Acad. Sci. U. S. A.* **2013,** *110*, 19342-19347.
  Abstract:



The cell cytoplasm contains a complex array of macromolecules at concentrations exceeding 300 g/L. The natural, most relevant state of a biological macromolecule is thus a “crowded” one. Moving

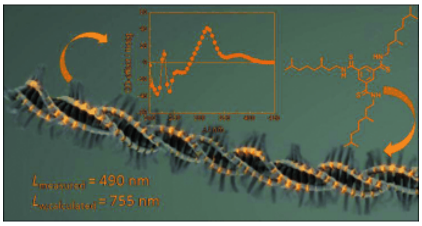
quantitative protein chemistry from dilute solution to the inside of living cells represents a major frontier that will affect not only our fundamental biological knowledge, but also efforts to produce and stabilize protein-based pharmaceuticals. We show that the bacterial cytosol actually destabilizes our test protein, contradicting most theoretical predictions, but in agreement with a novel *Escherichia coli* model.

- Columnar Self-Assembly in Electron-Deficient Heterotriangulenes
  Kivala, M.; Pisula, W.; Wang, S.; Mavrinskiy, A.; Gisselbrecht, J.-P.; Feng, X.; Müllen, K. *Chem. Eur. J.* **2013**, *19*, 8117–8128.
  Abstract:



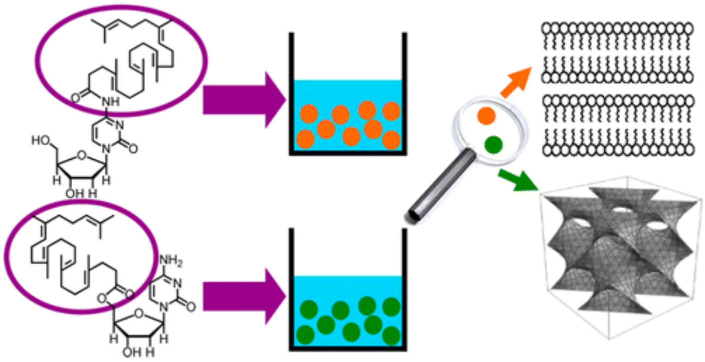
A series of soluble carbonyl-bridged heterotriangulenes, in which flexible *n*-dodecyl chains are attached through different spacers to the planar nitrogen-centered polycyclic core, have been synthesized. The introduction of triisopropylsilylethynyl moieties enabled, for the first time, the characterization of single-crystal columnar packing of a substituted heterotriangulene by X-ray crystallography. Electrochemical studies disclosed the carbonyl-bridged heterotriangulene core as a reasonably strong acceptor for a reversible two-electron transfer. The tendency of substituted heterotriangulenes to self-assemble in solution, on surfaces, and in the bulk appeared to sensitively depend on the nature of the lateral substituents, their steric demand, and the applied solution processing conditions. It can be concluded that 1) additional phenylene moieties between the heterotriangulene core and the *n*-dodecyl chains facilitate self-assembly by extending the π-conjugated polycyclic disc, 2) the rod-like ethynylene spacers introduce some additional flexibility and hence lower the overall aggregation tendency, and 3) the combination of both features in the phenylene–ethynylene moieties induces thermotropic liquid crystallinity.

- Thioamides: Versatile Bonds To Induce Directional and Cooperative Hydrogen Bonding in Supramolecular Polymers
  Mes, T.; Cantekin, S.; Balkenende, D. W. R.; Frissen, M. M. M.; Gillissen, M. A. J.; De Waal, B. F. M.; Voets, I. K.; Meijer, E. W.; Palmans, A. R. A. *Chem. Eur. J.* **2013**, *19*, 8642–8649.
  Abstract:



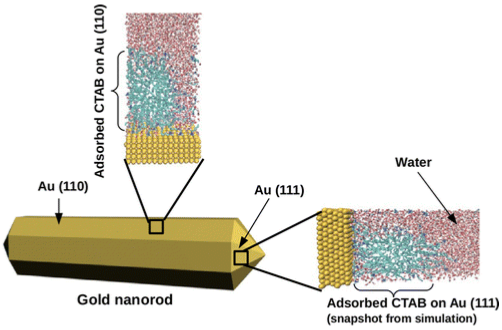
The amide bond is a versatile functional group and its directional hydrogen-bonding capabilities are widely applied in, for example, supramolecular chemistry. The potential of the thioamide bond, in contrast, is virtually unexplored as a structuring moiety in hydrogen-bonding-based self-assembling systems. We report herein the synthesis and characterisation of a new self-assembling motif comprising thioamides to induce directional hydrogen bonding. *N*,*N′*,*N″*-Trialkylbenzene-1,3,5-tris(carbothioamide)s (thioBTAs) with either achiral or chiral side-chains have been readily obtained by treating their amide-based precursors with P_2S_5. The thioBTAs showed thermotropic liquid crystalline behaviour and a columnar mesophase was assigned. IR spectroscopy revealed that strong, three-fold, intermolecular hydrogen-bonding interactions stabilise the columnar structures. In apolar alkane solutions, thioBTAs self-assemble into one-dimensional, helical supramolecular polymers stabilised by three-fold hydrogen bonding. Concentration- and temperature-dependent self-assembly studies performed by using a combination of UV and CD spectroscopy demonstrated a cooperative supramolecular polymerisation mechanism and a strong amplification of supramolecular chirality. The high dipole moment of the thioamide bond in combination with the anisotropic shape of the resulting cylindrical aggregate gives rise to sufficiently strong depolarised light scattering to enable depolarised dynamic light scattering (DDLS) experiments in dilute alkane solution. The rotational and translational diffusion coefficients, D_{trans} and D_{rot}, were obtained from the DDLS measurements, and the average length, L, and diameter, d, of the thioBTA aggregates were derived (L=490 nm and d=3.6 nm). These measured values are in good agreement with the value L_w=755 nm obtained from fitting the temperature-dependent CD data by using a recently developed equilibrium model. This experimental verification validates our common practice for determining the length of BTA-based supramolecular polymers from model fits to experimental CD data. The ability of thioamides to induce cooperative supramolecular polymerisation makes them effective and broadly applicable in supramolecular chemistry.

- Self-Assembly of Squalene-Based Nucleolipids: Relating the Chemical Structure of the Bioconjugates to the Architecture of the Nanoparticles
  Lepeltier, E.; Bourgaux, C.; Rosilio, V.; Poupaert, J. H.; Meneau, F.; Zouhiri, F.; Lepêtre-Mouehli, S.; Desmaële, D.; Couvreur, P. *Langmuir* **2013**, *48*, 14795–14803.
  Abstract:



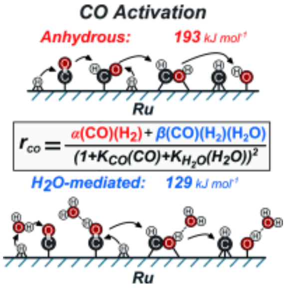
Squalene-based nucleolipids, including anticancer or antiviral prodrugs, gave rise to nanoparticles displaying a diversity of structures upon nanoprecipitation in water. Synchrotron small-angle X-ray scattering and cryo-TEM imaging revealed that both the nature of the nucleoside and the position of the squalene moiety relative to the nucleobase determined the self-assembly of the corresponding bioconjugates. It was found that small chemical differences resulted in major differences in the self-organization of nucleolipids when squalene was grafted onto the nucleobase whereas only lamellar phases were observed when squalene was linked to the sugar moiety. The key role of hydrogen bonds between nucleobases in the formation of the lamellar phases was suggested, in agreement with molecular simulations. These findings provide a way to fine tune the supramolecular organization of squalene-based prodrugs, with the aim of improving their pharmacological activity.

- Understanding the Microscopic Origin of Gold Nanoparticle Anisotropic Growth from Molecular Dynamics Simulations
  Meena, S. K.; Sulzipi, M. *Langmuir* **2013**, *48*, 14954–14961.
  Abstract:



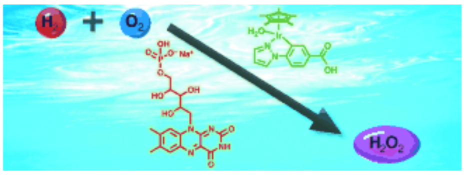
We use molecular dynamics simulations in order to understand the microscopic origin of the asymmetric growth mechanism in gold nanorods. We provide the first atomistic model of different surfaces on gold nanoparticles in a growing electrolyte solution, and we describe the interaction of the metal with the surfactants, namely, cetyltrimethylammonium bromide (CTAB) and the ions. An innovative aspect is the inclusion of the role of the surfactants, which are explicitly modeled. We find that on all the investigated surfaces, namely, (111), (110), and (100), CTAB forms a layer of distorted cylindrical micelles where channels among micelles provide direct ion access to the surface. In particular, we show how $AuCl_2^-$ ions, which are found in the growth solution, can freely diffuse from the bulk solution to the gold surface. We also find that the (111) surface exhibits a higher CTAB packing density and a higher electrostatic potential. Both elements would favor the growth of gold nanoparticles along the (111) direction. These findings are in agreement with the growth mechanisms proposed by the experimental groups of Murphy and Mulvaney.

- Mechanistic Role of Water on the Rate and Selectivity of Fischer–Tropsch Synthesis on Ruthenium Catalysts
  Hibbitts, D. D.; Loveless, B. T.; Neurock, M.; Iglesia, E. *Angew. Chem. Int. Ed.* **2013**, *52*, 12273–12278.
  Abstract



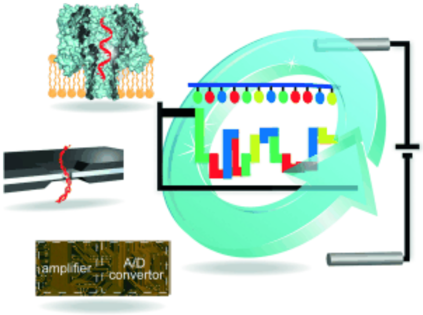
Water increases Fischer–Tropsch synthesis (FTS) rates on Ru through H-shuttling processes. Chemisorbed hydrogen (H*) transfers its electron to the metal and protonates the O-atom of CO* to form COH*, which subsequently hydrogenates to *HCOH* in the kinetically relevant step. H_2O also increases the chain length of FTS products by mediating the H-transfer steps during reactions of alkyl groups with CO* to form longer-chain alkylidynes and OH*.

- Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen by Using a Water-Soluble Iridium Complex and Flavin Mononucleotide
  Shibata, S.; Suenobu, T.; Fukuzumi, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 12327–12331.
  Abstract :



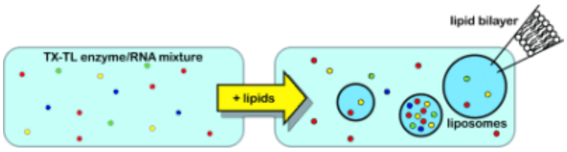
H_2, O_2 to H_2O_2: The direct synthesis of hydrogen peroxide from hydrogen and oxygen in water has been made possible by using an iridium(III) complex, $[Ir^{III}(Cp^*)(4\text{-}(1H\text{-pyrazol-1-yl-}\kappa N^2)\text{benzoic acid-}\kappa C^3)(H_2O)]_2SO_4$, and flavin mononucleotide. This method gives hydrogen peroxide with a high turnover number (847) and yield (19.2 %) under normal pressure and at room temperature.

- Nanopore-Based Sequencing and Detection of Nucleic Acids
  Ying, Y.-L.; Zhang, J.; Gao, R.; Long, Y.-T. *Angew. Chem. Int. Ed.* **2013**, *52*, 13154-13161.
  Abstract:



Nanopore-based techniques, which mimic the functions of natural ion channels, have attracted increasing attention as unique methods for single-molecule detection. The technology allows the real-time, selective, high-throughput analysis of nucleic acids through both biological and solid-state nanopores. In this Minireview, the background and latest progress in nanopore-based sequencing and detection of nucleic acids are summarized, and light is shed on a novel platform for nanopore-based detection.

- A Remarkable Self-Organization Process as the Origin of Primitive Functional Cells
  Stano, P.; D'Aguanno, E.; Bolz, J.; Fahr, A.; Luisi, P. L. *Angew. Chem. Int. Ed*. **2013**, *52*, 13397–13400.
  Abstract:

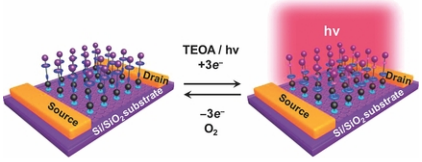


Encapsulation: The emergence of primitive cells remains an enigma of the origin of life. By modeling this key process as the encapsulation of a complex multimolecular mixture inside liposomes, a remarkable self-organization process has been revealed that brings about solute-rich compartments in which protein synthesis can take place.

- Interface-Engineered Bistable [2]Rotaxane-Graphene Hybrids with Logic Capabilities

Jia, C.; Li, H.; Jiang, J.; Wang, J.; Chen, H.; Cao, D.; Stoddart, J. F.; Guo, X. *Adv. Mater*. **2013**, *25*, 6752-6759.

Abstract:



The use of high-quality graphene as a local probe in combination with photo excitation helps to establish a deep mechanistic understanding of charge generation/quenching processes under lying the graphene/environment interface. By combining a non-destructive bottom-up assembly technique with sensitive graphene-based transistors, a bistable [2]rotaxane-graphene hybrid device, which exhibits a symmetric mirror-image photoswitching effect with logic capabilities, is produced.

- A Smart Hyperthermia Nanofiber with Switchable Drug Release for Inducing Cancer Apoptosis

  Kim, Y.-J.; Ebara, M.; Aoyagi, T. *Adv. Funct. Mater*. **2013**, *23*, 5753-5761.

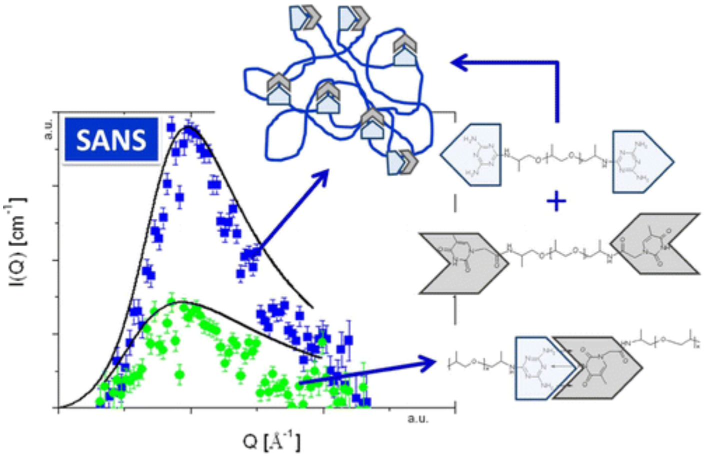
  Abstract :

A smart hyperthermia nanofiber is described with simultaneous heat generation and drug release in response to 'on-off' switching of alternating magnetic field (AMF) for induction of skin cancer apoptosis. The nanofiber is composed of a chemically-crosslinkable temperature-responsive polymer with an anticancer drug (doxorubicin; DOX) and magnetic nanoparticles (MNPs), which serve as a trigger of drug release and a source of heat, respectively. By chemical crosslinking, the nanofiber mesh shows switchable changes in the swelling ratio in response to alternating 'on-off' switches of AMF because the self-generated heat from the incorporated MNPs induces the deswelling of polymer networks in the nanofiber. Correspondingly, the 'on-off' release of DOX from the nanofibers is observed in response to AMF. The 70% of human melanoma cells died in only 5 min application of AMF in the presence of the MNPs and DOX incorporated nanofibers by double effects of heat and drug. Taken together these advantages on both the nano- and macroscopic scale of nanofibers demonstrate that the dynamically and reversibly tunable structures have the potential to be utilized as a manipulative hyperthermia material as well as a switchable drug release platform by simple switching an AMF 'on' and 'off'.

- Molecular Approach to Supramolecular Polymer Assembly by Small Angle Neutron Scattering

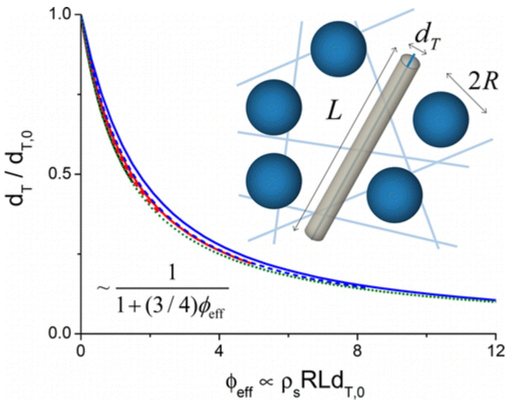
  Brás, A. R.; Hövelmann, C. H.; Antonius, W.; Teixeira, J.; Radulescu, A.; Allgaier, J.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D. *Macromolecules* **2013**, *46*, 9446–9454.

  Abstract:



We present a small angle neutron scattering (SANS) study of the association of heterocomplementary telechelic polypropylene glycol (PPG) polymers, bearing either diaminotriazine (DAT) or thymine (Thy) stickers as end-groups, both in the melt and in dilute solution. The SANS data are critically examined for the architecture and morphology as well as relative extent of linear assembly in the apolar solvent toluene. A random phase approximation (RPA) approach, adapted for a supramolecularly assembled multiblock copolymer is presented, which allows to extract the interaction parameters between the constituents and the medium. From the proposed approach, which describes very well heterocomplementary hydrogen-bonding telechelic polymers in both diluted toluene solution and in the melt, we conclude that linear association prevails.

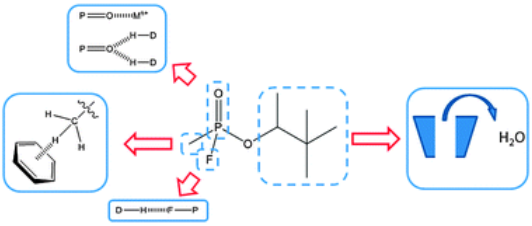
- Theory of Entanglements and Tube Confinement in Rod–Sphere Nanocomposites
  Yamamoto, U.; Schweizer, K. S. *ACS Macro Lett.* **2013**, *2*, 955–959.
  Abstract:



We formulate a microscopic theory for the polymer transverse confinement length and associated dynamic potential for a mixture of infinitely thin rods and hard spheres based solely on topological entanglements and excluded volume constraints. For fixed spheres, the needle effective tube diameter decreases with particle loading, and is largely controlled by a single dimensionless parameter involving all three key length-scales in the problem. A crossover from polymer entanglement to nanoparticle-controlled tube localization with increased loading is predicted. A preliminary extension to chain melts exhibits reasonable agreement with a recent simulation, and experimentally testable predictions are made. This work establishes a first-principles theoretical foundation to investigate a variety of dynamical problems in entangled polymer nanocomposites.

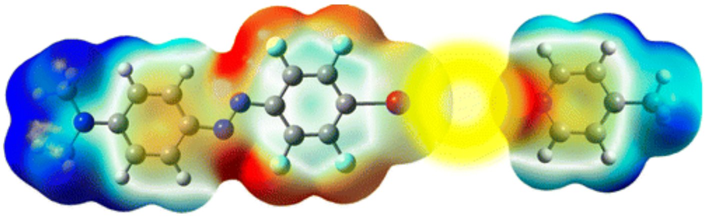
- Supramolecular chemistry and chemical warfare agents: from fundamentals of recognition to

catalysis and sensing
Sambrook, M. R.; Notman, S. *Chem. Soc. Rev.* **2013**, *42*, 9251-9267.
Abstract:



Supramolecular chemistry presents many possible avenues for the mitigation of the effects of chemical warfare agents (CWAs), including sensing, catalysis and sequestration. To-date, efforts in this field both to study fundamental interactions between CWAs and to design and exploit host systems remain sporadic. In this tutorial review the non-covalent recognition of CWAs is considered from first principles, including taking inspiration from enzymatic systems, and gaps in fundamental knowledge are indicated. Examples of synthetic systems developed for the recognition of CWAs are discussed with a focus on the supramolecular complexation behaviour and non-covalent approaches rather than on the proposed applications.

- The Halogen Bond in the Design of Functional Supramolecular Materials: Recent Advances
  Priimagi, A.; Cavallo, G.; Metrangolo, P.; Resnati, G. *Acc. Chem. Res.* **2013**, *46*, 2686–2695.
  Abstract:

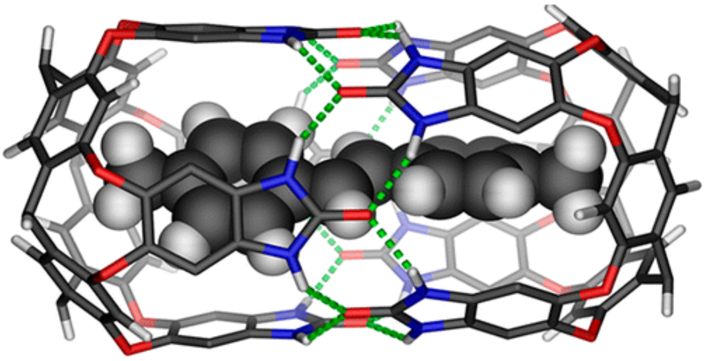


Halogen bonding is an emerging noncovalent interaction for constructing supramolecular assemblies. Though similar to the more familiar hydrogen bonding, four primary differences between these two interactions make halogen bonding a unique tool for molecular recognition and the design of functional materials. First, halogen bonds tend to be much more directional than (single) hydrogen bonds. Second, the interaction strength scales with the polarizability of the bond-donor atom, a feature that researchers can tune through single-atom mutation. In addition, halogen bonds are hydrophobic whereas hydrogen bonds are hydrophilic. Lastly, the size of the bond-donor atom (halogen) is significantly larger than hydrogen. As a result, halogen bonding provides supramolecular chemists with design tools that cannot be easily met with other types of noncovalent interactions and opens up unprecedented possibilities in the design of smart functional materials.

This Account highlights the recent advances in the design of halogen-bond-based functional materials. Each of the unique features of halogen bonding, directionality, tunable interaction strength, hydrophobicity, and large donor atom size, makes a difference. Taking advantage of the hydrophobicity, researchers have designed small-size ion transporters. The large halogen atom size provided a platform for constructing all-organic light-emitting crystals that efficiently generate triplet electrons and have a high phosphorescence quantum yield. The tunable interaction strengths provide tools for understanding light-induced macroscopic motions in photoresponsive azobenzene-containing polymers, and the directionality renders halogen bonding useful in the design on

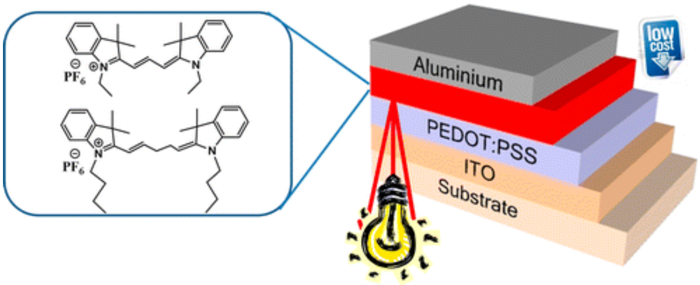
functional supramolecular liquid crystals and gel-phase materials. Although halogen bond based functional materials design is still in its infancy, we foresee a bright future for this field. We expect that materials designed based on halogen bonding could lead to applications in biomimetics, optics/photonics, functional surfaces, and photoswitchable supramolecules.

- Hydrogen-Bonded Capsules in Water
  Zhang, K-D.; Ajami, D.; Rebek, J. *Am. Chem. Soc.* **2013**, *135*, 18064–18066.
  Abstract:



Hydrogen-bonded capsules constrain molecules into small spaces, where they exhibit behavior that is inaccessible in bulk solution. Water competes with the formation of hydrogen bonds, and other forces for assembly, such as metal/ligand interactions or hydrophobic effects, have been applied. Here we report the reversible assembly of a water-soluble cavitand to a robust capsule host in the presence of suitable hydrophobic guests. The complexes are characterized by conventional NMR methods. Selectivity for guest length and fluorescence quenching of a stilbene guest are used as evidence for hydrogen bonding in the capsule.

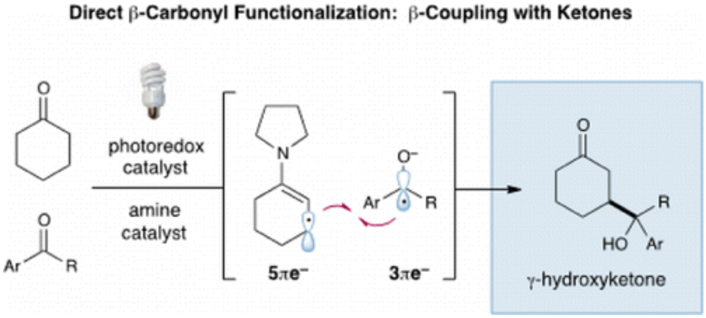
- Light-Emitting Electrochemical Cells Using Cyanine Dyes as the Active Components
  Pertegás, A.; Tordera, D.; Serrano-Pérez, J. J.; Ortí, E.; Bolink, H. J. *J. Am. Chem. Soc.* **2013**, *135*, 18008–18011.
  Abstract:



Light-emitting electrochemical cells (LECs) based on cyanine molecules were prepared. High photoluminescence quantum yields were obtained for host–guest films using two cyanine dyes, reaching 27%. Sandwiching these films in between two electrodes allows for very stable near-infrared emission with a maximum radiant flux of 1.7 W m–2 at an external quantum efficiency of 0.44%.

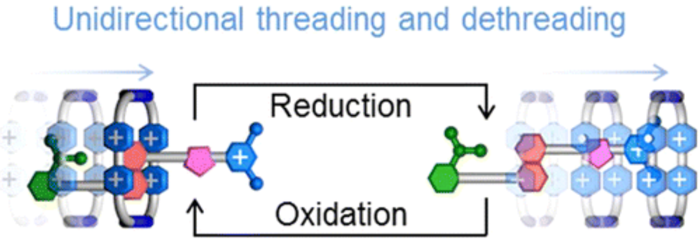
- Direct β-Functionalization of Cyclic Ketones with Aryl Ketones via the Merger of Photoredox and Organocatalysis
  Petronijević, F. R.; Nappi, M.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2013**, *135*, 18323-18326.

Abstract:



The direct β-coupling of cyclic ketones with aryl ketones has been achieved via the synergistic combination of photoredox catalysis and organocatalysis. Diaryl oxymethyl or aryl–alkyl oxymethyl radicals, transiently generated via single-electron reduction of ketone precursors, readily merge with β-enaminyl radical species, generated by photon-induced enamine oxidation, to produce γ-hydroxyketone adducts. Experimental evidence indicates that two discrete reaction pathways can be operable in this process depending upon the nature of the ketyl radical precursor and the photocatalyst.

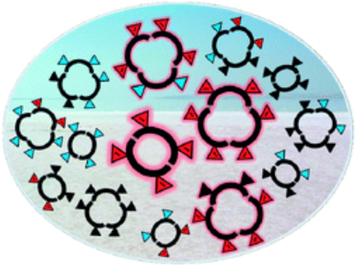
- Relative Unidirectional Translation in an Artificial Molecular Assembly Fueled by Light
  Li, H.; Cheng, C.; McGonigal, P. R.; Fahrenbach, A. C.; Frasconi, M.; Liu, W.-G.; Zhu, Z.; Zhao, Y.; Ke, C.; Lei, J.; Young, R. M.; Dyar, S. M.; Co, D. T.; Yang, Y.-W.; Botros, Y. Y.; Goddard, III, W. A.; Wasielewski, M. R.; Astumian, R. D.; Stoddart, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 18609-18620.
  Abstract:



Motor molecules present in nature convert energy inputs, such as a chemical fuel or incident photons of light, into directed motion and force biochemical systems away from thermal equilibrium. The ability not only to control relative movements of components in molecules but also to drive their components preferentially in one direction relative to each other using versatile stimuli is one of the keys to future technological applications. Herein, we describe a wholly synthetic small-molecule system that, under the influence of chemical reagents, electrical potential, or visible light, undergoes unidirectional relative translational motion. Altering the redox state of a cyclobis(paraquat-p-phenylene) ring simultaneously (i) inverts the relative heights of kinetic barriers presented by the two termini-one a neutral 2-isopropylphenyl group and the other a positively charged 3,5-dimethylpyridinium unit-of a constitutionally asymmetric dumbbell, which can impair the threading/dethreading of a [2]pseudorotaxane, and (ii) controls the ring's affinity for a 1,5-dioxynaphthalene binding site located in the dumbbell's central core. The formation and subsequent dissociation of the [2]pseudorotaxane by passage of the ring over the neutral and positively charged termini of the dumbbell component in one, and only one, direction relatively defined has been demonstrated by (i) spectroscopic (^{1}H NMR and UV/vis) means and cyclic voltammetry as well as with (ii) DFT calculations and by (iii) comparison with control compounds in the shape of constitutionally

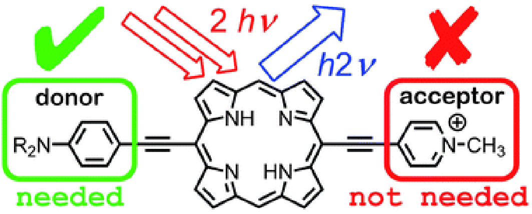
symmetrical [2]pseudorotaxanes, one with two positively charged ends and the other with two neutral ends. The operation of the system relies solely on reversible, yet stable, noncovalent bonding interactions. Moreover, in the presence of a photosensitizer, visible-light energy is the only fuel source that is needed to drive the unidirectional molecular translation, making it feasible to repeat the operation numerous times without the buildup of byproducts.

- The emergence of halophilic evolutionary patterns from a dynamic combinatorial library of macrocyclic pseudopeptides
  Atcher, J.; Moure, A.; Alfonso, I. *Chem. Commun.* **2013**, *49,* 487-489.
  Abstract:



The increase of the ionic strength amplifies the species bearing acidic side chains from a bio-inspired dynamic combinatorial library of macrocyclic pseudopeptides, in close resemblance to the evolution observed for the proteins of halophilic microorganisms.

- "Push-no-pull" porphyrins for second harmonic generation imaging
  Lopez-Duarte, I.; Reeve, J. E.; Perez-Moreno, J.; Boczarow, I.; Depotter, G.; Fleischhauer, J.; Clays, K.; Anderson, H. L. *Chem. Sci.* **2013**, *4*, 2024-2027.
  Abstract:



The established approach to design a molecule with strong second-order nonlinear optical (NLO) activity is to connect an electron-donor to an electron-acceptor *via* a π-conjugated bridge, to generate push-pull system. Surprisingly, we have found that dyes with large first hyperpolarizabilities, and which exhibit strong second harmonic generation (SHG), can be created just by attaching an electron-donor to a porphyrin. The free-base porphyrin core is sufficiently electron-deficient that the hyperpolarizability does not increase on addition of a pyridinium electron-acceptor.