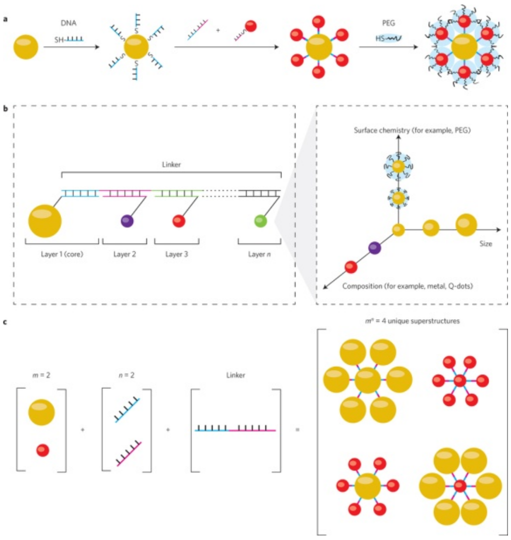
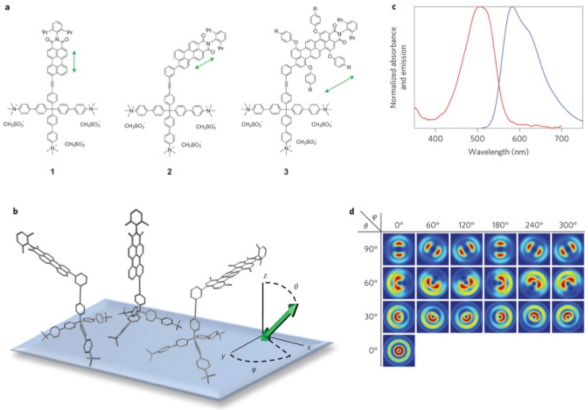
- DNA assembly of nanoparticle superstructures for controlled biological delivery and elimination
  Chou, L.Y.; Zagorovsky, K.; Chan, W. C. *Nature Nanotechnol.* **2014**, *9*, 148–155.
  Abstract:



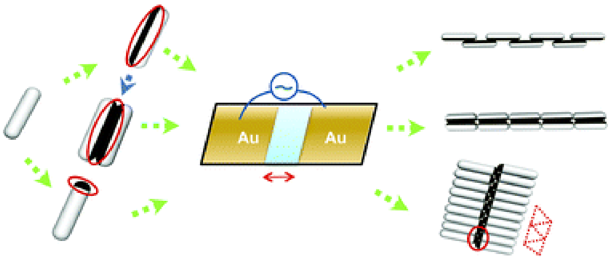
The assembly of nanomaterials using DNA can produce complex nanostructures, but the biological applications of these structures remain unexplored. Here, we describe the use of DNA to control the biological delivery and elimination of inorganic nanoparticles by organizing them into colloidal superstructures. The individual nanoparticles serve as building blocks, whose size, surface chemistry and assembly architecture dictate the overall superstructure design. These superstructures interact with cells and tissues as a function of their design, but subsequently degrade into building blocks that can escape biological sequestration. We demonstrate that this strategy reduces nanoparticle retention by macrophages and improves their in vivo tumour accumulation and whole-body elimination. Superstructures can be further functionalized to carry and protect imaging or therapeutic agents against enzymatic degradation. These results suggest a different strategy to engineer nanostructure interactions with biological systems and highlight new directions in the design of biodegradable and multifunctional nanomedicine.

- A surface-bound molecule that undergoes optically biased Brownian rotation
  Hutchison, J. A.; Uji-I, H.; Deres, A.; Vosch, T.; Rocha, S.; Müller, S.; Bastian, A. A.; Enderlein, J.; Nourouzi, H.; Li, C.; Herrmann, A.; Müllen, K.; De Schryver, F.; Hofkens, J. *Nature Nanotechnol.* **2014**, *9*, 131–136.
  Abstract:



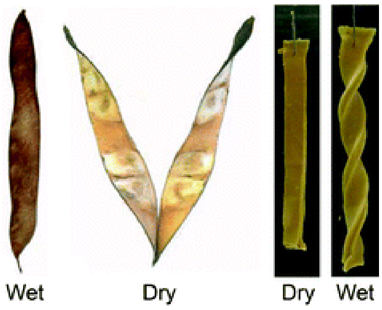
Developing molecular systems with functions analogous to those of macroscopic machine components, such as rotors, gyroscopes and valves, is a long-standing goal of nanotechnology. However, macroscopic analogies go only so far in predicting function in nanoscale environments, where friction dominates over inertia. In some instances, ratchet mechanisms have been used to bias the ever-present random, thermally driven (Brownian) motion and drive molecular diffusion in desired directions. Here, we visualize the motions of surface-bound molecular rotors using defocused fluorescence imaging, and observe the transition from hindered to free Brownian rotation by tuning medium viscosity. We show that the otherwise random rotations can be biased by the polarization of the excitation light field, even though the associated optical torque is insufficient to overcome thermal fluctuations. The biased rotation is attributed instead to a fluctuating-friction mechanism in which photoexcitation of the rotor strongly inhibits its diffusion rate.

- Reconfigurable assemblies of Janus rods in AC electric fields
  Chaudhary, K.; Juárez, J. J.; Chen, Q.; Granick, S.; Lewis, J. *Soft Matter* **2014**, *10,* 1320-1324.
  Abstract:



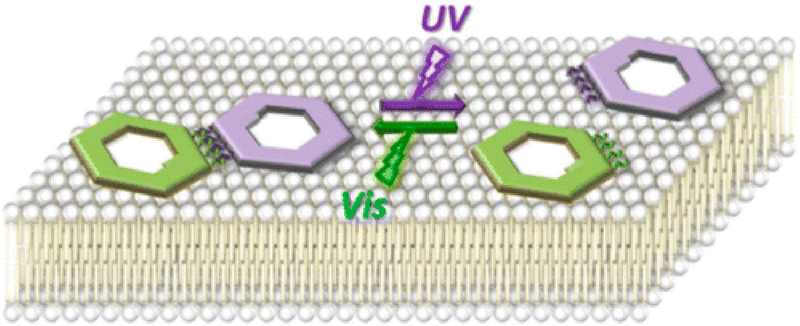
We investigate the electric field-induced assembly of Janus colloids composed of silica rods patterned with gold patches in both side- and tip-coated motifs. These shape and chemically anisotropic particles assemble into reconfigurable chains, whose structure depends on patch location, AC electric field strength, and frequency.

- Bioinspired materials that self-shape through programmed microstructures
  Studart, A. R.; Erb, R. M. *Soft Matter* **2014**, *10,* 1284-1294.
  Abstract:



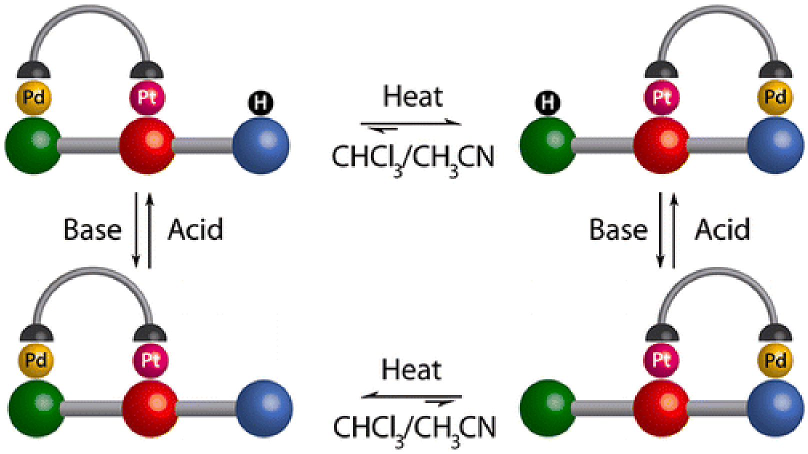
Nature displays numerous examples of materials that can autonomously change their shape in response to external stimuli. Remarkably, shape changes in biological systems can be programmed within the material's microstructure to enable self-shaping capabilities even in the absence of cellular control. Here, we revisit recent attempts to replicate in synthetic materials the shape-changing behavior of selected natural materials displaying deliberately tuned fibrous architectures. Simple processing methods like drawing, spinning or casting under magnetic fields are shown to be effective in mimicking the orientation and spatial distribution of reinforcing fibers of natural materials, thus enabling unique shape-changing features in synthetic systems. The bioinspired design and creation of self-shaping microstructures represent a new pathway to program shape changes in synthetic materials. In contrast to shape-memory polymers and metallic alloys, the self-shaping capabilities in these bioinspired materials originate at the microstructural level rather than the molecular scale. This enables the creation of programmable shape changes using building blocks that would otherwise not display the intrinsic molecular/atomic phase transitions required in conventional shape-memory materials.

- Dynamic Assembly/Disassembly Processes of Photoresponsive DNA Origami Nanostructures Directly Visualized on a Lipid Membrane Surface
  Suzuki, Y.; Endo, M.; Yang, Y.; Sugiyama, H. *J. Am. Chem. Soc.* **2014**, *136*, 1714-1717.
  Abstract:



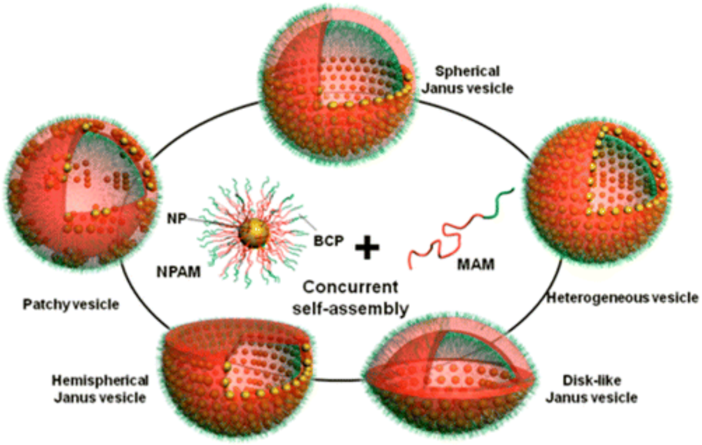
Here, we report the direct visualization of the assembly/disassembly processes of photoresponsive DNA origami nanostructures which can be placed on a lipid bilayer surface. The observation relies on controlled interactions between the bilayer components and cholesterol moieties introduced to the hexagonal origami structures, one of whose outer edges carries Azo-ODNs. The bilayer-placed hexagonal dimer was disassembled into monomer units by UV irradiation, and reversibly assembled again during visible light irradiation. These dynamic processes were directly monitored with high-speed atomic force microscopy. The successful application of our approach should facilitate studies of interactive and functional behaviors of various DNA nanostructures.

- Toward Metal Complexes That Can Directionally Walk Along Tracks: Controlled Stepping of a Molecular Biped with a Palladium(II) Foot
  Beves, J. E.; Blanco, V.; Blight, B. A.; Carrillo, R.; D'Souza, D. M.; Howgego, D.; Leigh, D. A.; Slawin, A. M. Z.; Symes, M. D. *J. Am. Chem. Soc.* **2014**, *136*, 2094-2100.
  Abstract:



We report on the design, synthesis, and operation of a bimetallic molecular biped on a three-foothold track. The "walker" features a palladium(II) complex "foot" that can be selectively stepped between 4-dimethylaminopyridine and pyridine ligand sites on the track via reversible protonation while the walker remains attached to the track throughout by means of a kinetically inert platinum(II) complex foot. The substitution pattern of the three ligand binding sites, together with the kinetic stability of the metal-ligand coordination bonds, affords the two positional isomers a high degree of metastability, meaning that altering the chemical state of the track does not automatically instigate stepping in the absence of an additional stimulus (heat in the presence of a coordinating solvent). The use of metastable metal complexes for foot-track interactions offers a promising alternative to dynamic covalent chemistry for the design of small-molecule synthetic molecular walkers.

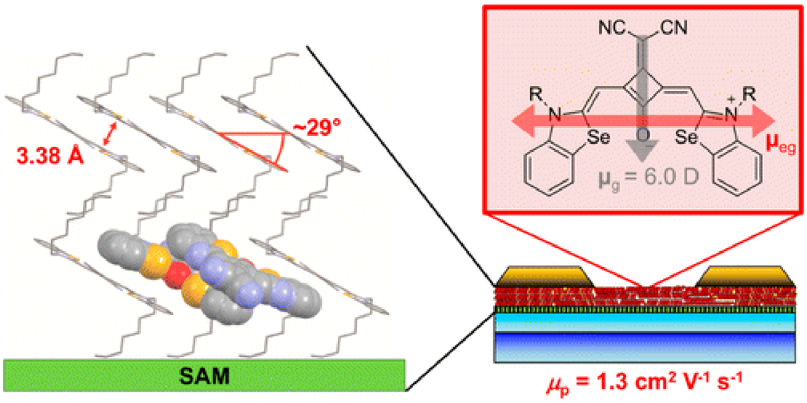
- Entropy-Driven Pattern Formation of Hybrid Vesicular Assemblies Made from Molecular and Nanoparticle Amphiphiles
  Liu, Y.; Li, Y.; He, J.; Duelge, K. J.; Lu, Z.; Nie, Z. *J. Am. Chem. Soc.* **2014**, *136*, 2602–2610.
  Abstract:



Although an analogy has been drawn between them, organic molecular amphiphiles (MAMs) and inorganic nanoparticle (NP) amphiphiles (NPAMs) are significantly different in dimension, geometry, and composition as well as their assembly behavior. Their concurrent assembly can synergetically combine the inherent properties of both building blocks, thus leading to new hybrid materials with increasing complexity and functionality. Here we present a new strategy to fabricate hybrid vesicles with well-defined shape, morphology, and surface pattern by coassembling MAMs of block copolymers (BCPs) and NPAMs comprising inorganic NPs tethered with amphiphilic BCPs. The assembly of binary mixtures generated unique hybrid Janus-like vesicles with different shapes, patchy vesicles, and heterogeneous vesicles. Our experimental and computational studies indicate that the different nanostructures arise from the delicate interplay between the dimension mismatch of the two types of amphiphiles, the entanglement of polymer chains, and the mobility of NPAMs. In addition, the entropic attraction between NPAMs plays a dominant role in controlling the lateral phase separation of the two types of amphiphiles in the membranes. The ability to utilize multiple distinct amphiphiles to construct discrete assemblies represents a promising step in the self-assembly of structurally complex functional materials.

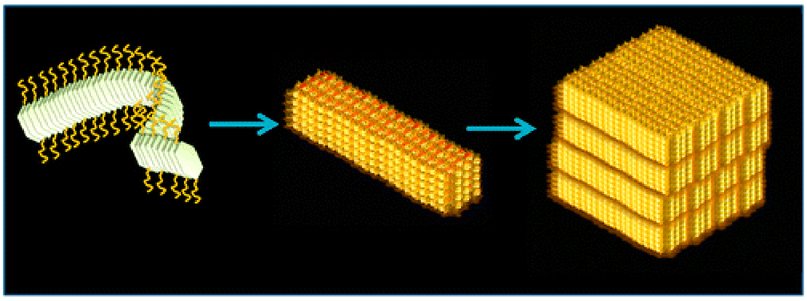
- High-Performance Organic Thin-Film Transistors of J-Stacked Squaraine Dyes
  Gsänger, M.; Kirchner, E.; Stolte, M.; Burschka, C.; Stepanenko, V.; Pflaum, J.; Würthner, F. *J. Am. Chem. Soc.* **2014,** *136*, 2351–2362.

Abstract:



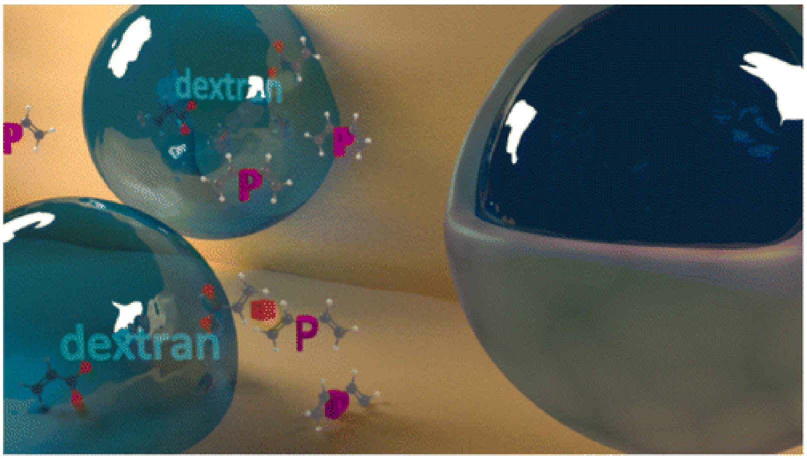
We have synthesized a series of dipolar squaraine dyes that contain dicyanovinyl groups as acceptor and benzannulated five-membered ring heterocycles with alkyl chains of varied length as donor moieties. Based on these squaraines, thin-film transistors (TFT) were fabricated by spin coating and solution shearing. Moreover, with one of these squaraine derivatives vacuum-deposited TFTs were prepared as well. Our detailed studies revealed that the transistor performance of the present series of squaraines is strongly dependent on their structural features as well as on the processing method of thin films. Thus, solution-sheared OTFTs of selenium squaraine bearing dodecyl substituents (denoted as Se-SQ-C12) performed best with a maximum hole mobility of 0.45 cm2 V–1 s–1, which is by far the highest value yet reported for OTFTs based on squaraines. This value was even surpassed by vacuum-deposited thin films of n-butyl-substituted selenium squaraine Se-SQ-C4, the only sublimable compound in this series, exhibiting a record hole mobility of 1.3 cm2 V–1 s–1. Furthermore, we have investigated the morphology of the thin films and the molecular packing of these squaraine dyes by optical spectroscopy, atomic force microscopy, and X-ray diffraction. These studies revealed a relationship between the molecular structure, packing motif, thin-film morphology, and transistor performance of the squaraine dyes. From the supramolecular point of view two packing features discovered in the single crystal structure of Se-SQ-C8 are of particular interest with regard to the structure–functionality relationship: The first is the slipped and antiparallel π-stacking motif which ensures cancellation of the molecules' dipole moments and J-type absorption band formation in thin films. The second is the presence of CN···Se noncovalent bonds which show similarities to the more common halogen-bonding interactions and which interconnect the individual one-dimensional slipped π-stacks, thus leading to two-dimensional percolation pathways along the source–drain direction.

- Hierarchical Self-Assembly of Amphiphilic Homopolymer into Unique Superstructures
  Mane, S. R.; Shunmugam, R. *ACS Macro Lett.* **2014**, *3*, 44–50.
  Abstract:



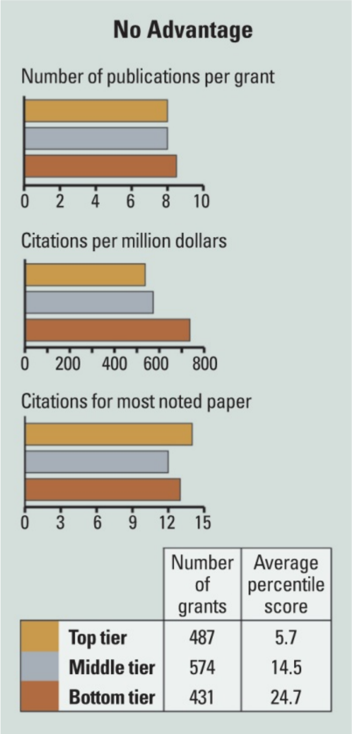
Supramolecular forces influence the morphologies of self-assemblies. Herein, self-assembled structures of an amphiphilic, norbornene-derived thiobarbiturate homopolymers (p-NTB) are discussed. The newly designed hompolymer shows self-assembled rod-like structures in tetrahydrofuran (THF) solvent. Formation of the rods are governed by hydrogen bonding motifs and amphiphilicity found in the molecular architecture. The solvent polarity controls their organization into cube-like and sphere-like structures at the next length scale. Encapsulation studies of hydrophobic magnetic particles as well as drug molecules into these superstructures demonstrate a novel route to fabricate multifunctional cube-like and sphere-like aggregates.

- Selective Interfacial Olefin Cross Metathesis for the Preparation of Hollow Nanocapsules
  Malzahn, K.; Marsico, F.; Koynov, K.; Landfester, K.; Weiss, C. K.; Wurm, F. R. *ACS Macro Lett.* **2014**, *3*, 40–43.
  Abstract:



The first synthesis of hollow nanocapsules with an aqueous core via olefin cross metathesis is presented. The reaction was tailored such that it proceeds selectively at the oil–water interface of aqueous nanodroplets in an inverse miniemulsion. The cross metathesis takes place between an acrylated polysaccharide and unsaturated organophosphates under mild conditions. This general protocol allows the synthesis of biocompatible and polyfunctional nanocapsules via the bioorthogonal olefin metathesis, thus generating a highly versatile methodology for the design of future materials for biomedical applications but also for materials science. Functionalization of the nanocapsules was demonstrated with fluorescent labels, which can be attached to the pendant phosphoester either within the cross-linker, exploiting the versatility of the phosphorus chemistry, or via coupling to the capsules’ surface.

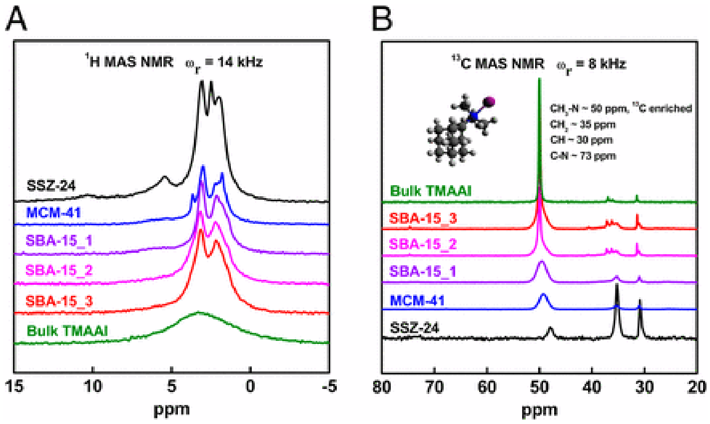
- Peering Into Peer Review
  Mervis, J. *Science* **2014**, *343*, 596-598.
  Abstract:



		Number of grants	Average percentile score
🟧	**Top tier**	487	5.7
⬜	**Middle tier**	574	14.5
🟫	**Bottom tier**	431	24.7

Lauer recently analyzed the citation record of papers generated by nearly 1500 grants awarded by NHLBI to individual investigators between 2001 and 2008. He was shocked by the results, which appeared online last month in *Circulation Research*: The funded projects with the poorest priority scores from reviewers garnered just as many citations and publications as those with the best scores. That was the case even though low-scoring researchers had been given less money than their top-rated peers.

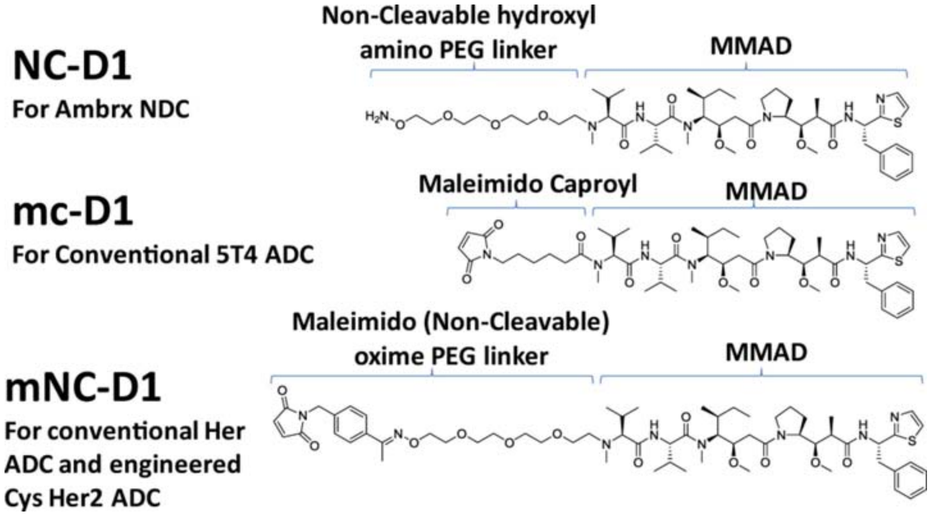
- Guest–host interactions of a rigid organic molecule in porous silica frameworks
  Wu, D.; Hwang, S.-J.; Zones, S. I.; Navrotsky, A. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 1720-1725.
  Abstract:



Confinement of molecules in nanoscale pores is important in both science and technology. This paper reports a systematic analysis of the structural, thermodynamic, and dynamic behavior on confinement of a rigid organic molecule in a series of silica frameworks with different pore sizes (0.8 to 20.0 nm). The comprehensive data set enables the strength of guest–host interactions to be calculated; structure, phase, and dynamics of confined guests in pores of various diameters to be analyzed; and different types of inclusion to be described. The evolution from single-molecule

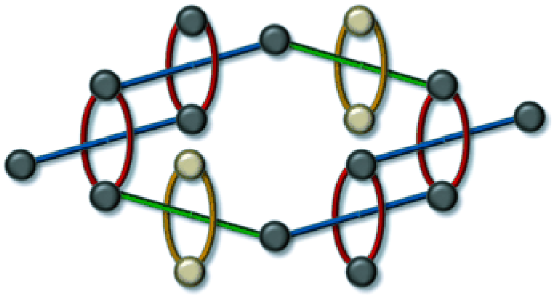
confinement to multimolecule adsorption/confinement to nanocrystal confinement is documented. This provides a conceptual model linking confinement on various length scales.

- A general approach to site-specific antibody drug conjugates
  Tian, F.; Lu, Y.; Manibusan, A.; Sellers, A.; Tran, H.; Sun, Y.; Phuong, T.; Barnett, R.; Hehli, B.; Song, F.; DeGuzman, M. J.; Ensari, S.; Pinkstaff, J. K.; Sullivan, L. M.; Biroc, S. L.; Cho, H.; Schultz, P. G.; DiJoseph, J.; Dougher, M.; Ma, D.; Dushin, R.; Leal, M.; Tchistiakova, L.; Feyfant, E.; Gerber, H.-P.; Sapra, P. *Proc. Natl. Acad. Sci. U. S. A.* **2014,** *111*, 1766-1771.
  Abstract:



Here we demonstrate the ability to genetically incorporate nonnative amino acids into proteins in mammalian cells using both transient and stable platform expression systems that provide yields and fidelities compatible with commercial applications. To illustrate the utility of this methodology we have generated chemically homogeneous antibody drug conjugates (NDCs) with precise control over the site and stoichiometry of drug conjugation. In rodent xenograft models these NDCs display improved properties, including half-life, efficacy and safety, relative to conventional heterogeneous ADCs. These advances allow the generation of therapeutic antibody drug conjugates with medicinal chemistry like control over structure, which should greatly facilitate the optimization of their pharmacological activities.

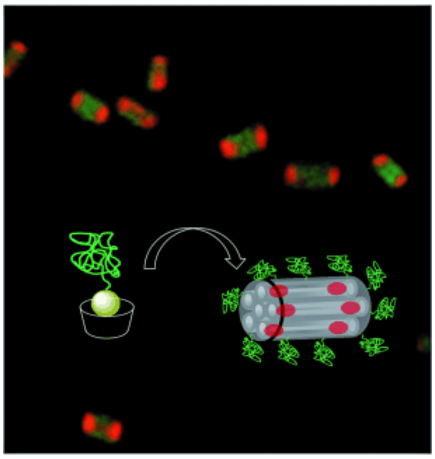
- An Interwoven Metal-Organic Framework Combining Mechanically Interlocked Linkers and Interpenetrated Networks
  Frank, N. C.; Mercer, D. J.; Loeb, S. J. *Chem. Eur. J.* **2013**, *19*, 14076–14080.
  Abstract:



New dibenzo[24]crown-8 ether derivatives were prepared that contain appendages with thioether donors that can coordinate to a metal ion. These macrocycles were then combined with 1,2-

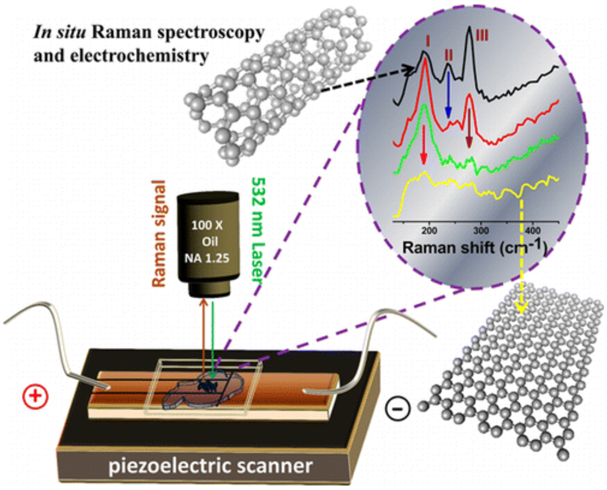
bis(pyridinium) ethane axles to create two types of [2]rotaxane ligands; those with the four thioether donors on the crown ether and those with six donor groups, four from the crown ether and two more attached to the stoppering groups of the dumbbell. The crown ethers and both types of [2]rotaxane ligands were allowed to react with Ag^I ions to form metal-organic rotaxane framework (MORF) style coordination polymers. The interlocked hexadentate ligand forms the first example of a new type of lattice containing interwoven frameworks resulting from both interpenetration of frameworks due to the presence of an interlocked ligand and more classical interpenetration of independent frameworks.

- Cyclodextrin-Modified Zeolites: Host–Guest Surface Chemistry for the Construction of Multifunctional Nanocontainers
  Szarpak-Jankowska, A.; Burgess, C.; De Cola, L.; Huskens, J., *Chem. Eur. J.* **2013**, *19*, 14925–14930.
  Abstract:



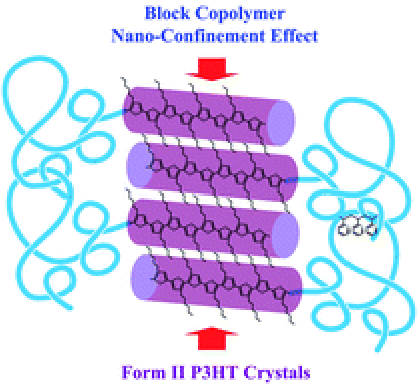
The functionalization of nanoporous zeolite L crystals with β-cyclodextrin (CD) has been demonstrated. The zeolite surface was first modified with amino groups by using two different aminoalkoxysilanes. Then, 1,4-phenylene diisothiocyanate was reacted with the amino monolayer and used to bind CD heptamine by using its remaining isothiocyanate groups. The use of the different aminoalkoxysilanes, 3-aminopropyl dimethylethoxysilane (APDMES) and 3-aminopropyl triethoxysilane (APTES), led to drastic differences in uptake and release properties. Thionine was found to be absorbed and released from amino- and CD-functionalized zeolites when APDMES was used, whereas functionalization by APTES led to complete blockage of the zeolite channels. Fluorescence microscopy showed that the CD groups covalently attached to the zeolite crystals could bind adamantyl-modified dyes in a specific and reversible manner. This strategy allowed the specific immobilization of His-tagged proteins by using combined host–guest and His-tag-Ni-nitrilotriacetic acid (NTA) coordination chemistry. Such multifunctional systems have the potential for encapsulation of drug molecules inside the zeolite pores and non-covalent attachment of other (for example, targeting) ligand molecules on its surface.

- Sequential Electrochemical Unzipping of Single-Walled Carbon Nanotubes to Graphene Ribbons Revealed by in Situ Raman Spectroscopy and Imaging
  John, R.; Shinde, D. B.; Liu, L.; Ding, F.; Xu, Z.; Vijayan, C.; Pillai, V. K.; Pradeep, T. *ACS Nano* **2014**, *8*, 234–242.
  Abstract:



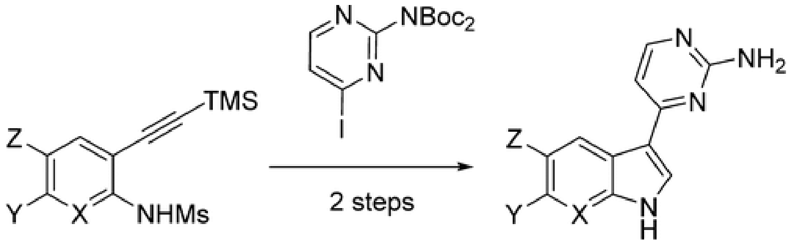
We report an in situ Raman spectroscopic and microscopic investigation of the electrochemical unzipping of single-walled carbon nanotubes (SWNTs). Observations of the radial breathing modes (RBMs) using Raman spectral mapping reveal that metallic SWNTs are opened up rapidly followed by gradual unzipping of semiconducting SWNTs. Consideration of the resonant Raman scattering theory suggests that two metallic SWNTs with chiralities (10, 4) and (12, 0) get unzipped first at a lower electrode potential (0.36 V) followed by the gradual unzipping of another two metallic tubes, (9, 3) and (10, 1), at a relatively higher potential (1.16 V). The semiconducting SWNTs with chiralities (11, 7) and (12, 5), however, get open up gradually at ±1.66 V. A rapid decrease followed by a subsequent gradual decrease in the metallicity of the SWNT ensemble as revealed from a remarkable variation of the peak width of the G band complies well with the variations of RBM. Cyclic voltammetry also gives direct evidence for unzipping in terms of improved capacitance after oxidation followed by more important removal of oxygen functionalities during the reduction step, as reflected in subtle changes of the morphology confirming the formation of graphene nanoribbons. The density functional-based tight binding calculations show additional dependence of chirality and diameter of nanotubes on the epoxide binding energies, which is in agreement with the Raman spectroscopic results and suggests a possible mechanism of unzipping determined by combined effects of the structural characteristics of SWNTs and applied field.

- Solution self-assembly and phase transformations of form II crystals in nanoconfined poly(3-hexyl thiophene) based rod-coil block copolymers
  Lee, Y.-H.; Yang, Y.-L.; Yen, W.-C.; Su, W.-F.; Dai, C.-A. *Nanoscale* **2014**, *6*, 2194–2200.
  Abstract:



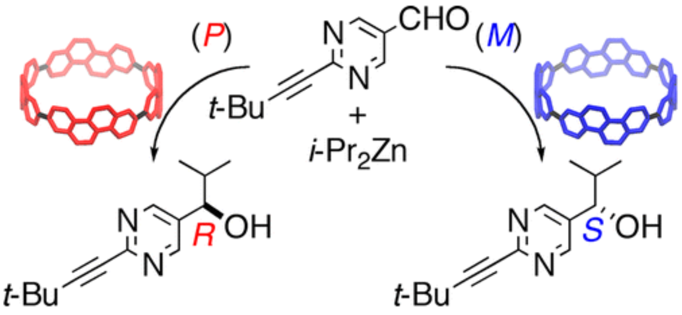
Solution processing of π-conjugated polymers constitutes a major low-cost manufacturing method for the fabrication of many new organic optoelectronic devices. The solution self-assembly kinetics of π-conjugated rod-coil block copolymers of symmetric poly(3-hexyl thiophene)-b-poly(2-vinyl pyridine) (P3HT-P2VP) during drying and the phase transformations of the subsequently dried samples were studied by using a combination of TEM, SAXS, WAXS and DSC measurements. During solution drying in chlorobenzene, a good solvent for the copolymer, P3HT-P2VP first formed nanoseed aggregates followed by the directional growth of nanofibrils driven by the formation of prevailing form II P3HT crystals within its nanofibril core confined by the surrounding domain of P2VP blocks. This result was in sharp contrast when a similar molecular weight P3HT homopolymer was solution self-assembled in chlorobenzene, nearly free from confinement, in which case the resulting nanofibrils consisted of a mixture of majority form I and form II crystals. Solvent-cast films of P3HT-P2VP nanofibrils with form II crystals were heat-/cold-treated and showed solid-state phase transformations from form II crystals to form I crystals, both within nanofibrils with annealing, indicating the metastability of the form II crystals with temperature. A disordered state followed with increasing temperatures which, when cooled, induced the formation of a thermodynamically stable lamellar phase with only form I P3HT crystals. Correspondingly, the study provides new strategies for controlling polymorphs and nanostructures of π-conjugated block copolymers for future applications using solution processing and subsequent heat treatment.

- Concise Syntheses of Meridianins and Meriolins Using a Catalytic Domino Amino-Palladation Reaction
  Walker, S. R.; Czyz, M. L.; Morris, J. C. *Org. Lett.* **2014,** *16*, 708-711.
  Abstract:



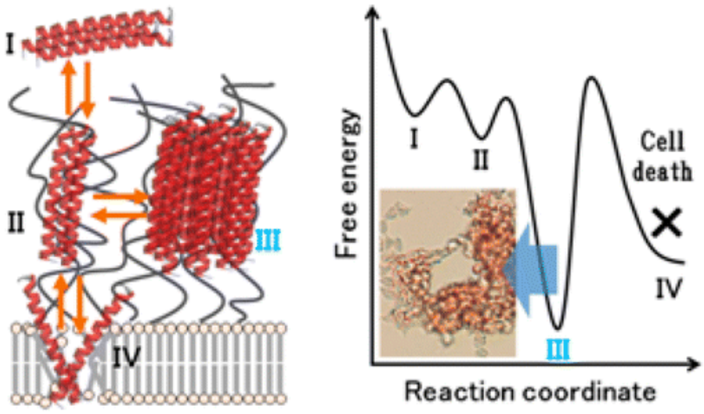
A synthesis of natural and synthetic members of the meridianin family of kinase inhibitory natural products has been developed. The sequence utilizes a variation of the Cacchi palladium-catalyzed domino reaction to efficiently construct the heterocyclic framework of the meridianins and meriolins from monocyclic precursors.

- Asymmetric Autocatalysis Initiated by Finite Single-Wall Carbon Nanotube Molecules with Helical Chirality
  Hitosugi, S.; Matsumoto, A.; Kaimori, Y.; Iizuka, R.; Soai, K.; Isobe, H. *Org. Lett.* **2014,** *16*, 645-647.
  Abstract:



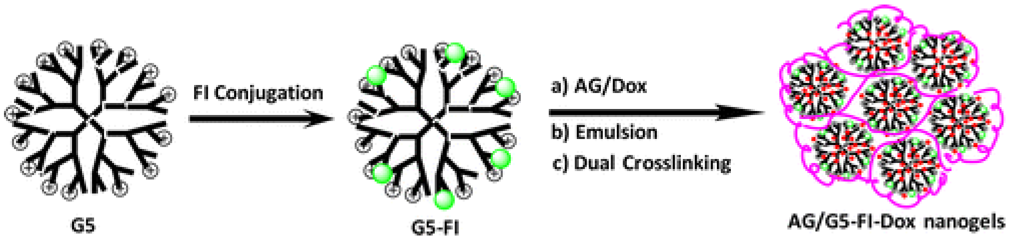
An asymmetric autocatalysis reaction was initiated by a finite single-wall carbon nanotube molecule with helical chirality. The asymmetric induction was initiated by the chiral environment arising from the planar chirality of the tubular polyaromatic hydrocarbons.

- Designing Cell-Aggregating Peptides without Cytotoxicity
  Yamamoto, N.; Tamura, A. *Biomacromolecules* **2014**, *15,* 512–523.
  Abstract:



We have designed α-helical peptides de novo that can induce aggregation of various kinds of cells by focusing on physicochemical properties such as hydrophobicity, net charges, and amphipathicity. It is shown that peptide hydrophobicity is the key factor to determine capabilities for cell aggregation while peptide net charges contribute to nonspecific electrostatic interactions with cells. On the other hand, amphipathic peptides tend to exhibit cytotoxicity such as antimicrobial activity and hemolysis, which are competitive with cell-aggregation capabilities. Different from the cases of living cells, aggregation of artificial anionic liposomes appears to be mainly determined by electrostatic interactions. This discrepancy might be due to the complex structure of surfaces of cell membranes consisting of macromolecular chains such as peptidoglycans, polysaccharides, or glycocalyx, which coexist with lipid bilayers. Our design strategy would pave the way to design peptides that lead aggregation of living cells without cytotoxicity.

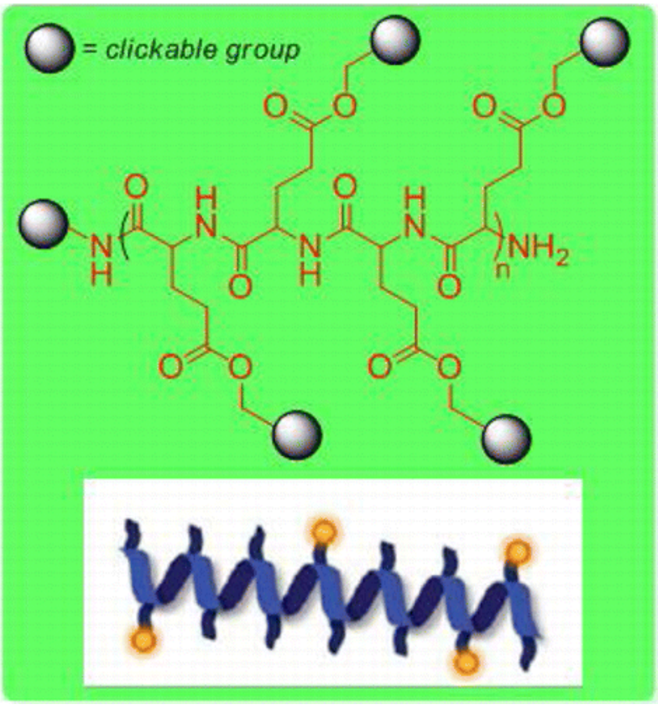
- Dendrimer-Assisted Formation of Fluorescent Nanogels for Drug Delivery and Intracellular Imaging
  Gonçalves, M.; Maciel, D.; Capelo, D.; Xiao, S.; Sun, W.; Shi, X.; Rodrigues, J.; Tomás, H.; Li, Y. *Biomacromolecules* **2014**, *15*, 492–499.
  Abstract:



Although, in general, nanogels present a good biocompatibility and are able to mimic biological tissues, their unstability and uncontrollable release properties still limit their biomedical applications. In this study, a simple approach was used to develop dual-cross-linked dendrimer/alginate nanogels (AG/G5), using $CaCl_2$ as cross-linker and amine-terminated generation 5 dendrimer (G5) as a cocrosslinker, through an emulsion method. Via their strong electrostatic interactions with anionic

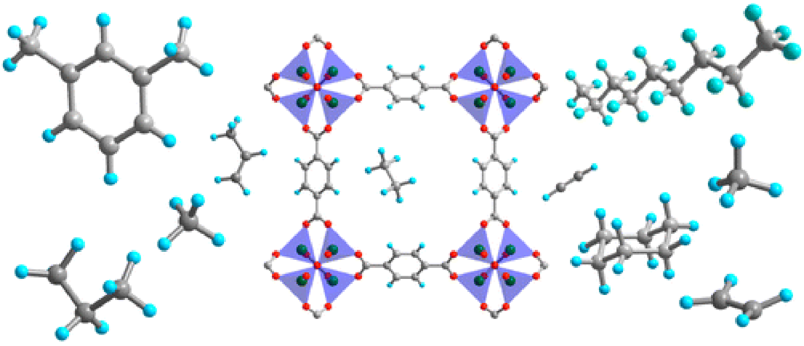
AG, together with cross-linker Ca^{2+}, G5 dendrimers can be used to mediate the formation of more compact structural nanogels with smaller size (433 ± 17 nm) than that (873 ± 116 nm) of the Ca^{2+}-cross-linked AG nanogels in the absence of G5. Under physiological (pH 7.4) and acidic (pH 5.5) conditions, the sizes of Ca^{2+}-cross-linked AG nanogels gradually decrease probably because of their degradation, while dual-cross-linked AG/G5 nanogels maintain a relatively more stable structure. Furthermore, the AG/G5 nanogels effectively encapsulate the anticancer drug doxorubicin (Dox) with a loading capacity 3 times higher than that of AG nanogels. The AG/G5 nanogels were able to release Dox in a sustained way, avoiding the burst release observed for AG nanogels. In vitro studies show that the AG/G5-Dox NGs were effectively taken up by CAL-72 cells (a human osteosarcoma cell line) and maintain the anticancer cytotoxicity levels of free Dox. Interestingly, G5 labeled with a fluorescent marker can be integrated into the nanogels and be used to track the nanogels inside cells by fluorescence microscopy. These findings demonstrate that AG/G5 nanogels may serve as a general platform for therapeutic delivery and/or cell imaging.

- Clickable Synthetic Polypeptides—Routes to New Highly Adaptive Biomaterials
  Quadir, M. A.; Martin, M.; Hammond, P. T. *Chem. Mater.* **2014***, 26*, 461–476.
  Abstract:



Synthetic polypeptides introduce a powerful capability to generate macromolecular species using the amino acid backbone found in nature, thus providing a route to biocompatible polymeric systems with highly programmable function. They can fold into stable secondary structures such as beta-sheets and α-helical structures, allowing the design of materials that optimally display surface groups that dictate cell signaling and molecular docking in biological systems and which undergo changes in chain stiffness and organization as well as complex hydrophobic and hydrophilic interactions that enable the intelligent design of responsive bioinspired materials. Until more recently, however, the versatility of these unique macromolecules was limited by the number, density, and type of functional groups which can be directly attached to the synthetic polypeptide backbone postpolymerization. In the past few years, researchers have introduced or utilized highly quantitative click chemistry to N-carboxy anhydride monomers used to generate synthetic polypeptide backbones, enabling direct and complete functionalization of macromolecular side-chains and side groups with a broader range of chemical functionality. These systems can yield charged polypeptides that exhibit pH responsive conformational changes and critical solution phase behavior, as well as densely grafted polypeptide macromolecules that mimic the behavior of naturally occurring proteins while introducing new function via facile synthetic modifications. Here we examine the significant advances in the design of bioinspired and biomimetic macromolecules presented by this capability, ranging from dynamic responsive micellar systems to biomimetic cell penetrating and antimicrobial peptides, and including structured hydrogel systems, and we look toward new possible areas of investigation and exploration utilizing the enabling combination of click chemistry with synthetic polypeptide materials.

- Hydrocarbon Separations in Metal–Organic Frameworks
  Herm, Z. R.; Bloch, E. D.; Long, J. R. *Chem. Mater.* **2014***, 26*, 323–338.
  Abstract:

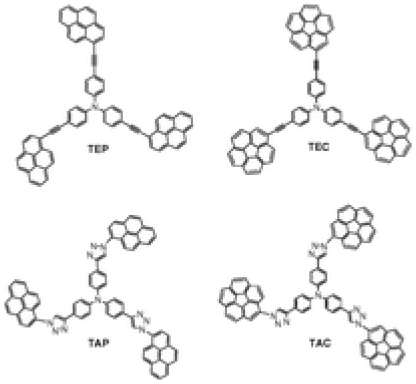


New materials capable of separating mixtures of saturated, unsaturated, and aromatic hydrocarbons can enable more efficient industrial processes and cleaner energy. Outstanding challenges in hydrocarbon separations stem from the similar structures, properties, and reactivities of the molecules comprising many of these mixtures. With high surface areas, tunable pore geometries, and adjustable surface functionality, metal–organic frameworks hold tremendous promise for effecting previously difficult or impossible separations. In this review, we provide a comprehensive account of the metal–organic frameworks that have been investigated for hydrocarbon separations within the context of their potential relevance for separating various industrial alkane-, alkene-, and aromatic-containing mixtures.

- Synthetic small-molecule walkers at work
  Qu, D.-H.; Tian, H. *Chem. Sci.* **2013***, 4,* 3031-3035.
  Abstract:

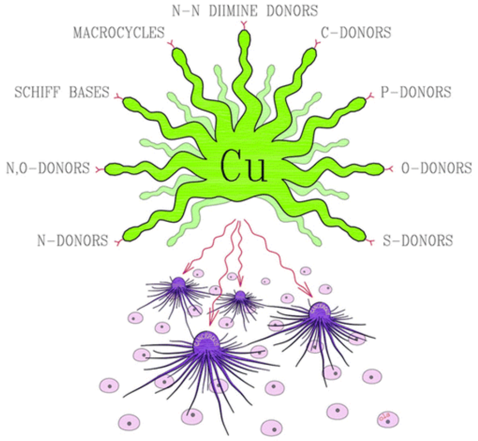
The naturally occurring molecular motors have been a source of inspiration for the development of a variety of artificial molecular machines and motors. Synthetic molecular walkers, in which a molecular fragment can walk along tracks, are emerging as a new class of artificial molecular motors. This minireview presents a brief introduction on synthetic small-molecule walkers and highlights recent significant accomplishments in developing synthetic small-molecule walkers that can perform specific tasks, such as quenching the fluorescence of the system or synthesizing a peptide in a sequence-specific manner.

- Florescence quenching detection and identification of nitro-aromatic explosives
  Niamnont, N.; Kimpitak, N.; Wongravee, K.; Rashatasakhon, P.; Baldridge, K. K.; Siegel, J. S.; Sukwattanasinitt, M. *Chem. Commun.* **2013**, *49,* 780-782.
  Abstract:



Triphenylamine-based fluorophores containing pyrene or corannulene show variable fluorescence quenching sensitivity toward nitro explosives. The most sensitive fluorophore is capable of detecting TNT on the ng cm^{-2} scale; the array is useful for identifying into aromatics.

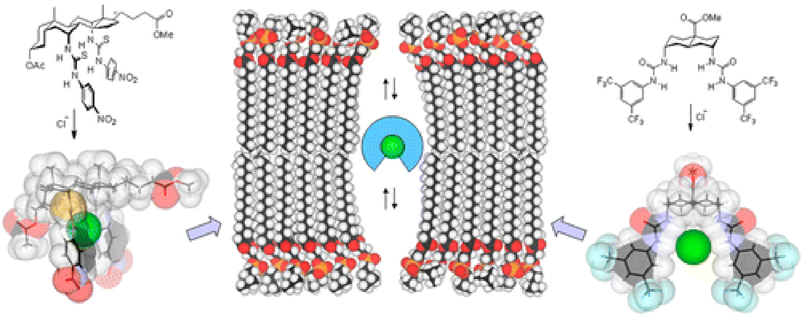
- Advances in Copper Complexes as Anticancer Agents
  Santini, C.; Pellei, M.; Gandin, V.; Porchia, M.; Tisato, F.; Marzano, C. *Chem. Rev.* ***2014**, 114*, 815-861.
  Abstract:



This review describes advances in the synthesis, design, and development of copper complexes as anticancer agents in the last 4 years (section 2). Interest in this field has rapidly grown in recent years, as illustrated by the increasing number of publications reported since 2000 (see Figure 1). This summary covers the period 2008–2012 and follows our previous efforts in the same area.

Although many copper complexes have been proposed as promising cytotoxic agents on the basis of in vitro assays very few data have been so far reported on their mechanisms of action. The final two sections (sections 3 and 4) summarize recent findings on (i) identification of the main molecular targets and cellular pathways involved in the copper complexes-induced antiproliferatice effects and (ii) the state of art of in vivo studies on the antitumor activity of copper compounds.
This overview would like to be a useful tool for the research community actively involved in the copper-based anticancer drug discovery.

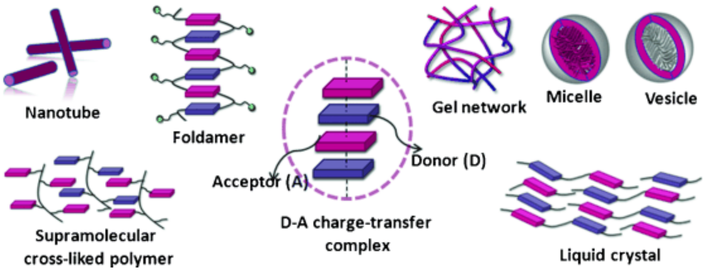
- Making a Match for Valinomycin: Steroidal Scaffolds in the Design of Electroneutral, Electrogenic Anion Carriers
  Valkenier, H.; Davis, A. P. *Acc. Chem. Res.* **2013**, *47*, 2898–2909.
  Abstract:



The natural product Valinomycin is a well-known transmembrane cation carrier. Despite being uncharged, this molecule can extract potassium ions from water without counterions and ferry them through a membrane interior. Because it only transports positive ions, it is electrogenic, mediating a flow of charge across the membrane. Equivalent agents for anions would be valuable research tools and may have therapeutic applications, especially in the treatment of “channelopathies” such as cystic fibrosis. However, no such molecules have been found in nature.
In this Account, we describe our research toward synthetic and rationally designed “anti-Valinomycins”. As our core approach to this problem, we used the steroid nucleus, provided by cholic acid, as a scaffold for the assembly of anion receptors. By positioning H-bond donors on this framework, especially urea and thiourea groups in conformationally constrained axial positions, we created binding sites capable of exceptionally high affinities (up to 10^{11} M^{-1} for $R_4N^+Cl^-$ in chloroform). The extended hydrocarbon surface of the steroid helped to maintain compatibility with nonpolar media. When we tested these “cholapods” for chloride transport in vesicles, they provided the first evidence for electrogenic anion transport mediated by electroneutral organic carriers: in other words, they are the first authenticated anti-Valinomycins. They also proved active in live cells that we grew and assayed in an Ussing chamber.
In subsequent work, we have shown that the cholapods can exhibit very high activities, with transport observed down to carrier/lipid ratios of 1:250 000. We also understand some of the effects of structure on the activity of these molecules. For example, in most cases, powerful transporters also act as powerful receptors. On the other hand, some modifications which favor binding do not promote transport. We gained functional advantages by cyclizing the cholapod architecture, which encloses the anion binding site. We could also simplify the structure without compromising function. A steroid-inspired *trans*-decalin framework has proved highly effective and may lead to agents with practical advantages. Changing an ester side-chain in this system revealed a

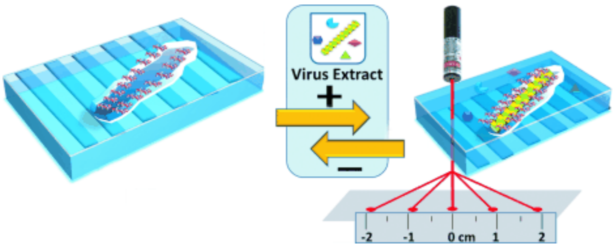
surprising effect, whereby increased length and/or lipophilicity resulted in substantially raised activity. Although much remains to be discovered about these anionophores, their high activities and intrinsic tuneabilities bode well for applications. In future work, we plan to develop and exploit these molecules as tools for biophysical research and to explore the possibility of useful biological activity.

- Supramolecular Assemblies by Charge-Transfer Interactions between Donor and Acceptor Chromophores
  Das, A.; Ghosh, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 2038–2054.
  Abstract:



We have collated various supramolecular designs that utilize organic donor–acceptor CT complexation to generate noncovalently co-assembled structures including fibrillar gels, micelles, vesicles, nanotubes, foldamers, conformationally restricted macromolecules, and liquid crystalline phases. Possibly inspired by nature, chemists have extensively used hydrogen bonding as a tool for supramolecular assemblies of a diverse range of abiotic building blocks. As a structural motif, CT complexes can be compared to hydrogen-bonded complexes in its directional nature and complementarities. Additional advantages of CT interactions include wider solvent tolerance and easy spectroscopic probing. Nevertheless the major limitation is their low association constant. This article shows different strategies have evolved over the years to overcome this drawback by reinforcing the CT interactions with auxiliary noncovalent forces without hampering the alternate stacking mode. Emerging reports on promising CT complexes in organic electronics are intimately related to various supramolecular designs that one can postulate based on donor–acceptor CT interactions.

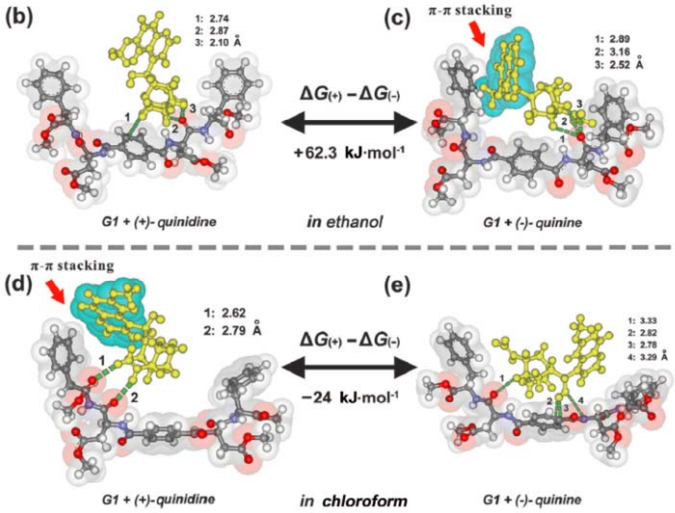
- A Double-Imprinted Diffraction-Grating Sensor Based on a Virus-Responsive Super-Aptamer Hydrogel Derived from an Impure Extract
  Bai, W.; Spivak, D. A. *Angew. Chem. Int. Ed.* **2014**, *53*, 2095–2098.
  Abstract:



The detection of viruses is of interest for a number of fields including biomedicine, environmental science, and biosecurity. Of particular interest are methods that do not require expensive equipment or trained personnel, especially if the results can be read by the naked eye. A new “double imprinting” method was developed whereby a virus-bioimprinted hydrogel is further micromolded into a diffraction grating sensor by using imprint-lithography techniques to give a “Molecularly

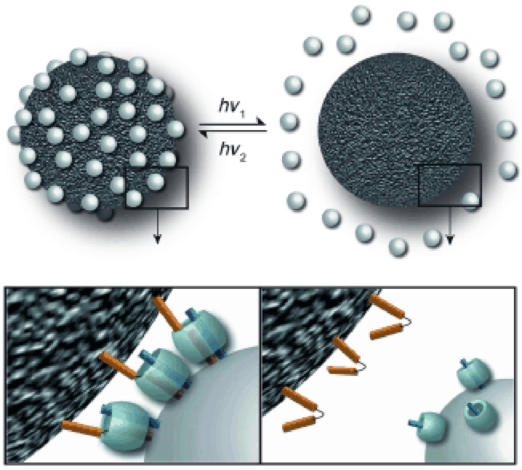
Imprinted Polymer Gel Laser Diffraction Sensor" (MIP-GLaDiS). A simple laser transmission apparatus was used to measure diffraction, and the system can read by the naked eye to detect the Apple Stem Pitting Virus (ASPV) at concentrations as low as 10 ng mL^{-1}, thus setting the limit of detection of these hydrogels as low as other antigen-binding methods such as ELISA or fluorescence-tag systems.

- Solvent-Driven Chiral-Interaction Reversion for Organogel Formation
  Qing, G.; Shan, X.; Chen, W.; Lv, Z.; Xiong, P.; Sun, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 2124–2129.
  Abstract:



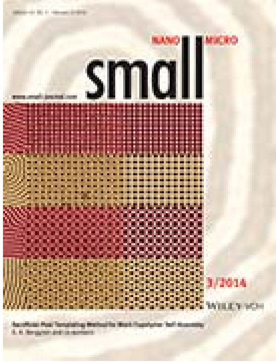
Get smart: A system for gel formation in which the solvent not only provides a medium but also determines the nature of the stereoselective interaction between a gelator and a chiral guest provides important insight into the assembly of chiral gelators. The solvent-driven preferential complexation of one or another chiral guest (see picture) enables the design of organogels with new "smart" features for various applications.

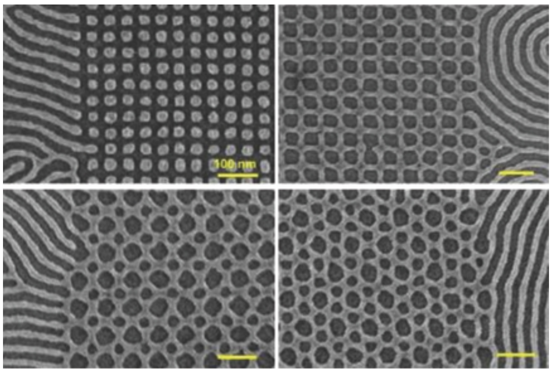
- Photoresponsive Hybrid Raspberry-Like Colloids Based on Cucurbit[8]uril Host–Guest Interaction
  Lan, Y.; Wu, Y.; Karas, A.; Scherman, O. A. *Angew. Chem. Int. Ed.* **2014**, *53*, 2166–2169.
  Abstract:



Reversible assembly of colloids: Hybrid raspberry-like colloids prepared by employing cucurbit[8]uril as a supramolecular linker to assemble functional polymeric nanoparticles onto silica microspheres can be disassembled and reassembled in an efficient and controllable manner (see picture). This supramolecular self-assembly method makes possible the preparation of colloids with sophisticated structures and properties.

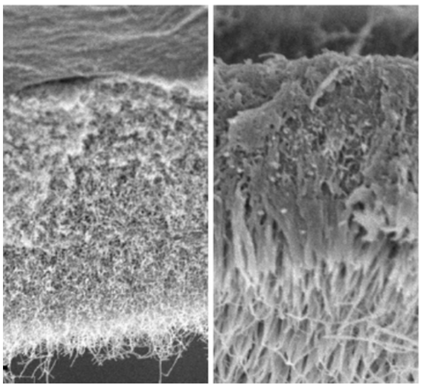
- Self-Assembly: Sacrificial-Post Templating Method for Block Copolymer Self-Assembly
  Tavakkoli, K. G.; Nicaise, S. M.; Hannon, A. F.; Gotrik, K. W.; Alexander-Katz, A.; Ross, C. A.; Berggren, K. K. *Small* **2014**, *3*, 493-499.
  Abstract:





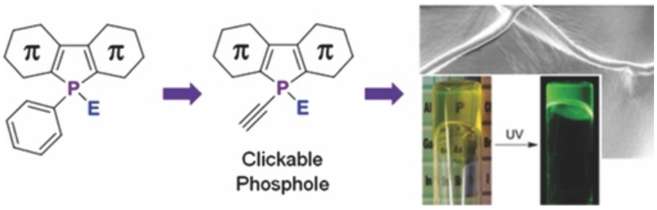
A sacrificial-post templating method is presented for directing block copolymer self-assembly to form nanostructures consisting of monolayers and bilayers of microdomains. In this approach, the topographical post template is removed after self-assembly and therefore is not incorporated into the final microdomain pattern. Arrays of nanoscale holes of different shapes and symmetries, including mesh structures and perforated lamellae with a bimodal pore size distribution, are produced. The ratio of the pore sizes in the bimodal distributions can be varied via the template pitch, and agrees with predictions of self consistent field theory.

- Electrostatic Control of Structure in Self-Assembled Membranes
  Bitton, R. ; Chow, L. W ; Zha, R. H. ; Velichko, Y. S. ; Pashuck, E. T ; Stupp, S. I. *Small*, **2014**, *3*, 500-505.
  Abstract:



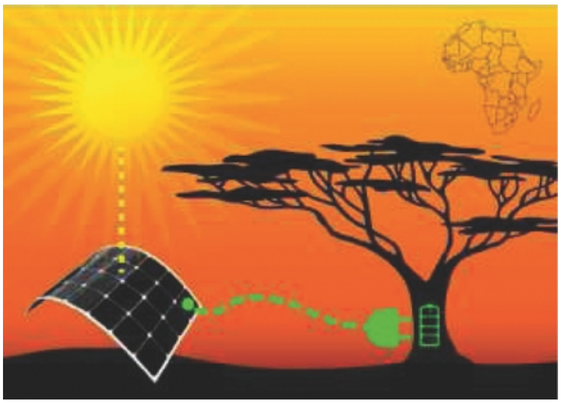
Self-assembling peptide amphiphiles (PAs) can form hierarchically ordered membranes when brought in contact with aqueous polyelectrolytes of the opposite charge by rapidly creating a diffusion barrier composed of filamentous nanostructures parallel to the plane of the incipient membrane. Following this event, osmotic forces and charge complexation template nanofiber growth perpendicular to the plane of the membrane in a dynamic self-assembly process. In this work, we show that this hierarchical structure requires massive interfacial aggregation of PA molecules, suggesting the importance of rapid diffusion barrier formation. Strong PA aggregation is induced here through the use of heparin-binding PAs with heparin and also with polyelectrolytes of varying charge density. Small angle X-ray scattering shows that in the case of weak PA-polyelectrolyte interaction, membranes formed display a cubic phase ordering on the nanoscale that likely results from clusters of PA nanostructures surrounded by polyelectrolyte chains.

- Molecular Engineering of “Click”-Phospholes Towards Self-Assembled Luminescent Soft Materials
  He, X.; Lin, J.-B.; Kan, W. H.; Dong, P.; Trudel, S.; Baumgartner, T. *Adv. Funct. Mater.* **2014**, *24*, 897–906.
  Abstract:



Inspired by the self-assembled bilayer structures of natural amphiphilic phospholipids, a new class of highly luminescent “click”-phospholes with exocyclic alkynyl group at the phosphorus center is reported. These molecules can be easily functionalized with a self-assembly group to generate neutral “phosphole-lipids”. This novel approach retains the versatile reactivity of the phosphorus center, allowing further engineering of the photophysical and self-assembly properties of the materials at a molecular level. The results of this study highlight the importance of being able to balance weak intermolecular interactions for controlling the self-assembly properties of soft materials. Only molecules with the appropriate set of intermolecular arrangement/interactions show both organogel and liquid crystal mesophases with well-ordered microstructures. Moreover, an efficient energy transfer of the luminescent materials is demonstrated and applied in the detection of organic solvent vapors.

- Organic Photovoltaic Modules and Biopolymer Supercapacitors for Supply of Renewable Electricity: A Perspective from Africa
  Inganäs, O.; Admassie, S. *Adv. Mater.* **2014**, *26*, 830–848.
  Abstract:



The role of materials in civilization is well demonstrated over the centuries and millennia, as materials have come to serve as the classifier of stages of civilization. With the advent of materials science, this relation has become even more pronounced. The pivotal role of advanced materials in industrial economies has not yet been matched by the influence of advanced materials during the

transition from agricultural to modern societies. The role of advanced materials in poverty eradication can be very large, in particular if new trajectories of social and economic development become possible. This is the topic of this essay, different in format from the traditional scientific review, as we try to encompass not only two infant technologies of solar energy conversion and storage by means of organic materials, but also the social conditions for introduction of the technologies. The development of organic-based photovoltaic energy conversion has been rapid, and promises to deliver new alternatives to well-established silicon photovoltaics. Our recent development of organic biopolymer composite electrodes opens avenues towards the use of renewable materials in the construction of wooden batteries or supercapacitors for charge storage. Combining these new elements may give different conditions for introduction of energy technology in areas now lacking electrical grids, but having sufficient solar energy inputs. These areas are found close to the equator, and include some of the poorest regions on earth.