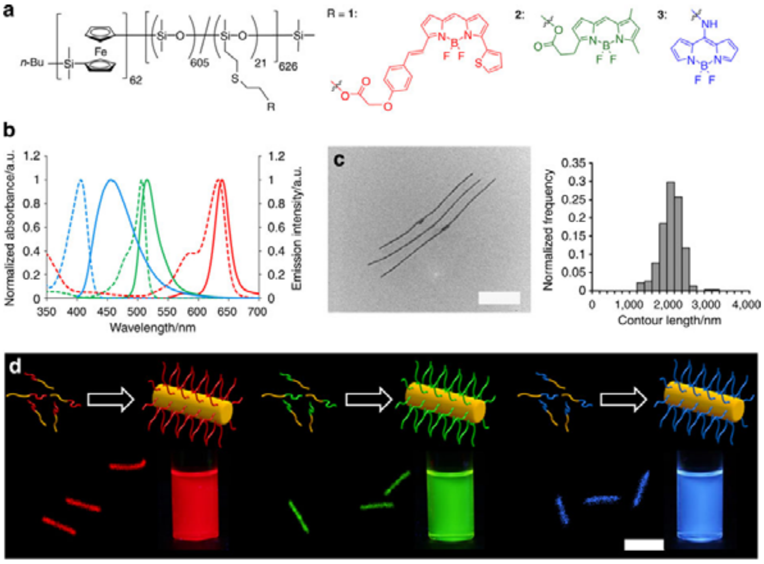
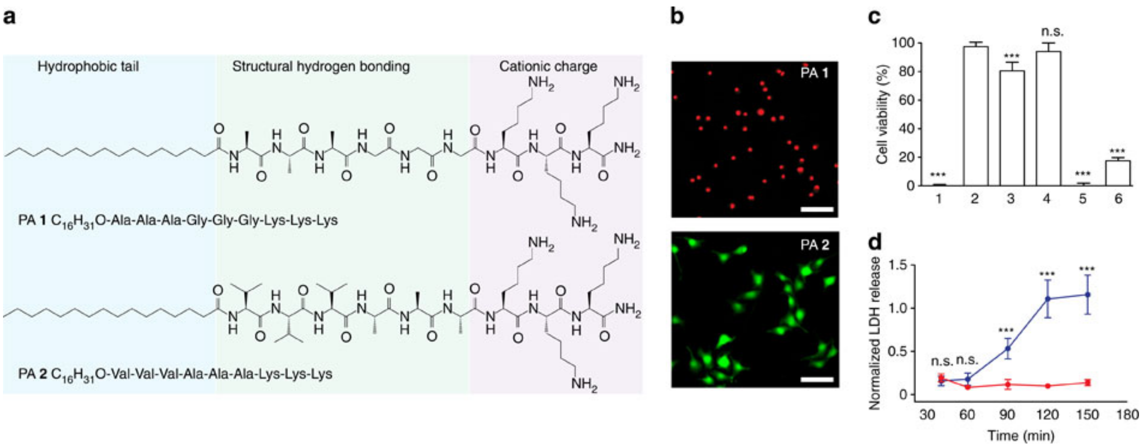
- Colour-tunable fluorescent multiblock micelles
  Hudson, Z. M.; Lunn, D. J.; Winnik, M. A.; Manners, I. *Nature Commun.* **2014**, *5*, 3372.
  Abstract:



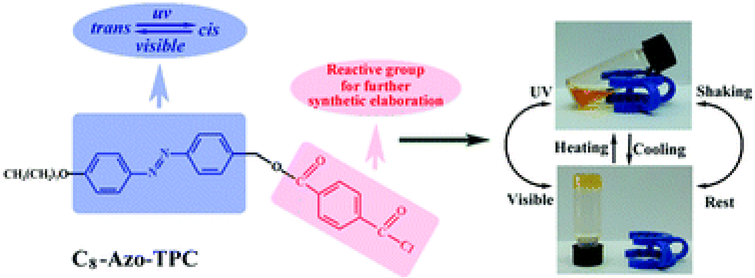
Emerging strategies based on the self-assembly of block copolymers have recently enabled the bottom-up fabrication of nanostructured materials with spatially distinct functional regions. Concurrently, a drive for further miniaturization in applications such as optics, electronics and diagnostic technology has led to intense interest in nanomaterials with well-defined patterns of emission colour. Using a series of fluorescent block copolymers and the crystallization-driven living self-assembly approach, we herein describe the synthesis of multicompartment micelles in which the emission of each segment can be controlled to produce colours throughout the visible spectrum. This represents a bottom-up synthetic route to objects analogous to nanoscale pixels, into which complex patterns may be written. Because of their small size and high density of encoded information, these findings could lead to the development of new materials for applications in, for example, biological diagnostics, miniaturized display technology and the preparation of encoded nanomaterials with high data density.

- Cell Death Versus Cell Survival Instructed by Supramolecular Cohesion of Nanostructures
  Newcomb, C. J.; Sur, S.; Ortony, J. H.; Lee, O-S.; Matson, J. B.; Boekhoven, J.; Yu, J-M.; Schatz, G. C.; Stupp, S. I. *Nature Commun.* **2014**, *5*, 3321.
  Abstract:



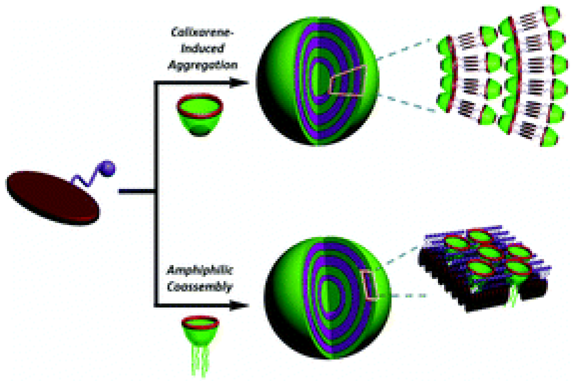
Many naturally occurring peptides containing cationic and hydrophobic domains have evolved to interact with mammalian cell membranes and have been incorporated into materials for non-viral gene delivery, cancer therapy or treatment of microbial infections. Their electrostatic attraction to the negatively charged cell surface and hydrophobic interactions with the membrane lipids enable intracellular delivery or cell lysis. Although the effects of hydrophobicity and cationic charge of soluble molecules on the cell membrane are well known, the interactions between materials with these molecular features and cells remain poorly understood. Here we report that varying the cohesive forces within nanofibres of supramolecular materials with nearly identical cationic and hydrophobic structure instruct cell death or cell survival. Weak intermolecular bonds promote cell death through disruption of lipid membranes, while materials reinforced by hydrogen bonds support cell viability. These findings provide new strategies to design biomaterials that interact with the cell membrane.

- Multistimuli responsive organogels based on a reactive azobenzene gelator
  Yang, R.; Peng, S.; Hughes, T. C. *Soft Matter* **2014**, *10,* 2188-2196.
  Abstract:



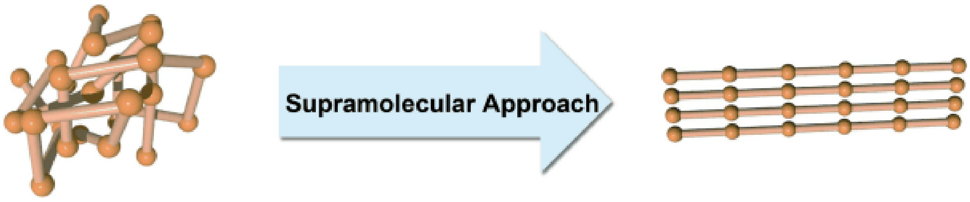
A reactive azobenzene based super organogelator was found to rapidly and reversibly transform a range of hydrophobic solvents from gels to solutions upon changes in temperature, light and shear force. More specifically they formed gels at concentrations as low as 0.08 wt%. Upon heating, exposure to UV light, or application of shear, the π–π bonding was disrupted which resulted in a rapid drop of both modulus and viscosity. This was confirmed by 1H NMR, SAXS, and rheological measurements. Although many examples of organogelators are known in the literature, this is the first time that a reactive group, a benzoyl chloride, has been incorporated in a supramolecular organogel structure. Moreover, this group is available for subsequent synthetic modifications. The presence of benzoyl chloride groups showed a remarkable effect on the formation and properties of the gels. Compared with other approaches, this strategy is advantageous in terms of structural design since it not only produces a multi-responsive soft material but also allows facile modifications which may expand the applications of organogels to other fields.

- Supra-amphiphilic aggregates formed by p-sulfonatocalix[4]arenes and the antipsychotic drug chlorpromazine
  Qin, Z.; Guo, D.-S.; Gao, X.-N.; Liu, Y. *Soft Matter* **2014**, *10,* 2253-2263.
  Abstract:



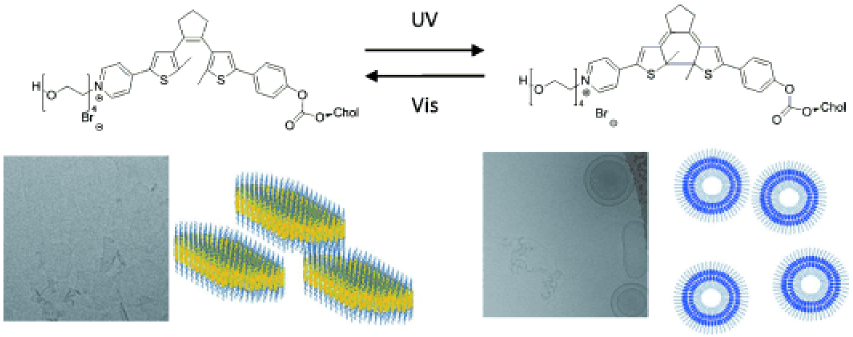
We report here a supramolecular strategy to directly assemble the small molecular antipsychotic drug chlorpromazine (CPZ) into nanostructures, induced by p-sulfonatocalix[4]arene (SC4A) and p-sulfonatocalix[4]arene tetraheptyl ether (SC4AH), with high drug loading efficiencies of 61% and 46%, respectively. The binary host–guest assembly process was monitored using optical transmittance measurements, and the size and morphology of these two kinds of supra-amphiphilic assemblies were identified using a combination of light scattering and high-resolution transmission electron microscopy, which showed solid spherical micelles. This strategy presents new opportunities for the development of high loading drug-containing carriers with easy processability for drug delivery.

- Supramolecular Approaches towards Ordered Polymer Materials
  Uemura, T., *Chem. Eur. J.* **2014**, *20*, 1482–1489.
  Abstract:



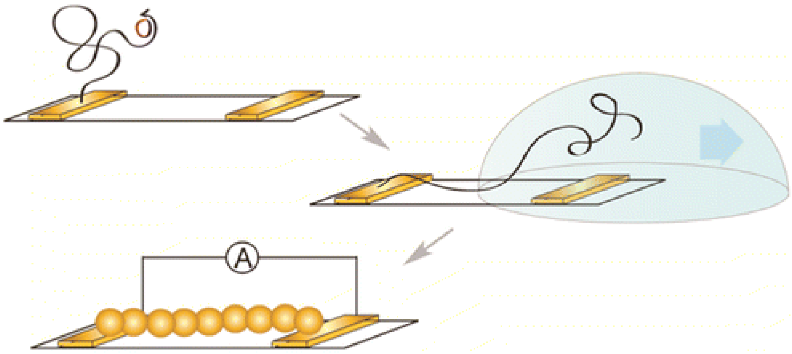
Controlled organization of polymer chains into ordered structures is highly important to tune or enhance the properties of the polymeric materials. A supramolecular approach using host–guest chemistry has allowed rational design of chain assemblies with many functional properties. Nanoporous materials with ordered channel structures are particularly useful for attaining precise assemblies of polymer chains through nanoconfinement.

- Light-Controlled Formation of Vesicles and Supramolecular Organogels by a Cholesterol-Bearing Amphiphilic Molecular Switch
  van Herpt, J. T., Areephong, J., Stuart, M. C. A., Browne, W. R. and Feringa, B. L., *Chem. Eur. J.* **2014**, *20*, 1737–1742.
  Abstract:



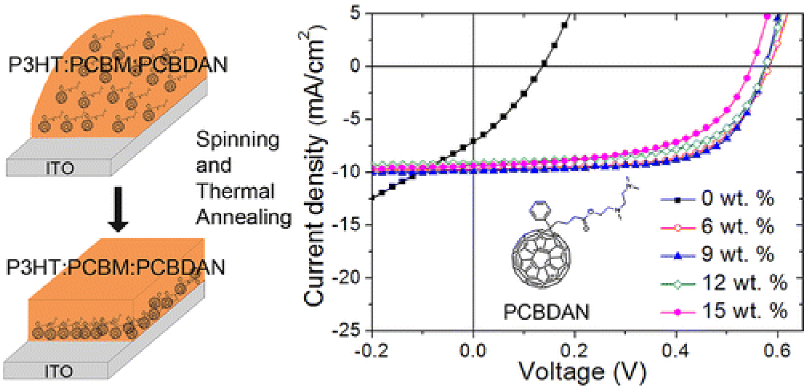
A new responsive material composed of an amphiphilic light-switchable dithienylethene unit functionalized with a hydrophobic cholesterol unit and a hydrophilic poly(ethylene glycol)-modified pyridinium group has been designed. This unique single-molecule system shows responsive light-switchable self-assembly in both water and organic solvents. Light-triggered reversible vesicle formation in aqueous solutions is reported. The molecule shows a different behavior in apolar aromatic solvents, in which light-controlled formation of organogel fibers is observed. The light-triggered aggregation behavior of this molecule demonstrates that control of a supramolecular structure with light can be achieved in both aqueous and organic media and that this ability can be present in a single molecule. This opens the way toward the effective development of new strategies in soft nanotechnology for applications in controlled chemical release systems.

- Gold Nanowire Based Electrical DNA Detection Using Rolling Circle Amplification
  Russell, C.; Welch, K.; Jarvius, J.; Cai, Y.; Brucas, R.; Nikolajeff, F.; Svedlindh, P.; Nilsson, M. *ACS Nano* **2014**, *8*, 1147–1153.
  Abstract:



We present an electrical sensor that uses rolling circle amplification (RCA) of DNA to stretch across the gap between two electrodes, interact with metal nanoparticle seeds to generate an electrically conductive nanowire, and produce electrical signals upon detection of specific target DNA sequences. RCA is a highly specific molecular detection mechanism based on DNA probe circularization. With this technique, long single-stranded DNA with simple repetitive sequences are produced. Here we show that stretched RCA products can be metalized using silver or gold solutions to form metal wires. Upon metallization, the resistance drops from TΩ to kΩ for silver and to Ω for gold. Metallization is seeded by gold nanoparticles aligned along the single-stranded DNA product through hybridization of functionalized oligonucleotides. We show that combining RCA with electrical DNA detection produces results in readout with very high signal-to-noise ratio, an essential feature for sensitive and specific detection assays. Finally, we demonstrate detection of 10 ng of Escherichia coli genomic DNA using the sensor concept.

- Self-Organization of Amine-Based Cathode Interfacial Materials in Inverted Polymer Solar Cells
  Ma, D.; Lv, M.; Lei, M.; Zhu, J.; Wang, H.; Chen, X. *ACS Nano* **2014**, *8*, 1601–1608.
  Abstract:

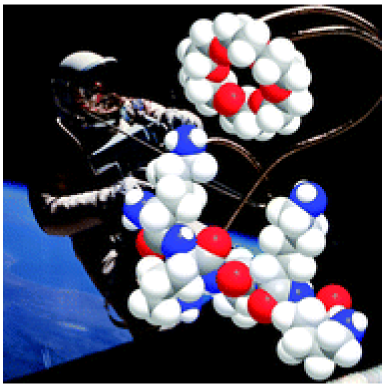


We present a strategy to fabricate polymer solar cells in inverted geometry by self-organization of alcohol soluble cathode interfacial materials in donor–acceptor bulk heterojunction blends. An amine-based fullerene [6,6]-phenyl-C61-butyric acid 2-((2-(dimethylamino)-ethyl)(methyl)amino)ethyl ester (PCBDAN) is used as an additive in poly(3-hexylthiophene) (P3HT) and 6,6-phenyl C61-butyric acid methyl ester (PCBM) blend to give a power conversion efficiency of 3.7% based on devices ITO/P3HT:PCBM:PCBDAN/MoO3/Ag where the ITO alone is used as the cathode. A vertical phase separation in favor of the inverted device architecture is formed: PCBDAN is rich on buried ITO surface reducing its work function, while P3HT is rich on air interface with the hole-collecting electrode. The driving force of the vertical phase separation is ascribed to the surface energy and its components of the blend compositions and the substrates. Similar results are also found with another typical alcohol soluble cathode interfacial materials, poly[(9,9-bis(3′-(N, N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN), implying that self-organization may be a general phenomenon in ternary blends. This self-organization procedure could eliminate the fabrication of printing thin film of interlayers or printing on such thin interlayers and would have potential application for roll-to-roll processing of polymer solar cells.

- Functional π-Gelators and Their Applications
  Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. *Chem. Rev.* **2014**, *114*, 1973–2129.
  Abstract:

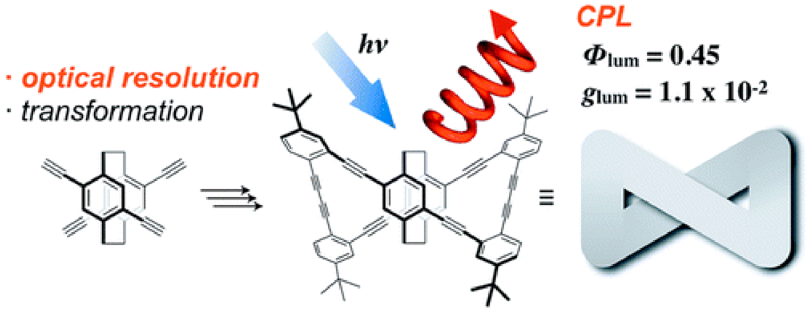
The progress achieved in gel chemistry has been tremendous and almost every class of molecules has been touched so far in search of new gelators. Atleast one new molecule may be getting added everyday as judged from the frequency of reports appearing in various scientific journals. Therefore, it is difficult to discuss all of them at one place. Due to this reason, while discussing different types of π-gelators, we have excluded gelators based on metallo supramolecular assemblies, hydrogels, and ionic gels derived from simple amino acids, peptides, and carbohydrates since several recent reviews are available on these topics. We rather focus on π-gelators based on photoresponsive chromophores, functional dyes, fused polyaromatics, heterocycles, functional dyes, oligomeric conjugated π-systems, and carbon allotrops. We have minimized discussions related to gelators obtained from simple functional derivatives of aromatic molecules such as benzene, pyrrole, or thiophene. However, we have included peptide and sugar based gelators having fused aromatics and functional dyes attached to them as borderline cases of π-gelators for the benefit of readers. The nonaromatic diacetylenes and several miscellaneous systems such as DNA bases and riboflavines are also included in this review to give a wider perspective of the topic to readers. For a better understanding, we have classified gelators discussed in this review into different categories according to the general nomenclature of molecules.

- Supramolecular reactivity in the gas phase: investigating the intrinsic properties of non-covalent complexes
  Cera, L.; Schalley, C. A. *Chem. Soc. Rev.* **2014**, *43*, 1800-1812.
  Abstract:



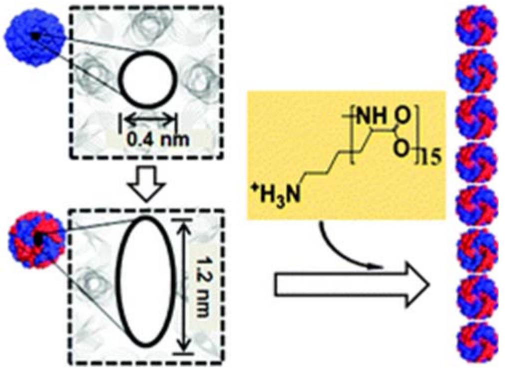
The high vacuum inside a mass spectrometer offers unique conditions to broaden our view on the reactivity of supramolecules. Because dynamic exchange processes between complexes are efficiently suppressed, the intrinsic and intramolecular reactivity of the complexes of interest is observed. Besides this, the significantly higher strength of non-covalent interactions in the absence of competing solvent allows processes to occur that are unable to compete in solution. The present review highlights a series of examples illustrating different aspects of supramolecular gas-phase reactivity ranging from the dissociation and formation of covalent bonds in non-covalent complexes through the reactivity in the restricted inner phase of container molecules and step-by-step mechanistic studies of organocatalytic reaction cycles to cage contraction reactions, processes induced by electron capture, and finally dynamic molecular motion within non-covalent complexes as unravelled by hydrogen–deuterium exchange processes performed in the gas phase.

- Planar Chiral Tetrasubstituted [2.2]Paracyclophane: Optical Resolution and Functionalization
  Morisaki, Y.; Gon, M.; Sasamori, T.; Tokitoh, N.; Chujo, Y. *J. Am. Chem. Soc.*, **2014**, *136*, 3350-3353.
  Abstract:



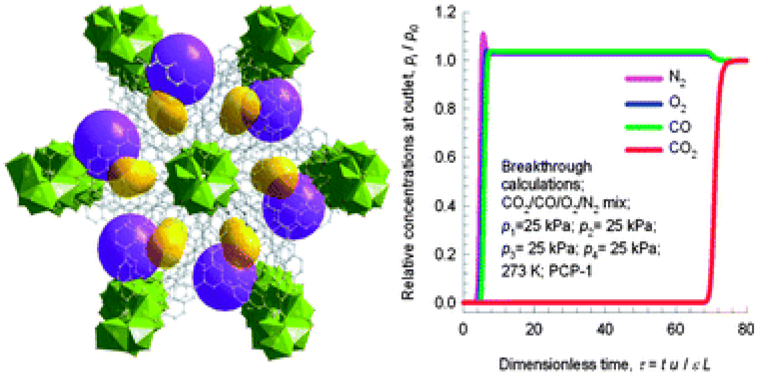
We achieved optical resolution of 4,7,12,15-tetrasubstituted [2.2]paracyclophane and subsequent transformation to planar chiral building blocks. An optically active propeller-shaped macrocyclic compound containing a planar chiral cyclophane core was synthesized, showing excellent chiroptical properties such as high fluorescence quantum efficiency and a large circularly polarized luminescence dissymmetry factor.

- Self-assembly of ferritin nanocages into linear chains induced by poly(α, L-lysine)
  Yang, R.; Chen, L.; Zhang, T.; Yang, S.; Leng, X.; Zhao, G. *Chem. Commun.* **2014**, *50,* 481-483.
  Abstract:



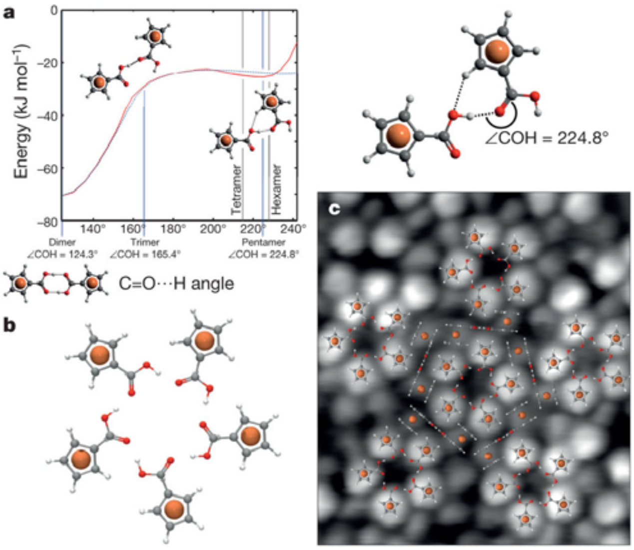
The widespread occurrence of protein channels offers a good opportunity to fabricate protein architectures. Herein, we have developed a novel strategy for linear self-assembly of ferritin cages induced by poly(α, L-lysine) through channel-directed electrostatic interactions at pH 7.0. The length of the formed filaments can be controlled.

- High $CO_2/N_2/O_2/CO$ separation in a chemically robust porous coordination polymer with low binding energy
  Duan, J.; Higuchi, M.; Krishna, R.; Kiyonaga, T.; Tsutsumi, Y.; Sato, Y.; Kubota, Y.; Takata, M.; Kitagawa, S. *Chem. Sci.* **2014**, *5,*660-666.
  Abstract:



Porous coordination polymers (PCPs), constructed from organic linkers and metal ions, can provide special pore environments for selective CO_2 capture. Although many PCPs have been reported, a rational design for identifying PCPs that adsorb CO_2 molecules with a low binding energy, high separation ability and high chemical stability remains a great challenge. Here, we propose and validate, experimentally and computationally, a new PCP, [La(BTN)DMF]·guest (PCP-1⊃guest), that has a large aromatic organic surface and a low binding energy for high CO_2 separation from four-gas mixtures (CO_2–N_2–O_2–CO) at ambient temperature. In addition, it shows good water and chemical stability; in particular, it is stable from pH = 2 to 12 at 100 °C, which is unprecedented for carboxylate-based PCPs.

- Self-assembly of hydrogen-bonded two-dimensional quasicrystals
  Wasio, N. A.; Quardokus, R. C.; Forrest, R. P.; Lent, C. S.; Corcelli, S. A.; Christie, J. A.; Henderson, K. W.; Kandel, S. A. *Nature* **2014,** *507*, 86-89.
  Abstract:



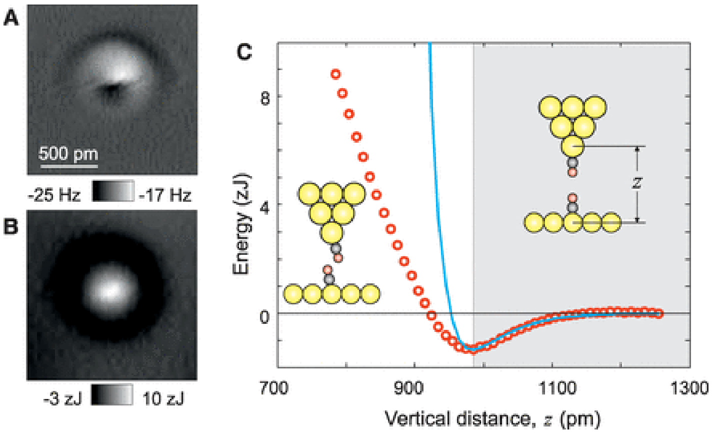
The process of molecular self-assembly on solid surfaces is essentially one of crystallization in two dimensions, and the structures that result depend on the interplay between intermolecular forces and the interaction between adsorbates and the underlying substrate. Because a single hydrogen bond typically has an energy between 15 and 35 kilojoules per mole, hydrogen bonding can be a strong driver of molecular assembly; this is apparent from the dominant role of hydrogen bonding in nucleic-acid base pairing, as well as in the secondary structure of proteins. Carboxylic acid functional groups, which provide two hydrogen bonds, are particularly promising and reliable in creating and maintaining surface order, and self-assembled monolayers of benzoic acids produce structure that depends on the number and relative placement of carboxylic acid groups. Here we use scanning tunnelling microscopy to study self-assembled monolayers of ferrocenecarboxylic acid (FcCOOH), and find that, rather than producing dimeric or linear structures typical of carboxylic acids, FcCOOH forms highly unusual cyclic hydrogen-bonded pentamers, which combine with simultaneously formed FcCOOH dimers to form two-dimensional quasicrystallites that exhibit local five-fold symmetry and maintain translational and rotational order (without periodicity) for distances of more than 400 ångströms.

- Sabotaged Scientist Sues Yale and Her Lab Chief

Enserink, M., *Science* **2014,** *343*, 1065-1066.
Abstract:

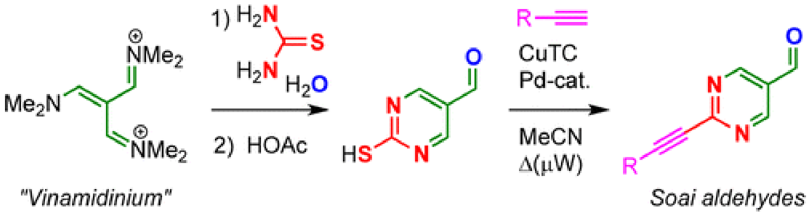
Magdalena Koziol, a former postdoc at Yale University, was the victim of scientific sabotage. Now, she is suing the alleged perpetrator, who she claims poisoned her zebrafish, as well as her former boss at Yale, who she says became hostile and unsupportive after the sabotage was discovered, and Yale University. The complex case raises a host of questions about research sabotage, a type of misbehavior that some scientists believe is more common than the few known cases suggest.

- Quantifying Molecular Stiffness and Interaction with Lateral Force Microscopy
  Weymouth, A. J.; Hofmann, T.; Giessibl, F. J. *Science* **2014,** *343*,1120-1122.
  Abstract:



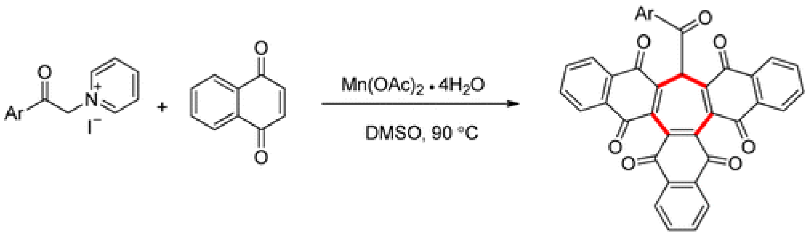
The spatial resolution of atomic force microscopy (AFM) can be drastically increased by terminating the tip with a single carbon monoxide (CO) molecule. However, the CO molecule is not stiff, and lateral forces, such as those around the sides of molecules, distort images. This issue begs a larger question of how AFM can probe structures that are laterally weak. Lateral force microscopy (LFM) can probe lateral stiffnesses that are not accessible to normal-force AFM, resulting in higher spatial resolution. With LFM, we determined the torsional spring constant of a CO-terminated tip molecule to be 0.24 newtons per meter. This value is less than that of a surface molecule and an example of a system whose stiffness is a product not only of bonding partners but also local environment.

- Synthesis of Soai Aldehydes for Asymmetric Autocatalysis by Desulfurative Cross-Coupling.
  Maltsev, O. V.; Pöthig, A.; Hintermann, L. *Org. Lett.* **2014,** *16*, 1282-1285.
  Abstract:



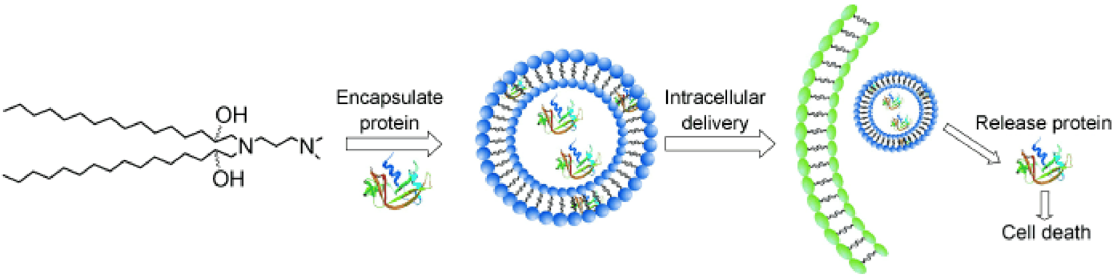
Palladium-catalyzed dehydrosulfurative Liebeskind–Srogl coupling of terminal alkynes with 2-mercapto-1,3-pyrimidine-5-carbaldehyde under base-free conditions provides 2-(alkynyl)-1,3-pyrimidine-5-carbaldehydes, which are substrates for autocatalytic amplification of chirality according to Soai et al. The mercapto aldehyde acceptor is obtained by condensation of Arnold's vinamidinium salt with thiourea.

- An Efficient Synthesis of Novel Fused Cycloheptatrienes through Mn(II)-Mediated Formal Intermolecular [2 + 2 + 2 + 1] Cycloaddition.
  Shu, W.-M.; Ma, J.-R.; Yang, Y.; Wu, A.-X. *Org. Lett.* **2014,** *16*, 1286-1289.
  Abstract:



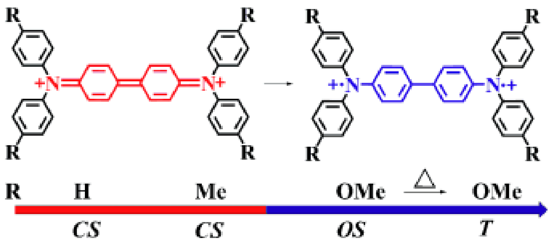
A new method for manganous acetate tetrahydrate mediated formal intermolecular [2 + 2 + 2 + 1] cycloaddition was developed for the synthesis of fused cycloheptatriene derivatives from *N*-(acylmethyl)pyridinium iodides and naphthoquinone. This method provides an innovative route for the efficient and convenient construction of fused seven-membered carbocycles from simple starting materials.

- Combinatorially Designed Lipid-like Nanoparticles for Intracellular Delivery of Cytotoxic Protein for Cancer Therapy
  Wang, M.; Alberti, K.; Sun, S.; Arellano, C. L.; Xu, Q. *Angew. Chem. Int. Ed.* **2014**, *53*, 2893–2898.
  Abstract:



An efficient and safe method to deliver active proteins into the cytosol of targeted cells is highly desirable to advance protein-based therapeutics. A novel protein delivery platform has been created by combinatorial design of cationic lipid-like materials (termed “lipidoids”), coupled with a reversible chemical protein engineering approach. Using ribonuclease A (RNase A) and saporin as two representative cytotoxic proteins, the combinatorial lipidoids efficiently deliver proteins into cancer cells and inhibit cell proliferation. A study of the structure–function relationship reveals that the electrostatic and hydrophobic interactions between the lipidoids and the protein play a vital role in the formation of protein–lipidoid nanocomplexes and intracellular delivery. A representative lipidoid (EC16-1) protein nanoparticle formulation inhibits cell proliferation in vitro and suppresses tumor growth in a murine breast cancer model.

- Tuning Ground States of Bis(triarylamine) Dications: From a Closed-Shell Singlet to a Diradicaloid with an Excited Triplet State
  Su, Y.; Wang, X.; Zheng, X.; Zhang, Z.; Song, Y.; Sui, Y.; Li, Y.; Wang, X. *Angew. Chem. Int. Ed.* **2014**, *53*, 2857–2861.
  Abstract:

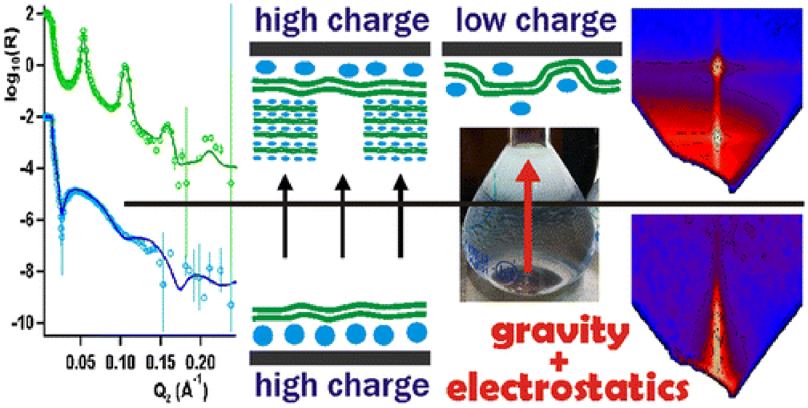


Three bis(triarylamine) dications were isolated by using weakly coordinating anions. Their electronic structures in the ground state were investigated by various experiments in conjunction with theoretical calculations. The ground-state electronic structures of these species were tunable by substituent effects, with two of them as closed-shell singlets and one of them as an open-shell singlet in the solid state. The excited state of the latter is thermally accessible, indicated by EPR and SQUID measurements. The work provides a new and stable diradicaloid structure motif with an excited triplet state.

- Key Factors Regulating the Mass Delivery of Macromolecules to Model Cell Membranes: Gravity and Electrostatics

  Campbell, R. A.; Watkins, E. B.; Jagalski, V.; Åkesson-Runnsjö, A.; Cárdenas, M. *ACS Macro Lett.* **2014**, *3*, 121–125.

  Abstract:

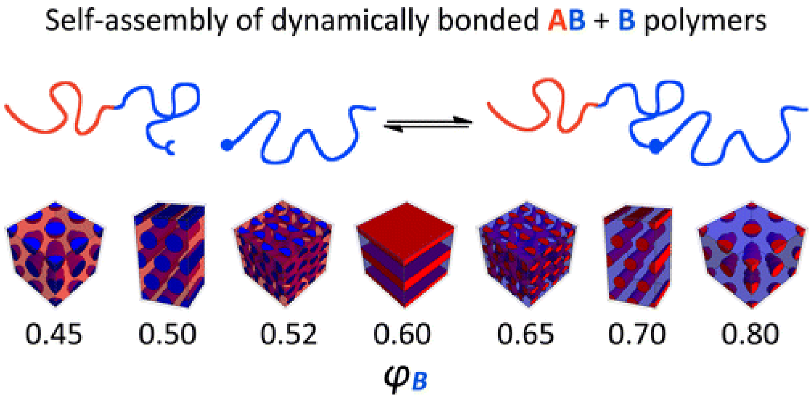


We show that both gravity and electrostatics are key factors regulating interactions between model cell membranes and self-assembled liquid crystalline aggregates of dendrimers and phospholipids. The system is a proxy for the trafficking of reservoirs of therapeutic drugs to cell membranes for slow diffusion and continuous delivery. Neutron reflectometry measurements were carried out on supported lipid bilayers of varying charge and on hydrophilic silica surfaces. Translocation of the macromolecule across the membrane and adsorption of the lamellar aggregates occur only when the membrane (1) is located above the bulk liquid and (2) has sufficient negative charge. The impact of such dramatic directionality effects due to bulk phase separation and gravity is emphasized for future biochemical investigations. Further, the potential to switch on the interaction mechanism through tuning the charge of the aggregates to activate endocytosis pathways on specific cell types is discussed in the context of targeted drug delivery applications.

- Phase Coexistence Calculations of Reversibly Bonded Block Copolymers: A Unit Cell Gibbs Ensemble Approach

  Mester, Z.; Lynd, N. A.; Delaney, K. T.; Fredrickson, G. H. *Macromolecules* **2014**, *47*, 1865–1874.

Abstract:



A self-consistent field theory (SCFT) technique for calculating the compositions of coexisting phases in melt blends of reversibly bonding block polymers is presented. This new method is obtained by deriving a canonical model for reaction equilibrium and incorporating it into the previously reported Gibbs ensemble unit-cell SCFT for investigating macrophase separation. We use our new technique to attack the phase behavior of an incompressible melt blend of AB diblock copolymers that reversibly react at their B termini with monofunctional B homopolymers to produce longer ABB diblock copolymers. We find that reaction equilibrium favoring the product polymer stabilizes a rich variety of ordered phases with little macrophase separation. Reaction equilibrium favoring the reactants, however, leads to macrophase separation over a broad range of compositions.