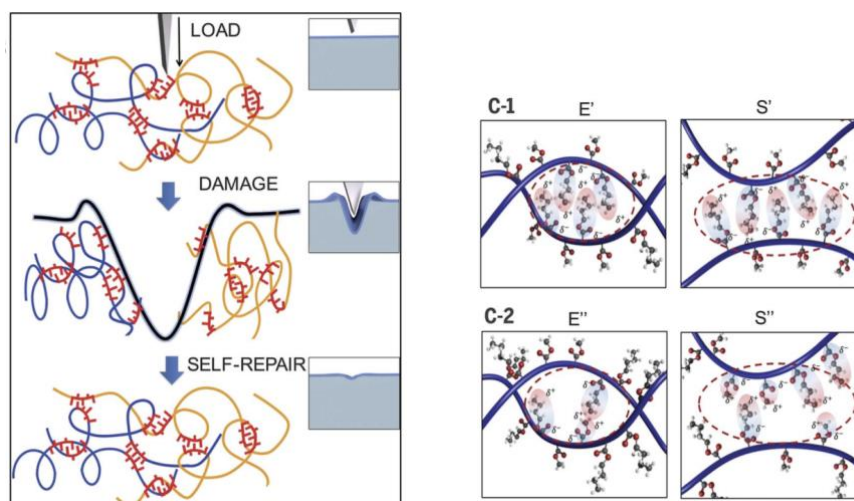


Key-and-lock Commodity Self-Healing Copolymers

Urban, M. W.*; Davydovich, D.; Yang, Y.; Demir, T.; Zhang, Y.; Casabianca, L. [*Science* 2018, 362, 220.](#)

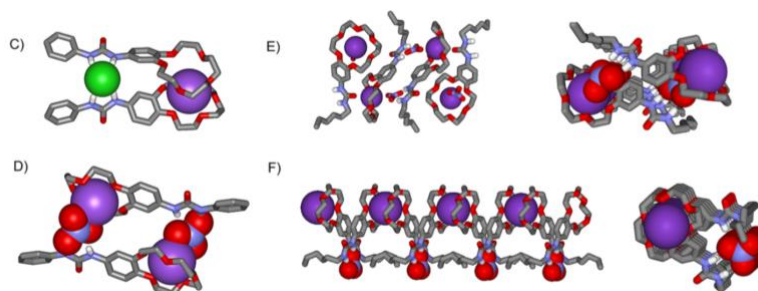


Self-healing materials are notable for their ability to recover from physical or chemical damage. We report that commodity copolymers, such as poly(methyl methacrylate)/*n*-butyl acrylate [p(MMA/*n*BA)] and their derivatives, can **self-heal upon mechanical damage**. This behavior occurs in a narrow compositional range for copolymer topologies that are preferentially alternating with a random component (alternating/random) and is attributed to favorable interchain van der Waals forces forming key-and-lock interchain junctions. **The use of van der Waals forces instead of supramolecular or covalent rebonding or encapsulated reactants eliminates chemical and physical alterations and enables multiple recovery upon mechanical damage without external intervention.** Unlike other self-healing approaches, perturbation of ubiquitous van der Waals forces upon mechanical damage is energetically unfavorable for interdigitated alternating/random copolymer motifs that facilitate self-healing under ambient conditions.

Comment: One of the most amazing things I've seen recently: to replace "strong" non-covalent interactions with Van der Waals interactions for a self-healing polymer. There are other examples of researchers using more and more weak interactions to do the same thing as with strong ones, and whenever someone will be able to use them all sequentially in a controlled manner, we will finally see the advent of real supramolecular chemistry. Or not.

Encapsulation versus Self-Aggregation toward Highly Selective Artificial K⁺ Channels

Barboiu, M.* [*Acc. Chem. Res.* 2018, ASAP.](#)



Natural ion-channel proteins allow ion transport across cell membranes at rates very close to those for ionic diffusion in water. Among them, natural KcsA K^+ channels present high transport rates and total selectivity for K^+ cations, rejecting all other cations. Most of the reported artificial ion channels cannot reach this type of activity because of their low selectivity. Several synthetic channels have been designed to mimic the natural KcsA channels, but those presenting an important K^+/Na^+ selectivity are limited. High-selectivity issues are determinant for the performance of natural protein channels, but they have been not considered as determinant in controlling the transport activity of the artificial ion channels. This Account discusses the last developments of artificial supramolecular carriers or channels that selectively transport K^+ cations against other cations. Mimicking the complex structures of protein channels is an important research area. These studies are related to such adaptive biomimetic systems that can self-select their functions, with a specific emphasis on artificial superstructures enabling K^+ transport like in the natural ones. Alternatively, it is more than interesting to synthetically construct only the active key structures of protein filters or gates that give the chemical selectivity or lead us to describe their dynamic role in the ion pumping and translocation along the channel. Several self-assembled macrocyclic channels are presented here.

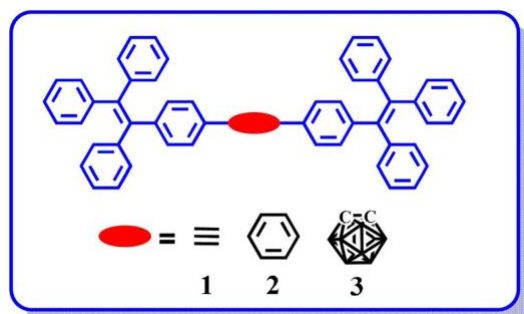
The macrocyclic binding sites may selectively encapsulate the K^+ cations or form aggregated H-bonded central pores of self-assembled macrocycles that coordinate the K^+ cations as hydrating water molecules in aqueous solution, compensating for the energetic cost of cation dehydration.

These macrocyclic channels are responsive in the presence of K^+ cations, even when a large excess of Na^+ is present. From the mechanistic point of view, these systems express a synergistic dynamic feature: addition of K^+ cations drives the selection and emergence of specific ion channels that selectively conduct the K^+ cations that promoted the formation of channel superstructures in the first place. These highly permeable and K^+ -selective artificial channels may be considered as simple primitive biomimetic alternatives of natural KcsA channels that may find interesting applications in chemical separations, selective sensing, and biomedical materials.

Comment: It is a remarkably short Accounts, but it discusses the interplay of encapsulation vs transport. I guess it's relevance with Wenzhi's research is the main reason for the paper to appear here.

Tetraphenylethylene–Carborane–Tetraphenylethylene Triad: Influence of Steric Bridge on Aggregation-Induced Emission Properties

Yin, Y.; Li, X.; Yan, S.; Yan, H.*; Lu, C.*; [Chem. Asian J. 2018, Early View](#)



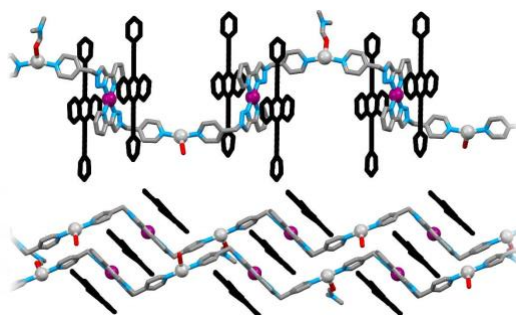
A novel tetraphenylethylene (TPE)–bridge–tetraphenylethylene triad has been synthesized, where the o-carboranyl moiety functions as a central bridge and two TPE units are in the lateral positions. This molecular triad has been characterized by various spectroscopic methods, and its structure

has been studied by X-ray crystallography as well as theoretical calculations. The impact of the bridging carboranyl unit on the aggregation-induced emission (AIE) characteristics of the TPE–bridge–TPE triad has been investigated. When the central bridge is changed from one-dimensional (1D) alkynyl to three-dimensional (3D) carboranyl, the absolute luminescent quantum yield of the triad increased from 21.2 % to 54.7 % in the solid state, accompanied by a luminescence color change from blue to yellow (94 nm red-shift). Building bridges: The impact of a carboranyl linker on the AIE characteristics of tetraphenylethylene (TPE)–bridge–TPE has been investigated. The luminescent quantum yield can be tuned from 21.2 % to 54.7 % in the solid state, and a red-shift emission of 94 nm is observed.

Comment: The results was unexpected but interesting.

Recognition Properties and Self-assembly of Planar $[M(2\text{-pyridyl-1,2,3-triazole})_2]^{2+}$ Metallo-ligands

Preston, D.*; Findlay, J. A.; Crowley, J. D.; [Chem. Asian J. 2018, Early View](#)



Molecular recognition continues to be an area of keen interest for supramolecular chemists. The investigated $[M(L)_2]^{2+}$ metallo-ligands ($M = Pd^{II}$, Pt^{II} , $L = 2\text{-}(1\text{-(pyridine-4-methyl)-1-}H\text{-1,2,3-triazol-4-yl)pyridine}$) form a planar cationic panel with vacant pyridyl binding sites. They interact with planar neutral aromatic guests through $\pi\text{--}\pi$ and/or metallophilic interactions. In some cases, the metallo-ligands also interacted in the solid state with Ag^I either through coordination to the pendant pyridyl arms, or through metal–metal interactions, forming coordination polymers. We have therefore developed a system that reliably recognises a planar electron-rich guest in solution and in the solid state, and shows the potential to link the resultant host–guest adducts into extended solid-state structures. The facile synthesis and ready functionalisation of 2-pyridyl-1,2,3-triazole ligands through copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) “click” chemistry should allow for ready tuning of the electronic properties of adducts formed from these systems.

Comment: This work is interesting: ligand and metal salts self-assemble into an extensive network by separated steps and only when formed in the solid state can recognize guest molecules.

Design, Synthesis, and Applications of DNA–Macrocyclic Host Conjugates

Zhou, X.; Pathak, P.; Jayawickramarajah, J.* [Chem. Commun., 2018, Advance Article](#).

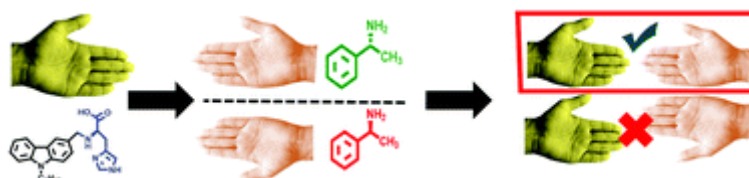


With this Feature Article we **review**, for the first time, the **development of DNA-host conjugates**—a nascent yet rapidly growing research focus within the ambit of **DNA supramolecular chemistry**. Synthetic hosts (such as cyclodextrins, cucurbiturils, and calixarenes) are well-suited to be partnered with DNA, since DNA assembly and host-guest binding both thrive in aqueous media, are largely orthogonal, and exhibit controllable and input-responsive properties. The covalent braiding of these two supramolecular synthons thus leads to advanced self-assemblies and nanostructures with exciting function that range from drug delivery agents to input-triggered switches. The latter class of DNA-host conjugates have been demonstrated to precisely control protein activity, and have also been used as modulable catalysts and versatile biosensors.

Comment: This article is a nice and quite understandable review and explains well the different issues. It may even inspire us for the elaboration of future systems including DNA as a regulator in order to form physical gels (in particular, the 4th part: “**Application of DNA-Macrocyclic Host Conjugates**”).

Preferential Intermolecular Interactions Lead to Chiral Recognition: Enantioselective Gel Formation and Collapse

Gambhir, D.; Kumar, S.; Dey, G.; Krishnan, V.; Koner, R. R.* [Chem. Commun., 2018, Advance Article](#).

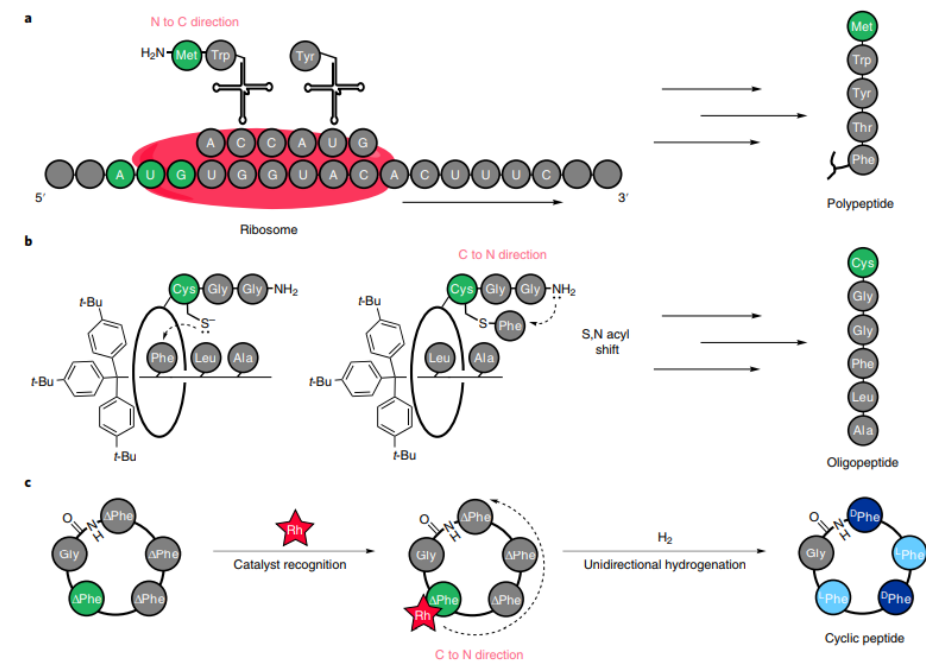


Interesting **self-assembly** of an **amino acid** based molecular material into a **hydrogel** in the **presence of selective enantiomeric chiral amines** leading to **chiral recognition** has been demonstrated. Moreover, **collapse of a metallogel** formed from the same material in the **presence of selective enantiomers** validated its **enantioselective affinity**. Importantly, in addition to relevant experimental techniques, DFT studies have been successfully explored to establish chiral recognition through enantioselective gelation.

Comment: This paper describes the formation of a hydrogel obtained from the self-assembly of a chiral amino acid. As in the previous article, this system could be useful in the motor project inducing an enantiomeric control.

Hydrogenation Catalyst Generates Cyclic Peptide Stereocentres in Sequence

Le, D. N.; Hansen, E.; Khan, H. A.; Kim, B.; Wiest, O.; * Dong, V. M.* [Nat. Chem. 2018 10, 968](#).



Molecular recognition plays a key role in enzyme-substrate specificity, the regulation of genes, and the treatment of diseases. Inspired by the power of molecular recognition in enzymatic processes, we sought to exploit its use in organic synthesis. Here we demonstrate how a synthetic rhodium-based catalyst can selectively bind a dehydroamino acid residue to initiate a sequential and stereoselective synthesis of cyclic peptides. Our combined experimental and theoretical study reveals the underpinnings of a cascade reduction that occurs with high stereocontrol and in one direction around a macrocyclic ring. As the catalyst can dissociate from the peptide, the C to N directionality of the hydrogenation reactions is controlled by catalyst-substrate recognition rather than a processive mechanism in which the catalyst remains bound to the macrocycle. This mechanistic insight provides a foundation for the use of cascade hydrogenations.

Comment: In this study, they provide a good example for the construction of cyclic peptides by cascade catalysis.

Peptide-Based Multifunctional Nanomaterials for Tumor Imaging and Therapy

Zhang, C.; Wu, W.; Li, R. Q.; Qiu, W. X.; Zhuang, Z. N.; Cheng, S. X.; Zhang, X. Z.* *Adv. Funct. Mater.* **2018** 1804492.

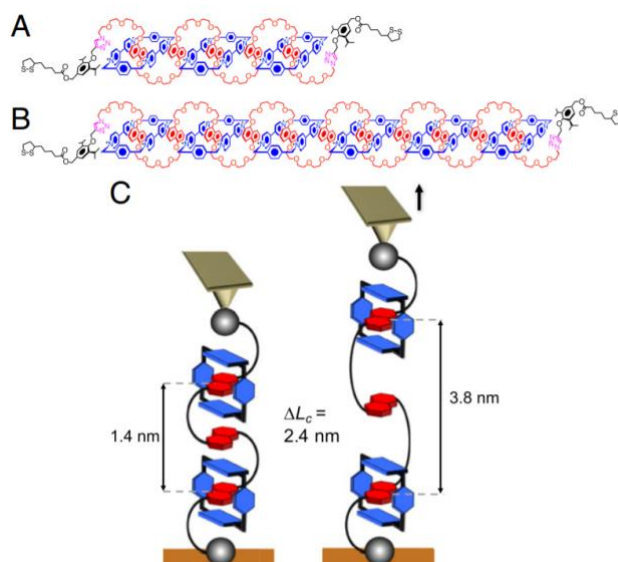


During the last decade, peptide-based nanomaterials are recognized as upcoming biomedical materials for tumor imaging and therapy. The rapid expansion of peptides and peptide derivatives is almost owing to their excellent biocompatibility, diverse bioactivity, potential biodegradability, specific biological recognition ability, and easy chemical modification characteristic. The present review outlines the development up to now concerning the design and biomedical applications of peptide-based multifunctional nanomaterials, with an emphasis on their variegated therapeutic methods.

Comment: In short, functional peptides have presented great potential for applications in tumor theranostics, we believe functional peptides will find more and more biomedical applications in the near future.

Dynamic Force Spectroscopy of Synthetic Oligorotaxane Foldamers

Sluysmansa, D.; Devauxa, F.; Brunsb, C.; Stoddart, J. F.; Duweza, A. S. *Proc. Nat. Acad. Sci. USA*, **2018**, *115*, 9362 - 9366.



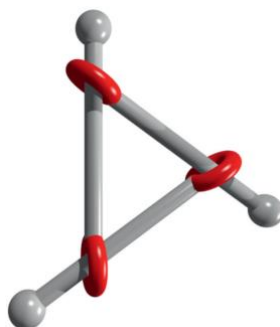
Wholly synthetic molecules involving both mechanical bonds and a folded secondary structure are one of the most promising architectures for the design of functional molecular machines with unprecedented properties. Here, we report dynamic single-molecule force spectroscopy experiments that explore the energetic details of donor–acceptor oligorotaxane foldamers, a class of molecular switches. The mechanical breaking of the donor–acceptor interactions responsible for the folded structure shows a high constant rupture force over a broad range of loading rates, covering three orders of magnitude. In comparison with dynamic force spectroscopy performed during the past 20 y on various (bio)molecules, the near-equilibrium regime of oligorotaxanes persists at much higher loading rates, at which biomolecules have reached their kinetic regime, illustrating the very fast dynamics and remarkable rebinding capabilities of the intramolecular donor–acceptor interactions. We focused on one single interaction at a time and probed the stochastic rupture and rebinding paths. Using the Crooks fluctuation theorem, we measured the mechanical work produced during the breaking and rebinding to determine a freeenergy difference, ΔG , of $6 \text{ kcal} \cdot \text{mol}^{-1}$ between the two local conformations around a single bond.

Comment: By using AFM-based dynamic force spectroscopy, donor–acceptor oligorotaxane foldamers, synthetic prototypes of molecular switches have been probed in this work. Their

findings ‘highlight the importance of the molecular design in the synthesis of efficient molecular machines’.

Triangular Cyclic Rotaxanes: Size, Fluctuations, and Switching Properties

Reddy, D.; Sevick, E. M.; Williams, D. [*Proc. Nat. Acad. Sci. USA*, 2018, 115, 9367 - 9372.](#)

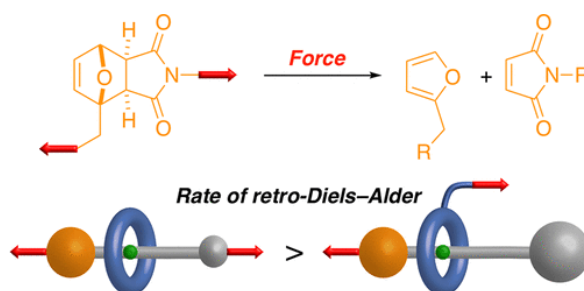


We examine one of the simplest cyclic rotaxanes—a molecule made from three rods with variable length between 0 and L . This [3]rotaxane, unlike a traditional molecule, shows significant size and shape fluctuations. We quantify these using a number of different measures. In particular, we show that the average angles are 100, 52, and 28 and the most populated lengths lie at L , $2L=3$, and $L=3$. The triangles are usually obtuse. We discuss the area allowed within the triangle for inclusion compounds. Inspired by the linear rotaxane switches, we also consider the statistical mechanics of switching when stations with attractive interactions promote small-cycle areas.

Comment: This newly designed [3]rotaxane not only enriches the rotaxane library, but also provides a new way to construct mechanical switches. However, the properties of cyclic rotaxanes still need to be investigated thoroughly.

Impact of a Mechanical Bond on the Activation of a Mechanophore

Zhang, M. ; De Bo, G.* [*J. Am. Chem. Soc.* 2018, 140, 12724-12727.](#)

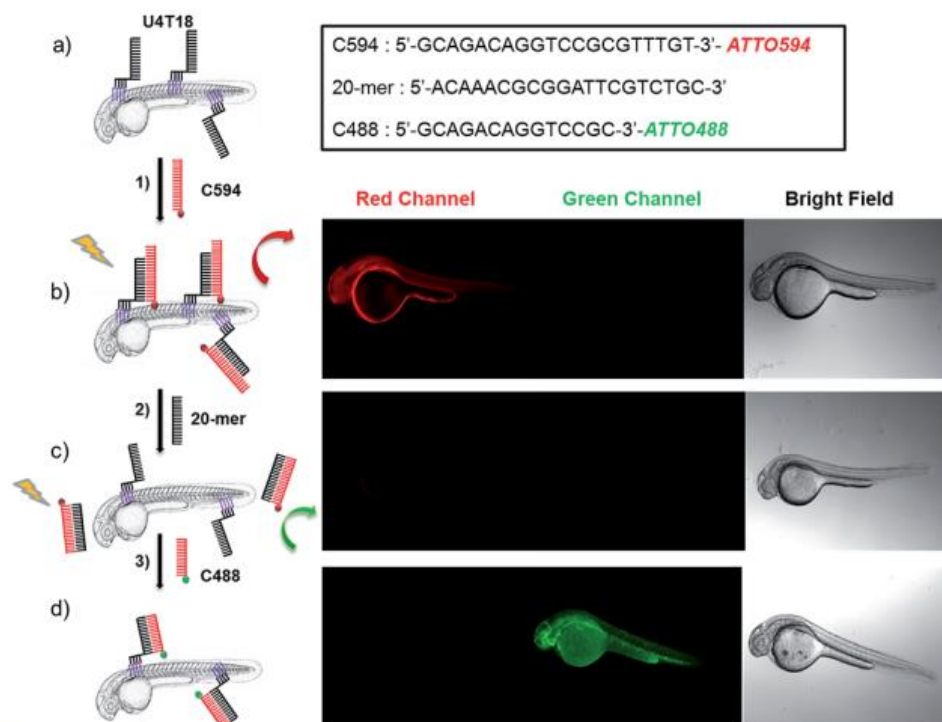


Mechanical bonds are known to efficiently absorb mechanical energy at low forces, but their behavior at high forces is unknown. Here we investigate the impact of a mechanical bond on the rate of activation of a Diels–Alder mechanophore. Using a combination of experimental and computational techniques, we found that the rate of a retro-Diels–Alder reaction under tension is decreased when the mechanophore is embedded in the axle of a rotaxane due to the presence of a competing high-stress region at the junction between the macrocycle and the axle.

Comment: This paper shows how it is possible to modulate the rate of a mechanically-triggered reaction (retro Diels Alder) through the incorporation of a mechanical bond. This will allow us to tune the mechanical resistance of a polymer chain playing on the position of mechanical bonds in the chain.

Performing DNA Nanotechnology Operations on a Zebrafish

Yang, J.*; Meng, Z.*; Liu, Q.; Shimada, Y.; Olsthoorn, R. C. L.; Spaink, H. P.; Herrmann, A.; Kros, A. [*Chem. Sci.* **2018**, *9*, 7271–7276.](#)

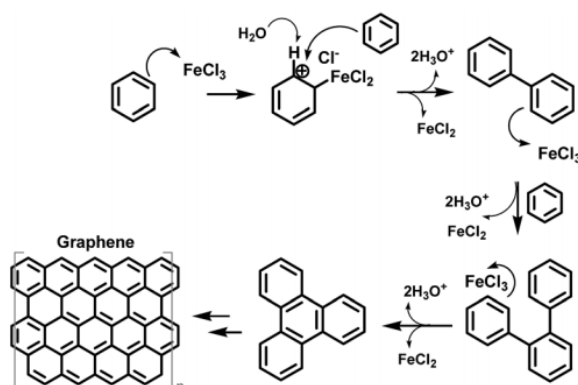


Nanoscale engineering of surfaces is becoming an indispensable technique to modify membranes and, thus cellular behaviour. Here, such membrane engineering related was explored on **the surface of a living animal** using DNA nanotechnology. We demonstrate the immobilization of oligonucleotides functionalized with a membrane anchor on 2 day old zebrafish. The protruding single-stranded DNA on the skin of zebrafish served as a handle for complementary DNAs, which allowed the attachment of small molecule cargo, liposomes and dynamic relabeling by DNA hybridization protocols. Robust anchoring of the oligonucleotides was proven as DNA-based amplification processes were successfully performed on the outer membrane of the zebrafish enabling the multiplication of surface functionalities from a single DNA-anchoring unit and the dramatic improvement of fluorescent labeling of these animals. As **zebrafish are becoming an alternative to animal models in drug development, toxicology and nanoparticles characterization**, we believe the platform presented here allows amalgamation of DNA nanotechnology tools with live animals and this opens up yet unexplored avenues like efficient bio-barcoding as well as in vivo tracking.

Comment: Technically, the work presented here is not significantly more complicated than functionalizing any cell membrane. However, working with a zebrafish embryo sounds classier than HeLa cells, isn't it? The interesting point in this article resides also in the fact that **the labels can be reversibly attached**.

Facile Room Temperature Synthesis of Large Graphene Sheets from Simple Molecules

Lopes, L. C.; da Silva, L. C.; Vaz, B. G.; Oliveira, A. R. M.; Oliveira, M. M.; Rocco, M. L. M.; Orth, E. S.; Zarkin, A. J. G.* [*Chem. Sci.* **2018**, *9*, 7297–7303.](#)

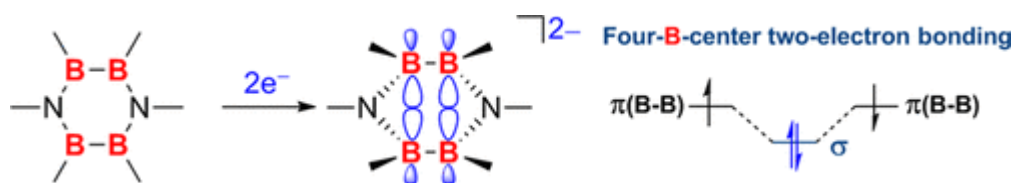


The largest graphene sample obtained through a chemical reaction under ambient conditions (temperature and pressure), using simple molecules such as benzene or n-hexane as precursors, is reported. Starting from a heterogeneous reaction between solid iron chloride and the molecular precursor (benzene and n-hexane) at a water/oil interface, **graphene sheets with micrometric lateral size** are obtained as a film deposited at the liquid/liquid (L/L) interface. The pathway involving the cyclization and aromatization of n-hexane to benzene at the L/L interface, and the sequence of conversion of benzene to biphenyl and biphenyl to condensed rings (which originates the graphene structures) was followed by different characterization techniques and a mechanistic proposal is presented. Finally, we demonstrate that this route can be extended for the synthesis of N-doped graphene, using pyridine as the molecular precursor.

Comment: While this abstract sounds amazing, and as the authors recognize it, there are still many problems to solve with this technique, mainly related to the purity of the graphene sheets. The most interesting point, in my opinion, was **the oxidation of n-hexane in such mild conditions**.

Zwitterionic Inorganic Benzene Valence Isomer with σ -Bonding between Two π -Orbitals

Su, B.; Ota, K.; Xu, K.; Hirao, H.*; Kinjo, R.* [*J. Am. Chem. Soc.* **2018**, *140*, 11921–11925.](#)



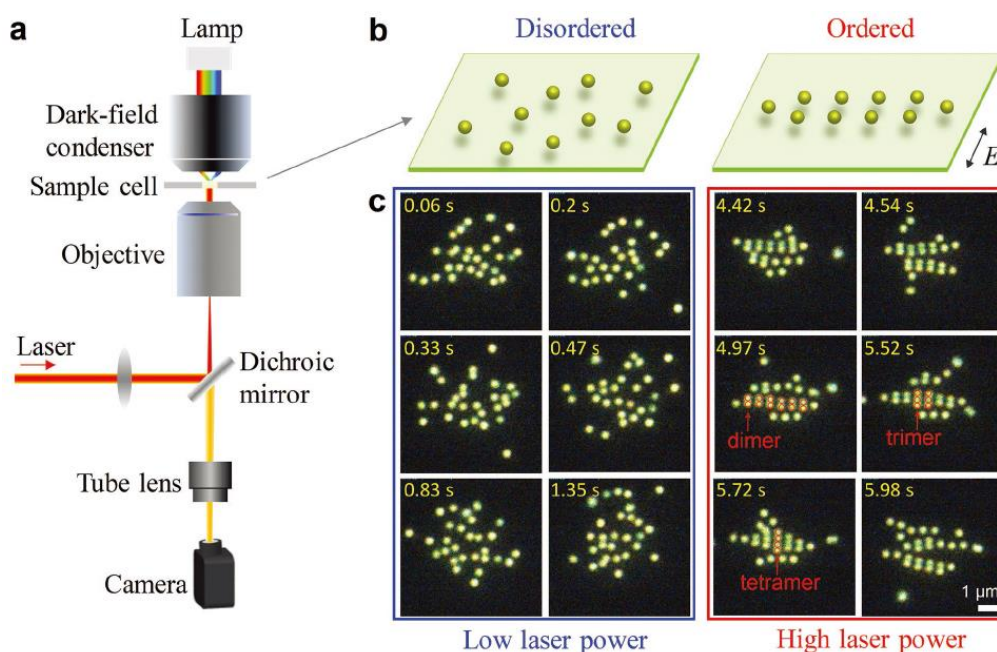
Despite the large number of plausible isomers of benzene (C_6H_6), only four valence isomers $[(CH)_6]$ have been experimentally detected, all of which are nonionic and possess skeletal frameworks built from localized C–C bonds. Herein, we present the isolation of a diazatetraborabenzene analogue of a hypothetical zwitterionic valence isomer of benzene. Therein, two electrons are delocalized over the four boron atoms in the six-membered B_4N_2 ring, which is a result of the σ -bonding interaction between two odd-electron B–B π -orbitals. Simple treatment

with a crown ether leads to the formation of a paramagnetic potassium-doped radical ion pair that exhibits a thermally populated triplet character.

Comment: I like this kind of papers as it challenges our classical understanding of chemical bonding. Here you have a σ -bond between two π -orbitals (2 electrons for 4 atoms).

Dissipative Self-Assembly of Anisotropic Nanoparticle Chains with Combined Electrodynamic and Electrostatic Interactions

Nan, F.; Han, F.; Scherer, N. F.; Yan, Z.* [Adv. Mater. 2018, 1803238](#).

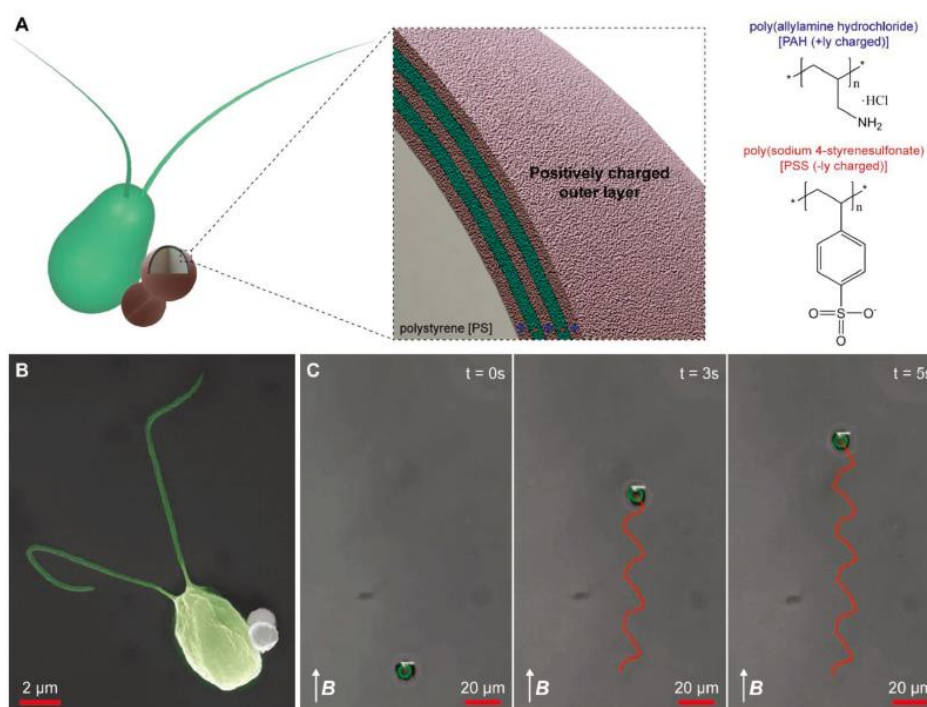


Dissipative self-assembly of colloidal nanoparticles offers the prospect of creating reconfigurable artificial materials and systems, yet the phenomenon only occurs far from thermodynamic equilibrium. Therefore, it is usually difficult to predict and control. Here, a dissipative colloidal solution system, where anisotropic chains with different interparticle separations in two perpendicular directions transiently arise among largely disordered silver nanoparticles illuminated by a laser beam, is reported. The optical field creates a nonequilibrium dissipative state, where a disorder-to-order transition occurs driven by anisotropic electrodynamic interactions coupled with electrostatic interactions. Investigation of the temporal dynamics and spatial arrangements of the nanoparticle system shows that the optical binding strength and entropy of the system are two crucial parameters for the formation of the anisotropic chains and responsible for adaptive behaviors, such as self-replication of dimer units. Formation of anisotropic nanoparticle chains is also observed among colloidal nanoparticles made from other metal (e.g., Au), polymer (e.g., polystyrene), ceramic (e.g., CeO₂), and hybrid materials (e.g., SiO₂@Au core-shell), suggesting that light-driven self-organization will provide a wide range of opportunities to discover new dissipative structures under thermal fluctuations and build novel anisotropic materials with nanoscale order.

Comment: I have seen a similar concept before (dissipative self-assembly of colloidal particles), but this paper describes a pure inorganic system. However, it's hard for me to fully understand all the analyses. Fortunately, the logic of this paper is quite straight forward to gradually understand what happened in this system and the critical factors for the formation of self-assemblies.

Microalga-Powered Microswimmers toward Active Cargo Delivery

Yasa, O.; Erkoc, P.; Alapan, Y.; Sitti, M.* [*Adv. Mater.* **2018**, 1804130.](#)

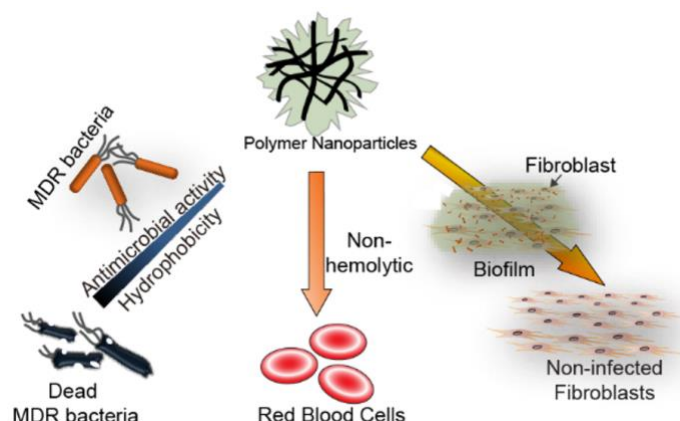


Nature presents intriguing biological swimmers with innate energy harvesting abilities from their local environments. Use of natural swimmers as cargo delivery agents presents an alternative strategy to transport therapeutics inside the body to locations otherwise difficult to access by traditional delivery strategies. Herein, a biocompatible biohybrid microswimmer powered by a unicellular freshwater green microalga, *Chlamydomonas reinhardtii*, is reported. Polyelectrolyte-functionalized magnetic spherical cargoes (1 μm in diameter) are attached to surface of the microalgae via noncovalent interactions without the requirement for any chemical reaction. The 3D swimming motility of the constructed biohybrid algal microswimmers is characterized in the presence and absence of a uniform magnetic fields. In addition, motility of both microalgae and biohybrid algal microswimmers is investigated in various physiologically relevant conditions, including cell culture medium, human tubal fluid, plasma, and blood. Furthermore, it is demonstrated that the algal microswimmers are cytocompatible when co-cultured with healthy and cancerous cells. Finally, fluorescent isothiocyanate-dextran (a water-soluble polysaccharide) molecules are effectively delivered to mammalian cells using the biohybrid algal microswimmers as a proof-of-concept active cargo delivery demonstration. The microswimmer design described here presents a new class of biohybrid microswimmers with greater biocompatibility and motility for targeted delivery applications in medicine.

Comment: This study describes a highly mobile biohybrid swimmer which contains a natural microalga and magnetic particles. It is a smart method to transport cargos, because this strategy avoids both complex synthesis and endows higher biocompatibility.

Engineered Polymer Nanoparticles with Unprecedented Antimicrobial Efficacy and Therapeutic Indices against Multidrug-Resistant Bacteria and Biofilms

Gupta, A.; Landis, R. F.; Li, C.-H.; Schnurr, M.; Das, R.; Lee, Y.-W.; Yazdani, M.; Liu, Y.; Kozlova, A.; Rotello, V. M.* *J. Am. Chem. Soc.* **2018**, *140*, 12137-12143.

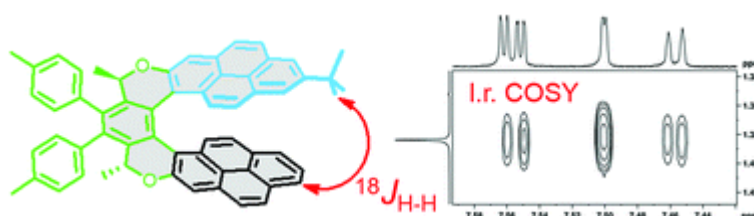


The rapid emergence of antibiotic-resistant bacterial “superbugs” with concomitant treatment failure and high mortality rates presents a severe threat to global health. The superbug risk is further exacerbated by chronic infections generated from antibiotic-resistant biofilms that render them refractory to available treatments. We hypothesized that efficient antimicrobial agents could be generated through careful engineering of hydrophobic and cationic domains in a synthetic semirigid polymer scaffold, mirroring and amplifying attributes of antimicrobial peptides. We report the creation of polymeric nanoparticles with highly efficient antimicrobial properties. These nanoparticles eradicate biofilms with low toxicity to mammalian cells and feature unprecedented therapeutic indices against red blood cells. Most notably, bacterial resistance toward these nanoparticles was not observed after 20 serial passages, in stark contrast to clinically relevant antibiotics where significant resistance occurred after only a few passages.

Comment: This paper describes the preparation of polymeric nanoparticles with antimicrobial properties. The mechanism of action (breaking of membranes) makes them very efficient against biofilms and doesn't leave any space for antibioresistance, which is one of the major challenges of today's medicine.

Dihydrogen Contacts Observed by Through-Space Indirect NMR Coupling

Dračínský, M.*; Buchta, M.; Buděšínský, M.; Vacek-Chocholoušová, J.; Stará, I. G.; Starý, I.; Malkina, O. L.* *Chem. Sci.* **2018**, *9*, 7437-7446.



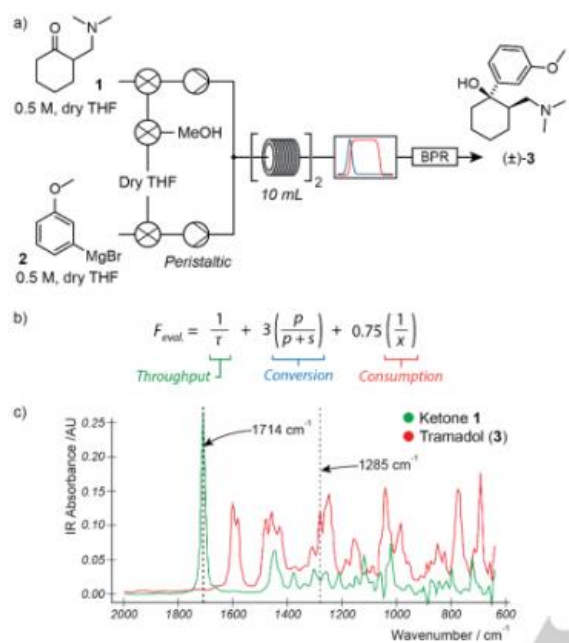
“Through-space” indirect spin–spin couplings between hydrogen atoms formally **separated by up to 18 covalent bonds** have been detected by NMR experiments in model helical molecules. It is demonstrated that this coupling can provide crucial structural information on the molecular conformation in solution. The coupling pathways have been visualised and analysed by

computational methods. The conformational dependence of the coupling is explained in terms of orbital interactions.

Comment: The authors explain that this kind of measurement allows to compare the structure of the molecule in solution to the ones obtained by crystallography and/or calculations. However, the main drawback is that it is limited to molecules with a **detectable steric hindrance**.

Across-the-world automated optimization and continuous flow synthesis of pharmaceutical agents operating through a cloud-based server

Fitzpatrick, E. D.; Maujean, T.; Evans, A.; Ley, V. S.* [Angew. Chem. Int. Ed. 2018, ASAP.](#)

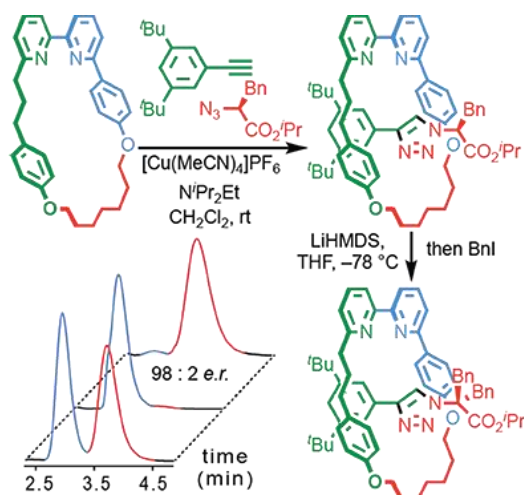


The power of the Cloud has been harnessed for pharmaceutical compound production with remote servers based in Tokyo, Japan being left to autonomously find optimal synthesis conditions for three active pharmaceutical ingredients (APIs) in laboratories in Cambridge, UK. A researcher located in Los Angeles, USA controlled the entire process via an internet connection. The constituent synthetic steps for Tramadol, Lidocaine and Bupropion were thus optimized with minimal intervention from operators within hours, yielding conditions satisfying customizable evaluation functions for all examples.

Comment: In this article the authors demonstrated that the use of an automated control system can assist drug synthesis and development. This automated synthetic method is the future of the Research and Development, especially for the pharmaceutical world, so each person going to this field should have a look at this article.

Stereoselective Synthesis of Mechanically Planar Chiral Rotaxanes

Jinks, A. M.; Juan, A.; Denis, M.; Fletcher, J. C.; Galli, M.; Jamieson, M. G. E.; Modicom, F.; Zhang, Z.; Goldup, M. S.* [Angew. Chem. Int. Ed. ASAP.](#)

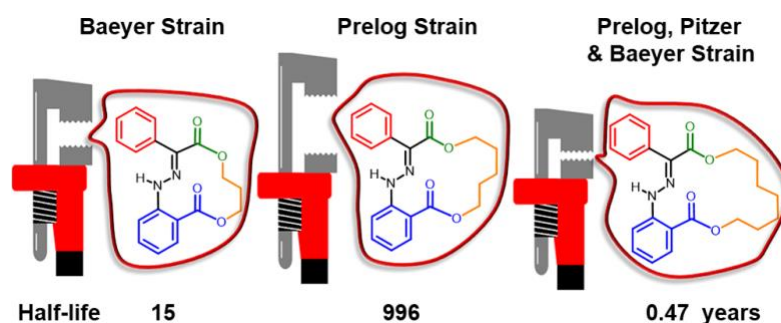


Chiral interlocked molecules in which the mechanical bond provides the sole stereogenic unit are typically produced with no control over mechanical stereochemistry. Here we report a stereoselective approach to mechanically planar chiral rotaxanes in up to 98: 2 d.r. using a readily available α amino acid-derived azide. Symmetrisation of the covalent stereocenter yields a rotaxane in which the mechanical bond provides the only stereogenic element.

Comment: Interesting paper reporting on the diastereoselective synthesis of a rotaxane by the reaction of a chiral azide linker and an achiral alkyne linker, leading to an asymmetric ring.

Building Strain with Large Macrocycles and Using It To Tune the Thermal Half-Lives of Hydrazone Photochromes

Li, Q.; Qian, H.; Shao, B.; Bussotti, L.; Di Donato, M.; Credi, A.*; Aprahamian, I.* *J. Am. Chem. Soc.* **2018**, *140*, 12323-12327.



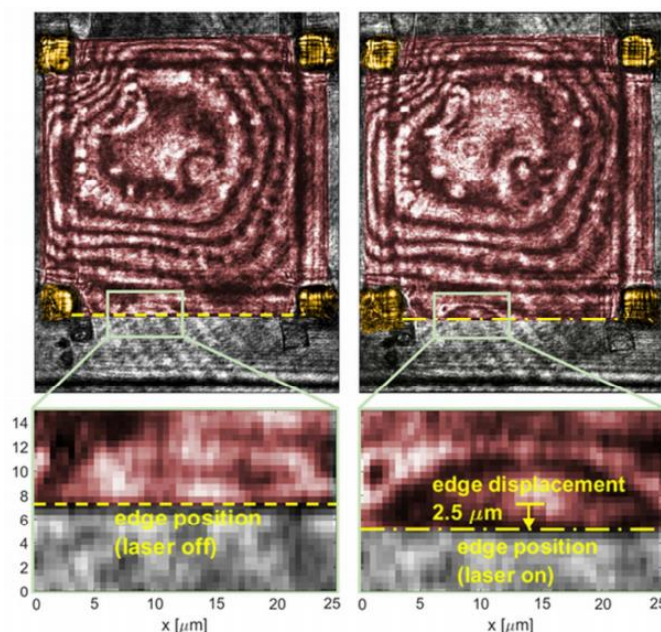
Strain has been used as a tool to modulate the reactivity (e.g., mechanochemistry) and thermal isomerization kinetics of photochromic compounds. Macrocyclization is used to build-up strain in such systems, and in general the reactivity and rates increase with the decrease in macrocycle size. To ascertain the effect of strain on recently reported bistable hydrazone photoswitches, we incorporated them into macrocycles having varying aliphatic linker lengths (C3–C7), and studied their switching behavior, and effect of macrocycle size on the thermal isomerization rate. Surprisingly, while the systems with C3–C5 linkers behave as expected (i.e., the rate is faster with smaller linkers), the isomerization rate in the systems with larger aliphatic linkers (C6–C8) is enhanced up to 4 orders of magnitude. NMR spectroscopy, X-ray crystallography and DFT calculations were used to elucidate this unexpected behavior, which on the basis of our analyses

results from the buildup of Pitzer (torsional), Prelog (transannular) and Baeyer (large angle) strain in the longer linkers.

Comment: The first postdoc paper from a previous SAMS member. They use macrocyclization to induce strain on photochromic hydrazine switches. Counterintuitively, for linkers longer than C6, the strain increases dramatically.

Photo-Responsive Suspended Micro-Membranes

Descrovi, E.; Pirani, F.; P. Rajamanickam, V.; Licheri, S.; Liberale, C.* [*J. Mater. Chem. C* **2018**, *6*, 10428–10434.](#)

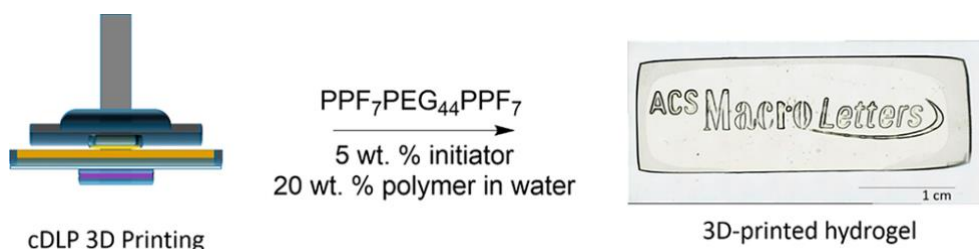


Light-responsive devices are becoming increasingly relevant in many applications ranging from soft-robotics, energy harvesting, regenerative medicine and tissue engineering. Here we present a two-photon fabrication process based on a photocurable azopolymeric compound that we successfully employed to manufacture suspended micro-membranes. Thanks to the incorporation of azobenzene units, the membranes are shown to exhibit a remarkable mechanical photo-responsivity despite the disordered, amorphous structure of the crosslinked network. When irradiated with a focused laser beam at 532 nm wavelength, a reversible shape modification is observed, with a linear expansion coefficient as large as 28%. This effect is accompanied by a refractive index decrease of about 0.16, as measured interferometrically. The initial state of the membrane is fully recovered when the irradiation is switched off, as the cyclic photoisomerization process is stopped. The presented approach can be extended to light-induce complex modifications of the mechanical features in 3D printed objects by remotely providing arbitrary illumination patterns.

Comment: This article presents another use of an azopolymer to induce mechanical responses in response to light. The interesting thing here is that, even though the material does not include some kind of organization (like in liquid crystals), the isomerization of the azobenzene is still amplified enough to induce a macroscopic motion.**END]**

Synthesis and 3D Printing of PEG–Poly(propylene fumarate) Diblock and Triblock Copolymer Hydrogels

Dilla, R. A.; Motta, C. M. M.; Snyder, S. R.; Wilson, J. A. Wesdemiotis, C.; Becker, M. L.* [ACS Macro Lett. 2018, 7, 1254–1260.](#)

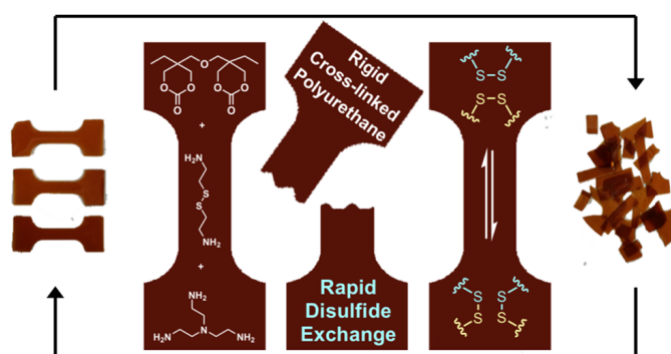


PEG-based hydrogels are used widely in exploratory tissue engineering applications but in general lack chemical and structural diversity. Additive manufacturing offers pathways to otherwise unattainable scaffold morphologies but has been applied sparingly to cross-linked hydrogels. Herein, monomethyl ether poly(ethylene glycol) (PEG) and PEG–diol were used to initiate the ring-opening copolymerization (ROCOP) of maleic anhydride and propylene oxide to yield well-defined diblock and triblock copolymers of PEG– poly(propylene maleate) (PPM) and ultimately PEG-poly(propylene fumarate) (PPF) with different molecular mass PEG macroinitiators and block length ratios. Using continuous digital light processing (cDLP), hydrogels were photochemically printed from an aqueous solution which resulted in a 10-fold increase in elongation at break compared to traditional diethyl fumarate (DEF) based printing. Furthermore, PPF–PEG–PPF triblock hydrogels were also found to be biocompatible in vitro across a number of engineered MC3T3, NIH3T3, and primary Schwann cells.

Comment: The materials described in this article show a good compatibility with different type of cells. This can promote them as biomaterial in medicine and nanomedicine.

Rapidly Reprocessable Cross-Linked Polyhydroxyurethanes Based on Disulfide Exchange

Fortman D. J.; Snyder, R. L.; Sheppard, D. T.; Dichtel, W. R.* [ACS Macro Lett. 2018, 7, 1226–1231.](#)



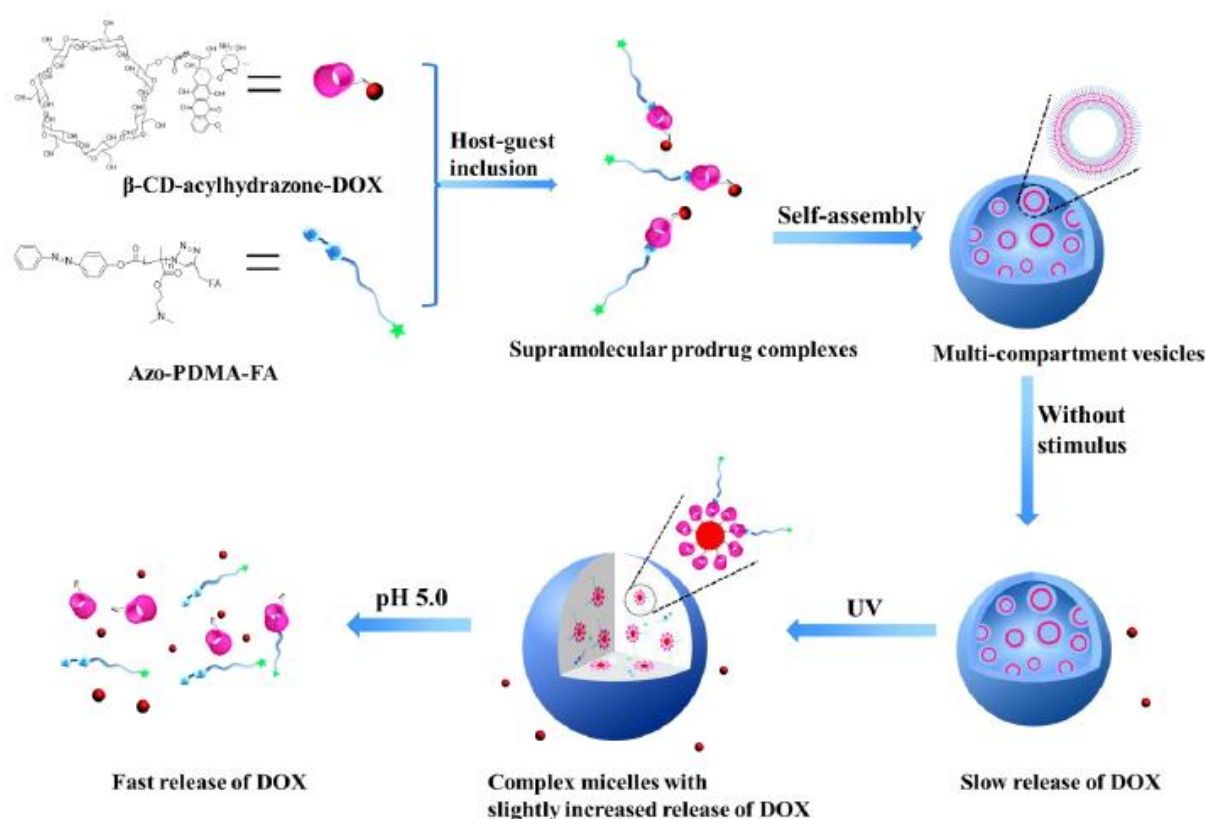
Polymer networks that are cross-linked by dynamic covalent bonds often sacrifice the robust mechanical properties of traditional thermosets in exchange for rapid and efficient reprocessability. **Polyurethanes are attractive materials for reprocessable cross-linked polymers because of their excellent mechanical properties,** widespread use, and ease of synthesis, but their syntheses

typically rely on harmful isocyanate precursors. Polyhydroxyurethanes (PHUs), derived from amines and cyclic carbonates, are promising alternative to traditional polyurethanes. PHU networks are reprocessable *via* transcarbamoylation reactions even in the absence of external catalysts, but this process occurs over hours at temperatures above 150 °C. We have dramatically shortened the reprocessing times of PHU networks by incorporating dynamic disulfide bonds. Using cystamine as a comonomer gives materials with similar thermal stability and mechanical properties to other rigid cross-linked PHUs. Despite their excellent mechanical properties, these materials show rapid stress relaxation and have characteristic relaxation times as low as 30 s at 150 °C. This property enables reprocessing with quantitative recovery of cross-link density as measured by DMTA after only 30 min of elevated-temperature compression molding. Disulfide incorporation is a promising approach to obtain reprocessable, crosslinked PHU resins that are not derived from isocyanates.

Comment: The authors demonstrate that the incorporation of disulfide-containing cystamine into PHU networks allow the reprocessing of the network with negligible changes in their chemical structure, good recovery of their cross-link density and moderate recovery of their mechanical properties.

Photo- and pH- dually-responsive β -cyclodextrin-based supramolecular prodrug complexes self-assemblies for programmed drug delivery

Bai, Y.*; Liu, C. P.; Song, X. I. N.; Zhuo, L.; Bu, H.; Tian, W.*; [Chem. Asian J. 2018, Accepted Article](#)



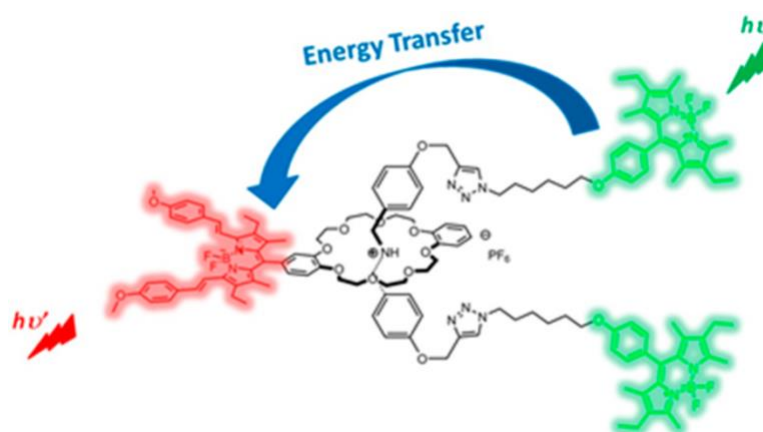
Despite the progress has been made in the application of supramolecular prodrug self-assemblies to enhance the functionality of drug delivery systems, the corresponding research on multiple responsive supramolecular prodrug self-assemblies for programmed drug delivery is still limited. In this paper, the synthesis and self-assembly behaviours of supramolecular prodrug complexes

(SPCs) with β -cyclodextrin-acylhydrazone-DOX and the targeting of azobenzene-terminated poly(2-(dimethylamino)ethyl methacrylate) (Azo-PDMA-FA) as building blocks are investigated and described. The obtained SPCs can further form self-assemblies based on their amphiphilic nature. Next, SPCs-based multi-compartment vesicles and complex micelles, which are confirmed by transmission electron microscopy (TEM) and dynamic/static light scattering (DLS/SLS), are obtained with good reversibility under alternative visible light or UV irradiation. Furthermore, three-stage programmed drug delivery behaviour was observed from dually responsive SPCs-based self-assemblies utilizing UV and pH stimuli. Specifically, SPCs first self-assembled into multi-compartment vesicles accompanied by a slow release of DOX. Next, UV light irradiation induced the dissociation of β -CD/Azo, leading to the morphology transition and slightly enhanced release of DOX. When the self-assemblies were transferred to PBS solution (pH 5.0), the release rates increased notably due to the broken acylhydrazone bond. Finally, basic cell experiments further demonstrated that the SPCs-based self-assemblies could be internalized into cancer cells, suggesting their promise for applications in cancer therapy.

Comment: This work is interesting. Programmed drug delivery based on supramolecular self-assembly is attractive.

Energy Harvesting in a Bodipy-Functionalized Rotaxane

Yesilgul, N.; Seven, O.; Guliyev, R.; Akkaya, E. U. *J. Org. Chem.* 2018, *ASAP*.

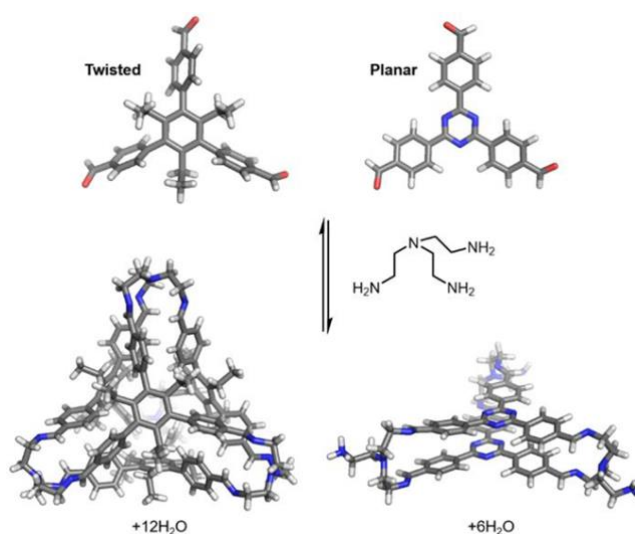


A rotaxane composed of two separate Bodipyfunctionalized units can be synthesized with a high yield. The resulting structure shows a very efficient through-space energy transfer (FRET), acting as an energy funnel. Thus, maximum solar output in the visible region can be collected and converted into red light, which can be transformed efficiently with a finetuned photovoltaic device. The versatility of the synthetic pathway demonstrates the potential utility of rotaxane-based energy harvesting supramolecules assemblies.

Comment: In this paper, authors succeed to synthesized a bodipy-containing rotaxane and envisage to have applications in the areas of energy harvesting supramolecular assemblies. The **awesome** Bodipy may have huge potential applications, e.g., James Tour has published a paper to use Bodipy as a pendant fluorophore on the stator portion of a motor for tracking their movements (*Nature*. 2017, 567-572.)

Precursor Control over the Self-Assembly of Organic Cages via Imine Condensation

Jiao, T.; Wu, G.; Chen, L.; Wang, C. Li. H. *J. Org. Chem.* 2018, *ASAP*.

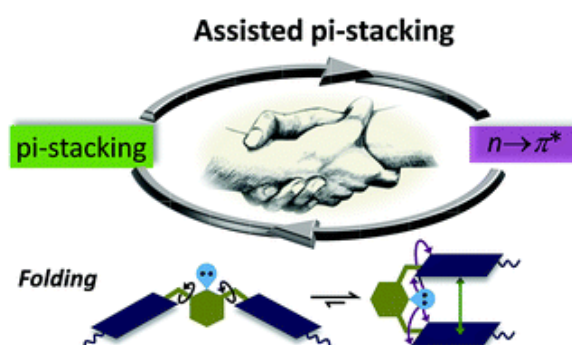


A series of tetrahedral cages and triangular prisms have been selfassembled by condensing ostensibly analogous triformyl precursors with tris or bis-amino linkers under the nominally reversible reaction conditions in the manner of either [4 + 4] or [2 + 3], respectively. We observed that the conformations of the triformyl precursors have great impact on the self-assembly pathway and product yields. More specifically, a rigid and planar precursor favors the formation of prisms while a more twisted one favors tetrahedron. As a comparison, a more flexible precursor, which is able to adopt both relatively planar and twisted conformations, is capable of producing both prisms and tetrahedrons in relatively high yields. Both experimental and theoretical results indicate that the selfassembly preference is ascribed to subtle variations in the level of π - π and CH- π interactions that act as the driving forces for the formation of prisms and tetrahedrons, respectively.

Comment: This paper shows how the shape of the precursor affects the formation of the cages either with a twisted triformyl precursor and a planar triformyl precursor respectively.

Assisted π -Stacking: a Strong Synergy Between Weak Interactions

Sao, S.; Naskar, S.; Mukhopadhyay, N.; Das, M.*; Chaudhuri, D.* *Chem. Commun.*, 2018, [Advance Article](#).



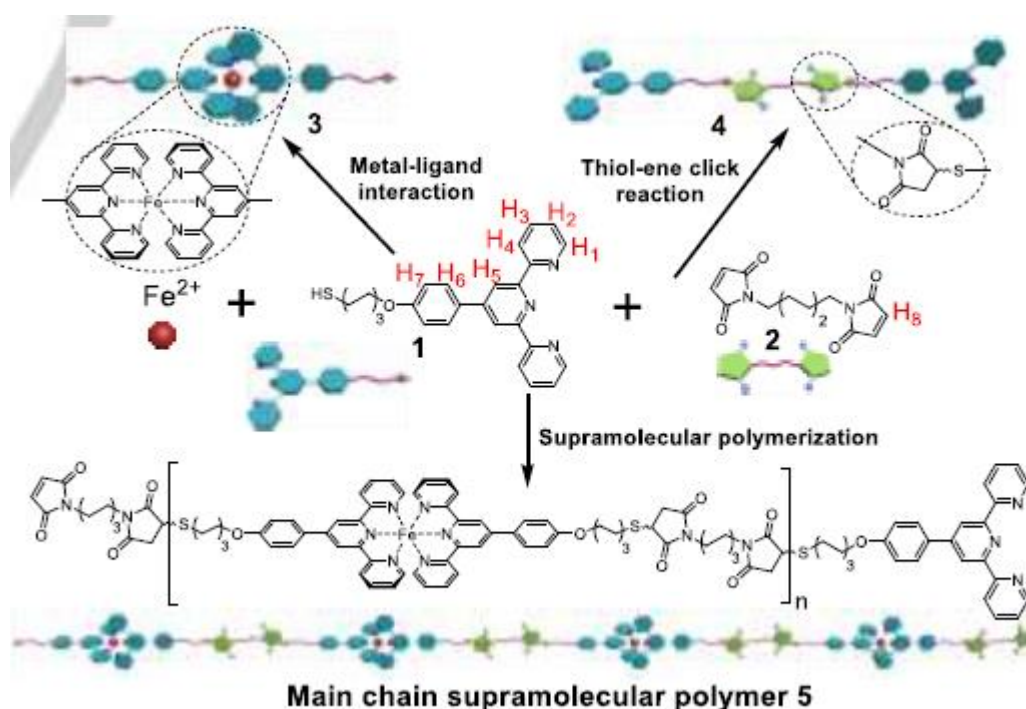
Synergy between a pair of **weak non-covalent interactions** can **predispose** a molecular **self-assembly** towards a specific pathway. We report **assisted p-stacking**, a synergy between

aromatic p-stacking and n - p* interactions that exhibits an unprecedented strength and thermal stability. Natural bond orbital analysis reveals the **non-additive nature** of the interaction.

Comment: I have to admit that I may have not fully understood this article, which is quite focused on a theoretical approach. However, what I can tell is that, one should not underestimate the strength of non-covalent interactions and that with a bit of fine tuning, one could control the self-assembly pathway.

Controlled formation of main chain supramolecular polymer based on metal–ligand interaction and thiol-ene click reaction

Chen, F.; Tian, Y.-K.*; Chen, Y.*, [Chem. Asian J. 2018, Accepted Article](#)



Supramolecular polymers with multi-functionalities and hierarchical structures have received considerable attention and become a hot research topic over the past years. Herein, a novel main-chain supramolecular polymer has been successfully fabricated by using metal–ligand interaction and thiol-ene click reaction. ^1H NMR, UV/Vis, DOSY, and viscosity measurements were carried out to investigate the molecular recognition and the process of supramolecular polymerization. From the study, the orthogonality between thiol-ene click reactions and terpyridine-metal ions complexation behavior was testified, and supramolecular polymeric assemblies could be constructed by one pot method. Meantime, due to the incorporation of metal-ligand interactions, the supramolecular polymer shows stimuli-responsive properties toward the chemical stimuli. Hence, this work will provide a novel methodology for developing supramolecular polymers as smart materials.

Comment: Supramolecular polymers are quite attractive. This work uses a simple way to construct a supramolecular polymer and it's interesting.

Light-Induced Cargo Release From a Cucurbit[8]uril Host by Means of a Sequential Logic Operation

Romero, M. A.; Fernandes, R. J.; Moro, A. J.; Basilico, N.*; Pischel U.* [Chem. Commun., 2018, Advance Article.](#)



The logically controlled and **light-induced** release of a **tripeptide model cargo** from a **cucurbit[8]uril host macrocycle** by means of a **photoswitch** was shown **in water**. This provides a new approach to **photoresponsive** and **selective release** in a meaningful **pH window**.

Comment: This short article presents the chalcone/flavylium switch. It is triggered by light and is also pH controlled (flavylium requires low pH in order to be formed). This type of control is interesting and should be kept in mind, especially concerning the motors subjects). Another part of this work concerns the use of such switches as logical operators. I think that even if this approach may work, it seems to be a really tedious method and remains far from real applications.