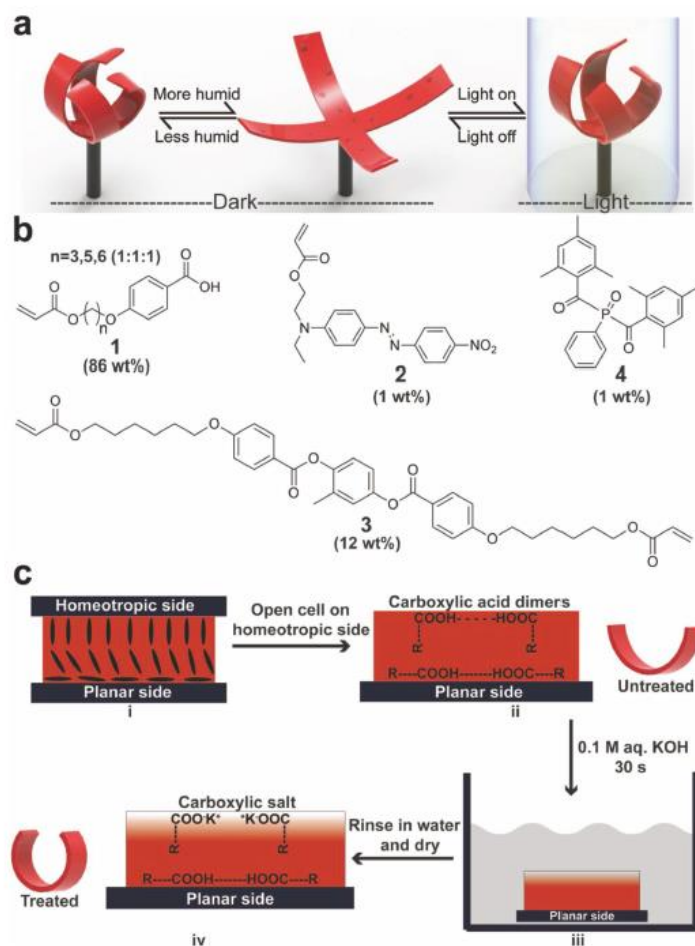


## An Artificial Nocturnal Flower via Humidity-Gated Photoactuation in Liquid Crystal Networks

Wani, O.-M.; Verpaalen, R.; Zeng, H.; Priimagi, A.\* ; Schenning, A. P. H. J.\* [Adv. Mater. 2018, 1804602.](#)



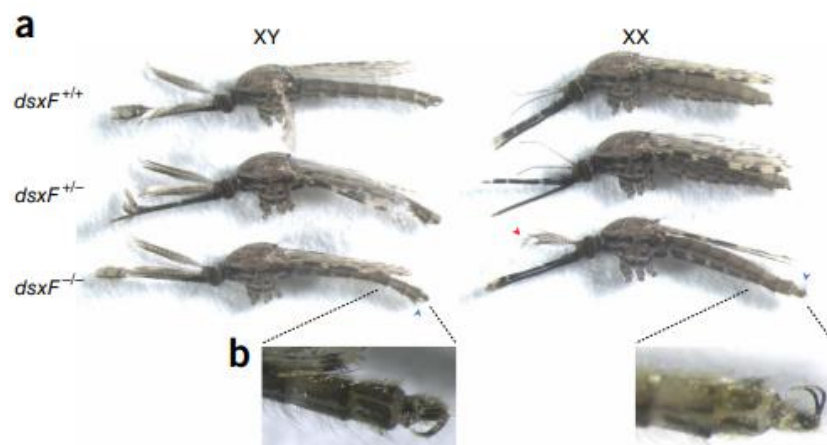
Beyond their colorful appearances and versatile geometries, flowers can self-shape-morph by adapting to environmental changes. Such responses are often regulated by a delicate interplay between different stimuli such as temperature, light, and humidity, giving rise to the beauty and complexity of the plant kingdom. Nature inspires scientists to realize artificial systems that mimic their natural counterparts in function, flexibility, and adaptation. Yet, many of the artificial systems demonstrated to date fail to mimic the adaptive functions, due to the lack of multi-responsivity and sophisticated control over deformation directionality. Herein, a new class of liquid-crystalnetwork (LCN) photoactuators whose response is controlled by delicate interplay between light and humidity is presented. Using a novel deformation mechanism in LCNs, humidity-gated photoactuation, an artificial nocturnal flower is devised that is closed under daylight conditions when the humidity level is low and/or the light level is high, while it opens in the dark when the humidity level is high. The humidity-gated photoactuators can be fueled with lower light intensities than conventional photothermal LCN actuators. This, combined with facile control over the speed, geometry, and directionality of movements, renders the “nocturnal actuator” promising for smart and adaptive bioinspired microrobotics.

**Comment:** A shape-morph material based on azobenzene again, which is different with the last paper. The authors introduced classical azobenzenes and treated the materials with a base, leading

the fast shape-morph and humidity responsive. Here, they used normal azo rather than (ortho-fluoro) oF-azo due to the fast thermal-relaxation of the normal azobenzene. So, the rational is important for any paper.

### A CRISPR–Cas9 Gene Drive Targeting *Doublesex* Causes Complete Population Suppression in Caged *Anopheles Gambiae* Mosquitoes

Kyrou, K.; Hammond, A. M.; Galizi, R.; Kranjc, N.; Burt, A.; Beaghton, A. K.; Nolan, T.; Crisanti, A.\* [Nat. Biotechnol. 2018, 36, 1062–1066.](#)

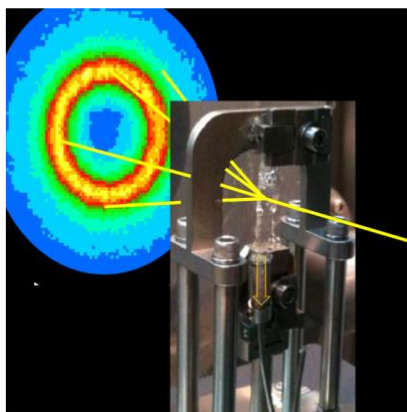


In the human malaria vector *Anopheles gambiae*, the gene *doublesex* (*Agdsx*) encodes two alternatively spliced transcripts, *dsx-female* (*AgdsxF*) and *dsx-male* (*AgdsxM*), that control differentiation of the two sexes. The female transcript, unlike the male, contains an exon (exon 5) whose sequence is highly conserved in all *Anopheles* mosquitoes so far analyzed. We found that CRISPR–Cas9-targeted disruption of the intron 4–exon 5 boundary aimed at blocking the formation of functional *AgdsxF* did not affect male development or fertility, whereas females homozygous for the disrupted allele showed an intersex phenotype and complete sterility. A CRISPR–Cas9 gene drive construct targeting this same sequence spread rapidly in caged mosquitoes, reaching 100% prevalence within 7–11 generations while progressively **reducing egg production to the point of total population collapse**. Owing to functional constraint of the target sequence, no selection of alleles resistant to the gene drive occurred in these laboratory experiments. Cas9-resistant variants arose in each generation at the target site but did not block the spread of the drive.

**Comment:** With the rumors of disappearance of He Jiankui, [the Chinese scientist who led to the birth of the world's first genome-edited babies](#), and who is kindly nicknamed the “Chinese Frankenstein” by the press, I thought it would be interesting to have an article about CRISPR (and a picture of cute dead mosquitoes). Roughly, the authors edited the gene responsible for the differentiation of sexes in a mosquito species, **leading ultimately to the death of all the population**. The mosquitoes were caged, meaning that there was no way to balance this gene “defect”; however, I think it stresses the fact that CRISPR may be powerful (and, with great power, comes great responsibilities).

### Stretching PEO–PPO Type of Star Block Copolymer Gels: Rheology and Small-Angle Scattering

Annaka, M.; Mortensen, K.\* [ACS Macro Lett. 2018, 7, 1438–1442.](#)

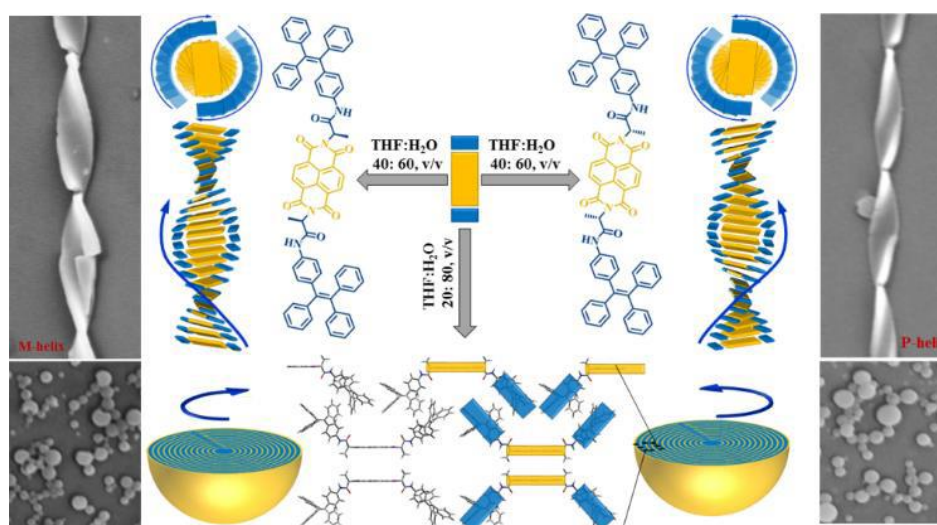


Cross-linked Tetronic star block copolymer gels, based on poly(ethylene oxide) and poly(propylene oxide), behave quite regular with respect to mechanical properties, but exhibits unusual absence of structural response to strain. The elastic response is linear up to more than 100% strain, with a steady-state modulus of the order of 0.01 MPa after an initial stress relaxation. Neutron and X-ray scattering experiments show a consistent but unexpected response to uniaxial strain, with no changes in characteristic molecular dimensions. Upon strain beyond about 100%, that is, when the stress–strain curve is no longer linear, structural texture appears and becomes even more pronounced upon further strain, thus, indicating alignment of the self-assembled hexagonally ordered cylindrical micelles with the cylinder-axis perpendicular to the strain. It is proposed that the main structural response to large-amplitude strain is related to a layer-dominated structure of cross-linked star molecules.

**Comment:** This paper gives a nice overview on the correlation between mechanical and structural properties of star block copolymer gels by measuring the structural response to uniaxial elongation.

### Supramolecular chiral helical ribbons of naphthalenediimide appended tetraphenylethylene controlled by solvent and induces via L- and D-alanine spacers

Bhosale, S. V.; Goskulwad, S. P.; Al Kobaisi, M.; La, D. D.; Bhosale, R. S.; Ratanlal, M.\*; Bhosale, S. V.\*; [Chem. Asian J. 2018, Accepted Article](#)

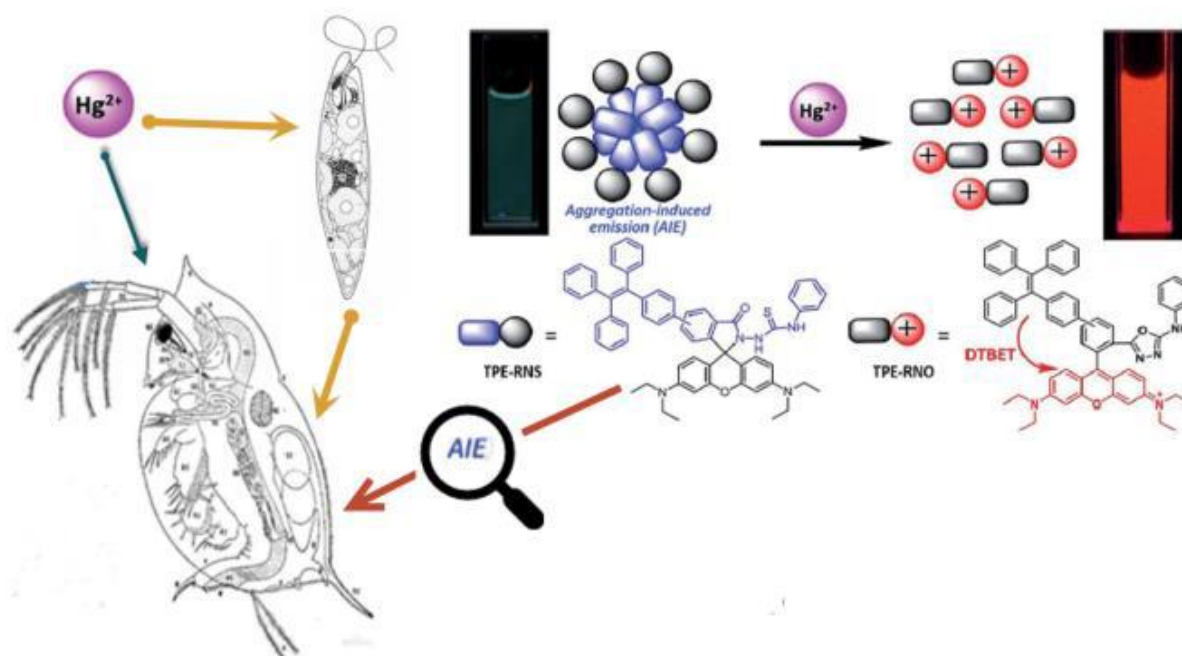


Naphthalenediimide-tetraphenylethylene with alanine spacer (coded as: NDI-(Ala-TPE)<sub>2</sub>) were synthesized to study the influence of the chirality of amino acid spacer on its self-assemblies. Here we particularly show that NDI-Ala-TPE bearing L-alanine gives left-handed (M-type) helical superstructure, while D-alanine produces right-handed (P-type) helical ribbons in THF:H<sub>2</sub>O at 40:60% v/v ratios. However, particular aggregates were observed at higher 20:80% v/v ratios. Circular dichroism is used to characterise induction of chirality and the handedness of the helical superstructures, and the microstructure of the self-assembled materials was visualised using scanning electron microscopy and DLS confirm formation of particular aggregates in solution.

**Comment:** It's a simple work just talking about the chiral self-assembly of the molecules and it's quite easy to understand and read.

### In vivo visualization of the process of Hg<sup>2+</sup> bioaccumulation in water flea *Daphnia carinata* by a novel aggregation-induced emission fluorogen

He, T.; Ou, W.; Tang, B. Z.\*; Qin, J.\*; Tang, Y.\*; [Chem. Asian J. 2018, Accepted Article](#)



This paper employs a specially designed aggregation-induced emission fluorogen (AIEgen) to in vivo visualize the process of Hg<sup>2+</sup> bioaccumulation in a common species of freshwater zooplankton *Daphnia carinata* (*D. carinata*) by two methods, direct Hg<sup>2+</sup> absorption and ingestion of Hg<sup>2+</sup> contaminated food. We analysed the relevance between photoluminescence (PL, I<sub>595</sub>/I<sub>480</sub>) ratios and Hg<sup>2+</sup> (C<sub>Hg2+</sub>) and developed the master curve for Hg<sup>2+</sup> determination based on measuring the PL intensity of the solution. Meanwhile, fluorescent image analysis showed that the major recipient organs of Hg<sup>2+</sup> in *D. carinata* were the compound eyes and carapace, followed by the intestine and shell gland, but not the brain or heart. The response of *D. carinata* to Hg<sup>2+</sup> via uptake from surrounding water differed distinctly from that through food intake of the algae (*Euglena gracilis*) contaminated by mercury. When Hg<sup>2+</sup> was encapsulated by algae membrane, no fluorescence was detected, and the carapace morphology remained intact after ingesting algae for 80 min, in contrast to the rapid carapace deformation by direct Hg<sup>2+</sup> absorption. The *D. carinata* showed higher mortality by direct Hg<sup>2+</sup> immersion than via food ingestion. The reason for the high mortality after

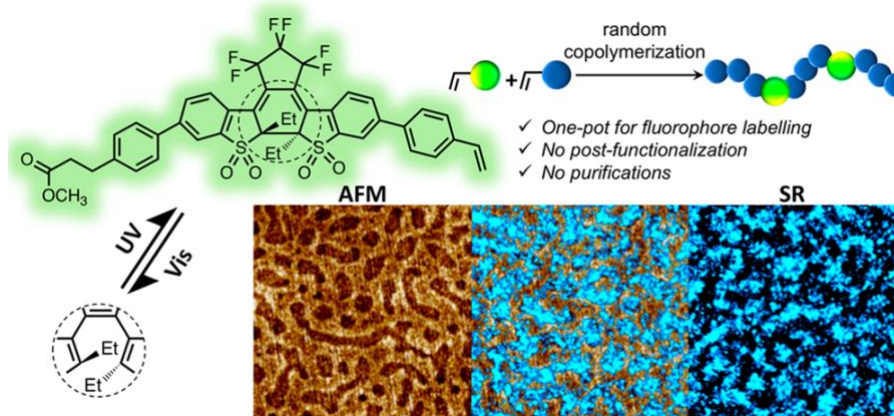


Hg<sup>2+</sup> immersion was possibly due to carapace deformity after chemical reaction between chitin and mercury, but the biochemical pathway leading to mortality needs further study.

**Comment:** It's interesting to use AIE in vivo visualize the process of Hg<sup>2+</sup> bioaccumulation.

### A Polymerizable Photoswitchable Fluorophore for Super-Resolution Imaging of Polymer Self-Assembly and Dynamics

Qiang, Z.; Shebek, K. M.; Irie, M.; Wang, M.\* [ACS Macro Lett. 2018, 7, 1432–1437.](#)

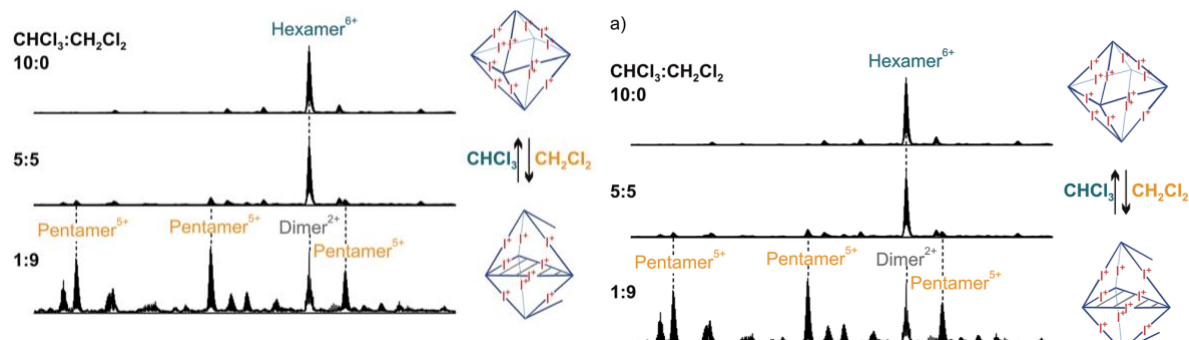


Single-molecule super-resolution microscopy has become a standard imaging tool in the life sciences for visualizing nanostructures in situ, but the application of this technique in polymer science is much less explored. A key bottleneck is the lack of fluorophores and simple covalent attachment strategies onto polymer chains. Here, we report a functional diarylethene-based photoswitchable fluorophore that can be directly incorporated into polymer backbones through copolymerization, which significantly streamlines the labeling strategy, with no further post-coupling reactions or purifications needed. The attachment of fluorophores onto selectively labeled polymers enables super-resolution imaging of a series of model polymer blend systems with different nanostructures and chemical compositions. As each individual fluorophore is able to switch several times on average between its bright and dark state, multiple time-lapse images can be acquired to observe the dynamic nanostructural evolution of polymer blends upon solvent vapor annealing. With this demonstration of a universal, simplified labeling strategy and the ability to image polymer assembly under native conditions, this reported fluorophore may promote the widespread use of super-resolution microscopy in the polymer community.

**Comment:** the authors describe a nice way to directly incorporate into polymer chains a fluorophore through a copolymerization strategy with no post-functionalization or purification needed. It provides a simple way to label and image polymeric systems.

### Surprising Solvent-Induced Structural Rearrangements in Large [N...I<sup>+</sup>...N] Halogen-Bonded Supramolecular Capsules: An Ion Mobility-Mass Spectrometry Study

Warzok, U.; Marianski, M.; Hoffmann, W.; Turunen, L.; Rissanen, K.; Pagel, K.; Schalley, C. A.\* [Chem. Sci. 2018, 9, 8343.](#)

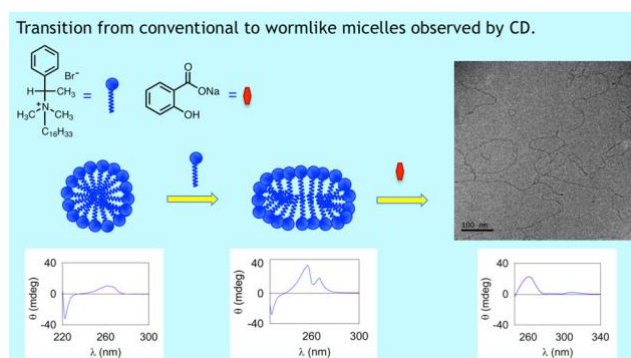


Coordinative halogen bonds have recently gained interest for the assembly of supramolecular capsules. **Ion mobility-mass spectrometry and theoretical calculations now reveal the well-defined gas-phase structures** of dimeric and hexameric  $[N \cdots I^+ \cdots N]$  halogen-bonded capsules with counterions located inside their cavities as guests. The solution reactivity of the large hexameric capsule shows the intriguing solvent-dependent equilibrium between the hexamer and an unprecedented pentameric  $[N \cdots I^+ \cdots N]$  halogen-bonded capsule, when the solvent is changed from chloroform to dichloromethane. The intrinsic flexibility of the cavitands enables this novel structure to adopt a pseudo-trigonal bipyramidal geometry with nine  $[N \cdots I^+ \cdots N]$  bonds along the edges and two pyridine binding sites uncomplexed.

**Comment:** Despite knowing this in the back of my head, it is good to be reminded that **mass spectrometry can give you way more information than just a number**. Here, as is the speciality of the Schalley group, they use it to reveal supramolecular structures. I'm mainly proposing this paper so that you can keep it in mind when planning experiments.

### Effect of the Hydrophobic Tail of a Chiral Surfactant on the Chirality of Aggregates and on the Formation of Wormlike

Creatto, E. J.; Ceccacci, F.; Mancini, G.; Sabadini, E.\* [Langmuir 2018, 34, 13288.](#)



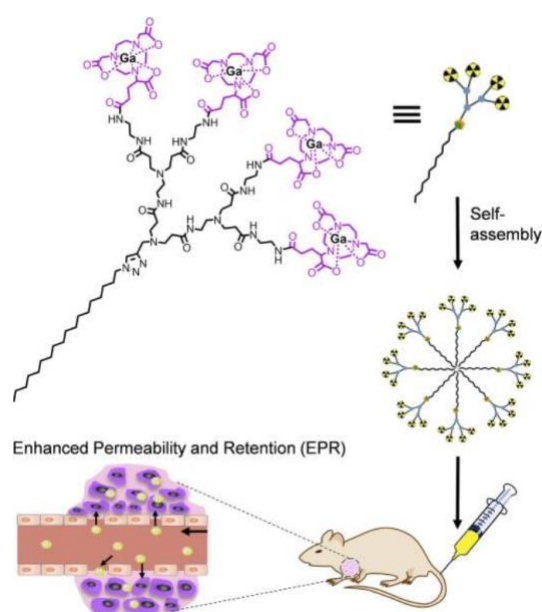
**The micellization of chiral enantiopure surfactants**, dodecyl-*N,N*-dimethyl-*N*-(*S*)-(1-phenyl)ethylammonium bromide and hexadecyl-*N,N*-dimethyl-*N*-(*S*)-(1-phenyl)ethylammonium bromide, was investigated by circular dichroism spectroscopy and isothermal titration calorimetry. The formation of wormlike micelles (WLMs) upon the addition of sodium salicylate to the aqueous solutions of the surfactant was observed only in the case of hexadecyl-*N,N*-dimethyl-*N*-(*S*)-(1-phenyl)ethylammonium bromide. The presence of WLMs was assessed by cryogenic transmission electron microscopy, rheology, and isothermal titration calorimetry experiments, and their supramolecular chirality was investigated by circular dichroism spectroscopy. **Depending on the length of the hydrophobic tail, molecular chirality is transferred into a different chiral**

**supramolecular trait.** Our findings demonstrate that hydrophobic interactions by controlling the organization and functions of self-assemblies also control the transcription of the chiral information from molecules to complex supramolecular systems.

**Comment:** Gentle reminder that micelles are, in fact, cooperative supramolecular polymers. While I'm not a fan of the paper itself – they chose a light blue background for the TOC – like concept.

### Self-assembling Supramolecular Dendrimer Nanosystem for PET Imaging of Tumors

Garrigue, P.; Tang, J.; Ding, L.; Bouhle, A.; Tintarud, A.; Laurinie, E.; Huang, Y.; Lyu, Z.; Zhang, M.; Fernandez, S.; Balasse, L.; Lan, W.; Masi, E.; Marsone, D.; Weng, Y.; Liu, X.; Giorgio, S.; Iovannai, J.; Pricle, S.; Guillet, B.; Peng, L.\* *Proc. Nat. Acad. Sci. USA.* **2018**, *115*, 11454 - 11459.

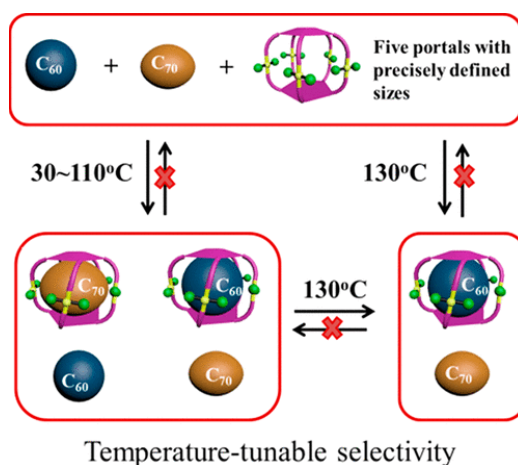


Bioimaging plays an important role in cancer diagnosis and treatment. However, imaging sensitivity and specificity still constitute key challenges. Nanotechnology-based imaging is particularly promising for overcoming these limitations because nanosized imaging agents can specifically home in on tumors via the “enhanced permeation and retention” (EPR) effect, thus resulting in enhanced imaging sensitivity and specificity. Here, we report an original nanosystem for positron emission tomography (PET) imaging based on an amphiphilic dendrimer, which bears multiple PET reporting units at the terminals. This dendrimer is able to self-assemble into small and uniform nanomicelles, which accumulate in tumors for effective PET imaging. Benefiting from the combined dendrimeric multivalence and EPR-mediated passive tumor targeting, this nanosystem demonstrates superior imaging sensitivity and specificity, with up to 14-fold increased PET signal ratios compared with the clinical gold reference 2-fluorodeoxyglucose ([<sup>18</sup>F]FDG). Most importantly, this dendrimer system can detect imaging-refractory low-glucose-uptake tumors that are otherwise undetectable using [<sup>18</sup>F]FDG. In addition, it is endowed with an excellent safety profile and favorable pharmacokinetics for PET imaging. Consequently, this dendrimer nanosystem constitutes an effective and promising approach for cancer imaging. Our study also demonstrates that nanotechnology based on self-assembling dendrimers provides a fresh perspective for biomedical imaging and cancer diagnosis.

**Comment:** In this paper, the workers have established an effective and excellent self-assembling supramolecular dendrimer nanosystem. Remarkably, the obtained PET images showed significantly higher quality in terms of sensitivity and specificity. It is a particularly interesting perspective on the design and construction of tailor-made self-assembling dendrimer nanosystems for various biomedical applications.

### Self-Assembled Carcerand-like Cage with a Thermoregulated Selective Binding Preference for Purification of High-Purity C60 and C70

Sun, W.; Wang, Y.; Ma, L.; Zheng, L.; Fang, W.; Chen, X.; Jiang, H.\* [J. Org. Chem. 2018 ASAP.](#)



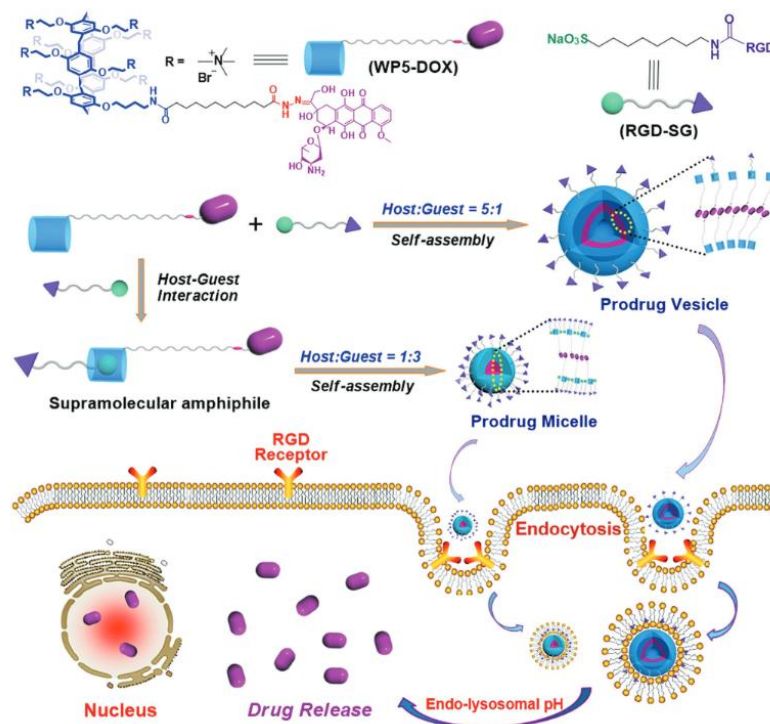
Fullerene molecules have attracted considerable interest because of the unique curved aromatic  $\pi$ -conjugated systems. However, the complicated and costly technologies for purification of highly pure fullerenes hamper easy access to these attractive molecules and consequently limit most of the fullerene applications. Here, we report the discovery of a carcerand-like cage acting as a stand-alone host for efficient separation and purification of C60 and C70 from fullerene soot. The cage, built through the self-assembly of metal coordination, is capable of quantitatively encapsulating fullerenes C60 and C70. The fullerene complexes are highly stable at high temperatures because of the small crevices with precisely defined sizes, multiple favorable CH- $\pi$  interactions, and concave-convex aromatic interaction between fullerenes and corannulenes. Importantly, the carcerand-like cage shows a temperature-dependent selective binding preference for C60 over C70, which allows us to develop an efficient and green procedure for isolating C60 and C70 with high purity and low mass loss from fullerene soot without the help of recrystallization or high-performance liquid chromatography.

**Comment:** By using the crevice size, multiple favorable CH- $\pi$  interactions, and concave-convex aromatic interaction between fullerenes and cages, the authors develop a new class of corannulene-based molecular cages that have unprecedentedly thermodynamic stability. The cage has unique properties that can easily and efficiently be used for separation and purification of C60 and C70 in high purity from fullerene soot, without the help of recrystallization or HPLC.

### From Supramolecular Vesicles to Micelles: Controllable Construction of Tumor-Targeting Nanocarriers Based on Host-Guest Interaction between a Pillar[5]arene-Based Prodrug and a RGD-Sulfonate Guest



Hu, X.-Y.\*; Gao, L.; Mosel, S.; Ehlers, M.; Zellermann, E.; Jiang, H.; Knauer, S. K.; Wang, L.; Schmuck, C.\* [Small 2018, e1803952](#).

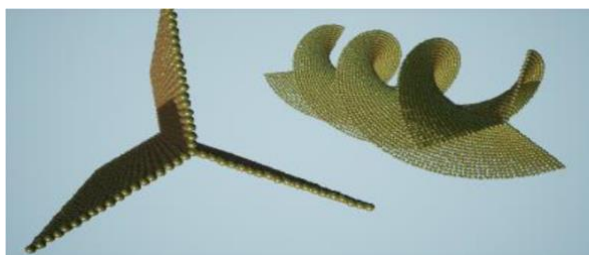


The targeting ability, drug-loading capacity, and size of the drug nanocarriers are crucial for enhancing the therapeutic index for cancer therapy. Herein, the morphology and size-controllable fabrication of supramolecular tumor-targeting nanocarriers based on host-guest recognition between a novel pillar[5]arene-based prodrug WP5-DOX and a Arg-Gly-Asp (RGD)-modified sulfonate guest RGD-SG is reported. The amphiphilic WP5-DOX⊃RGD-SG complex with a molar ratio of 5:1 self-assembles into vesicles, whereas smaller-sized micelles can be obtained by changing the molar ratio to 1:3. This represents a novel strategy of controllable construction of supramolecular nanovehicles with different sizes and morphologies based on the same host-guest interactions by using different host-guest ratios. Furthermore, *in vitro* and *in vivo* studies reveal that both these prodrug nanocarriers could selectively deliver doxorubicin to RGD receptor-overexpressing cancer cells, leading to longer blood retention time, enhanced antitumor efficacy, and reduced systematic toxicity in murine tumor model, suggesting their potential application for targeted drug delivery.

**Comment:** Drug delivery is a very fashionable topic. The main novelties here are the design of the vehicle which is a supramolecular assembly and the active release of the drug, improving the targeting ability and lowering the side effects.

### Controlled Synthesis and Supramolecular Organization of Conjugated Star-Shaped Polymers

Van Den Eede, M.-P.; De Winter, J.; Gerbaux, P.; Teyssandier, J.; De Feyter, S.; Van Goethem, C.; Vankelecom, I. F. J.; Koeckelberghs, G. [Macromolecules 2018, 51, 8689](#).

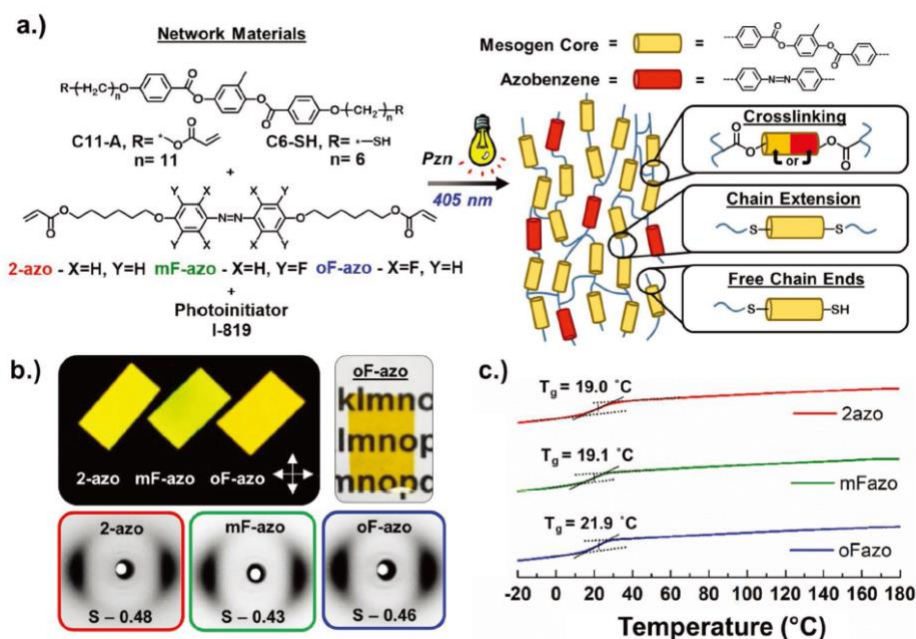


Through the incorporation of chiral and achiral poly(3-alkylthiophenes) (P3ATs) into a star-shaped system, a well-defined supramolecular organization is obtained lacking the unfavorable linear lamellar structure typically obtained for P3AT. Through the combination of a controlled chain-growth polymerization and efficient postpolymerization and click reactions, well-defined star-shaped P3ATs with a low dispersity of 1.1 were obtained. The combination of UV-vis, circular dichroism (CD), atomic force microscopy (AFM), and transmission electron microscopy (TEM) measurements showed the formation of a strong (chiral) supramolecular organization into fibers, different and stronger than those obtained with the linear P3ATs. The fact that the width of the fibers is in good agreement with the width of a single star-shaped P3AT excludes the formation of a linear lamellar structure. Furthermore, the particular supramolecular organization of the star-shaped polymers, which appears thanks to the precision polymer synthesis, triggers properties of the arms of the star-shaped molecule that are not present in the individual arms.

**Comment:** The authors show here that chirality at the supramolecular scale can be driven by only few chiral centers. Thus, they control the shape of their assemblies and improve their properties.

### All-Optical Control of Shape

Donovan, B. R.; Matavulj, V. M.; Ahn, S.-K.; Guin, T.; White, T. J.\* *Adv. Mater.* **2018**, [1804435](https://doi.org/10.1002/adma.201804435).



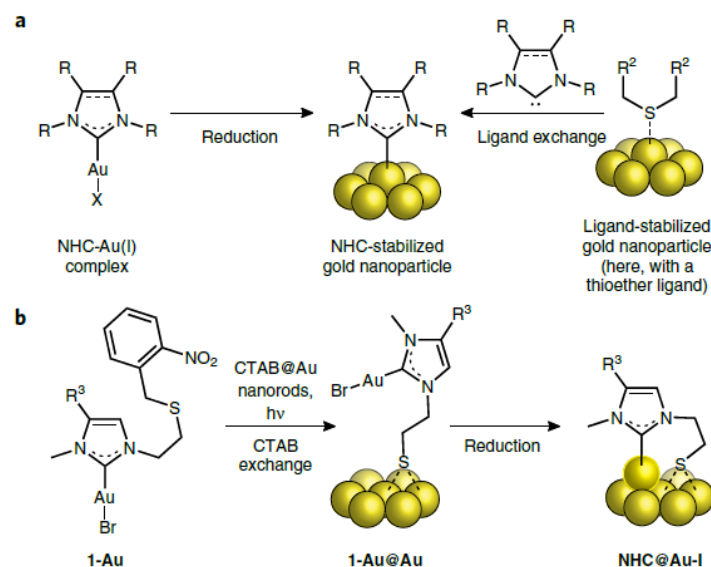
Photoresponsive liquid crystal elastomers (LCEs) are a unique class of anisotropic materials capable of undergoing large-scale, macroscopic deformations when exposed to light. Here, surface-

aligned, azobenzene-functionalized LCEs are prepared via a radical-mediated, thiol-acrylate chain transfer reaction. A long-lived, macroscopic shape deformation is realized in an LCE composed with an *o*-fluorinated azobenzene (oF-azo) monomer. **Under UV irradiation, the oF-azo LCE exhibits a persistent shape deformation for >72 h.** By contrasting the photomechanical response of the oF-azo LCE to analogs prepared from classical and *m*-fluorinated azobenzene derivatives, the origin of the persistent deformation is clearly attributed to the underlying influence of positional functionalization on the kinetics of *cis*-*trans* isomerization. Informed by these studies and enabled by the salient features of light-induced deformations, oF-azo LCEs are demonstrated to undergo all-optical control of shape deformation and shape restoration.

**Comment:** Introducing azobenzene into liquid crystalline materials is not rare any more, but if you find this kind of papers in high-level journals it must contain something amazing. In this paper, the introduction of *ortho*-fluorinated (oF) azobenzene made the LCEs bear long-lived photomechanical deformations due to the high stability of *cis*-isomer.

### Robust Gold Nanorods Stabilized by Bidentate N-Heterocyclic-Carbene–Thiolate Ligands

MacLeod, M.J.; Goodman, A.J.; Ye, H.Z.; Nguyen, H. V.; Van Voorhis, T; Johnson J.A.\*  
[Nat. Chem. 2018, ASAP.](#)



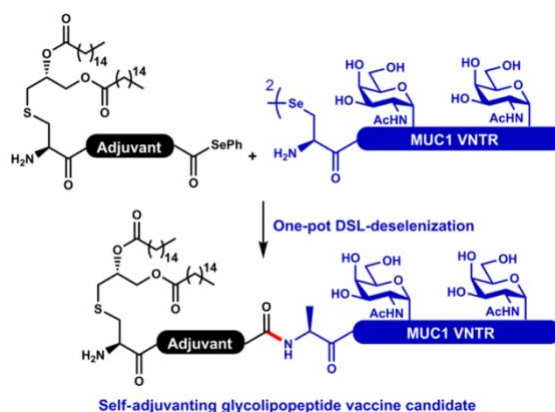
Although **N-heterocyclic carbenes (NHCs)** have demonstrated outstanding potential for use as surface anchors, synthetic challenges have limited their application to either large planar substrates or very small spherical nanoparticles. The development of **a strategy to graft NHCs onto non-spherical nanomaterials**, such as gold nanorods, would greatly expand their utility as surface ligands. Here, we use a bidentate thiolate–NHC–gold(i) complex that is easily grafted onto commercial cetyl trimethylammonium bromide-stabilized gold nanorods through ligand exchange. On mild reduction of the resulting surface-tethered NHC–gold(i) complexes, the gold atom attached to the NHC complex is added to the surface as an adatom, thereby precluding the need for reorganization of the underlying surface lattice upon NHC binding. The resulting thiolate–NHC-stabilized gold nanorods are stable towards excess glutathione for up to six days, and under conditions with large

variations in pH, high and low temperatures, high salt concentrations, or in biological media and cell culture. We also demonstrate the utility of these nanorods for in vitro photothermal therapy.

**Comment:** They show a new ligand strategy for the generation of NHC@Au surface linkages that overcomes the size, shape and solvent limitations of previous methods.

### Synthesis of a Self-Adjuvanting MUC1 Vaccine via Diselenide-Selenoester Ligation-Deselenization

McDonald, D. M.; Hanna, C. C.; Ashhurst, A. S.; Corcilius, L.; Byrne, S. N.; Payne, R. J. \* *ACS Chem. Biol.* **2018**.



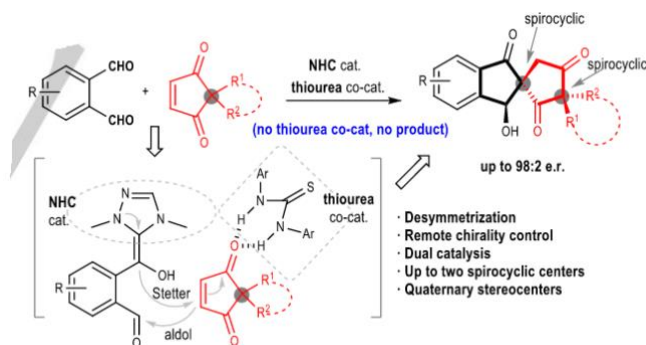
Access to lipopeptide-based vaccines for immunological studies remains a significant challenge owing to the amphipathic nature of the molecules, which makes them difficult to synthesize and purify to homogeneity. Here, we describe the application of a new peptide ligation technology, the diselenide-selenoester ligation (DSL), to access self-adjuvanting glycolipopeptide vaccines. We show that rapid ligation of glyco- and lipopeptides is possible via DSL in mixed organic solvent-aqueous buffer and, when coupled with deselenization chemistry, affords rapid and efficient access to a vaccine candidate possessing a MUC1 glycopeptide epitope and the lipopeptide adjuvant Pam2Cys. This construct was shown to elicit MUC1-specific antibody and cytotoxic T lymphocyte responses in the absence of any other injected lipids or adjuvants. The inclusion of the helper T cell epitope PADRE both boosted the antibody response and resulted in elevated cytokine production.

**Comment:** This is a new peptide ligation technology: the diselenide-selenoester ligation (DSL).

### Access to All-Carbon Spirocycles through a Carbene and Thiourea Cocatalytic Desymmetrization Cascade Reaction

Zhuo, S.; Zhu, T.; Zhou, L.; Mou, C.; Chai, H.; Lu, Y.; Pan, L.; Jin, Z.; Chi, Y. R. *Angew. Chem. Int. Ed.* **2018**, ASAP.



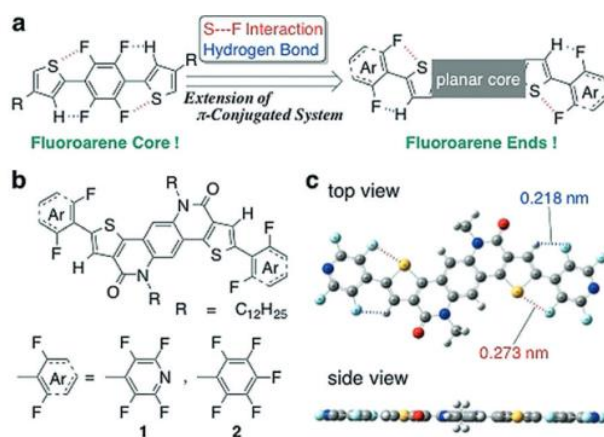


A new catalytic approach for asymmetric quick access to spirocycles is disclosed. The reaction involves a carbene and thiourea co-catalyzed desymmetrization process with simultaneous installation of a spirocyclic core. The use of a thiourea co-catalyst is critical to turn on this reaction, as no product was formed without the presence of the thioureas. Our study constitutes the first success in carbene-catalyzed enantioselective synthesis of all-carbon spirocycles. Products from our reactions can be readily transformed to sophisticated multi-cyclic molecules and chiral ligands.

**Comment:** The spirocycle scaffold has great interest in organocatalysis and as a bio-active molecule. In this article, they describe an asymmetric catalytic method through a chiral NHC catalysis to get access to such spirocycles. The products synthesized are rich in functionalities and can be used for further transformations.

### Substrate-Induced Self-Assembly of Cooperative Catalysts

Zhuo, S.; Zhu, T.; Zhou, L.; Mou, C.; Chai, H.; Lu, Y.; Pan, L.; Jin, Z.; Chi, Y. R. *Angew. Chem. Int. Ed.* **2018**, ASAP.



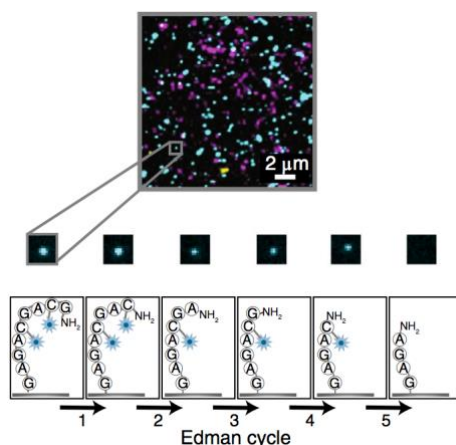
To create low band-gap, fluorescent, and elastic organic crystal emitters, we focused on an extended  $\pi$ -conjugated system based on: a) a planar conformation, b) a rigid structure, and c) controlled intermolecular interactions. Herein, we report on two fluorescent and highly flexible organic crystals (1 and 2) which could bend under an applied stress. The bent crystals rapidly recover their straight shape upon release of the stress. Crystal 1 with a tetrafluoropyridyl terminal unit and a lower band-gap energy (orange emission,  $\lambda_{em} = 573$  nm,  $\Phi_F = 0.50$ ), showed no bending mechanofluorochromism and had superior performance as an optical waveguide with reddish orange emission. The waveguide performance of the crystal did not decrease under bending stress. For crystal 2 with a pentafluorophenyl terminal unit (green emission,  $\lambda_{em} = 500$  nm,  $\Phi_F = 0.38$ ), the

original waveguide performance decreased under an applied bending stress; however, this crystal showed a unique bending mechanofluorochromism.

**Comment:** In this article, the authors describe the self-assembly of thiadiazole platform to control the packing in the solid state. They observed waveguide but the most surprising information is that the material keeps its efficiency under mechanical stress. Do the triarylamine crystals have some elastic properties in order to observe the same effect?

### Next-Generation Peptide Sequencing

Lei, T.\* [Nat. Meth., 2018,15, 997.](#)

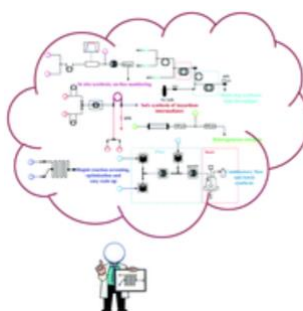


The concept of **massively parallel** single-molecule protein **sequencing** emerges.

**Comment:** This “research highlight” article is briefly presenting a novel approach in the sequencing of proteins. The complete work has recently been published in [Nature Biotech.](#) The main advantages for this technique are its extremely high sensitivity (around a million times higher than mass spectrometry) and the possibility to sequence an enormous number of peptide molecules in parallel. However, it requires a reference in the database. Thus, making the sequencing of new proteins more difficult or even impossible. I think this article still may interest the “biologists” of our team and I can recommend reading the corresponding [Nat. Biotech.](#) for further information.

### Continuous Flow Chemistry: Where are we now? Recent Applications, Challenges and Limitations

Akwi, F. M., Watts, P.\* [Chem. Commun. 2018, Advance Article.](#)

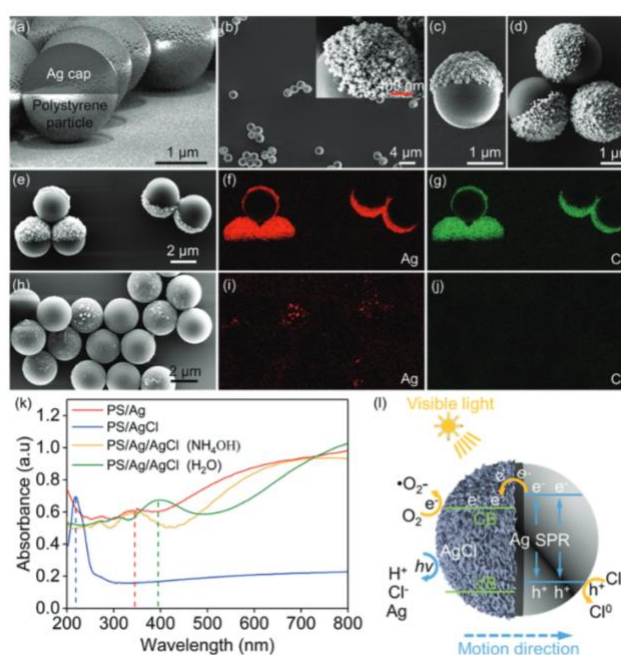


A general outlook of the changing face of chemical synthesis is provided in this article through recent applications of **continuous flow processing** in both industry and academia. The benefits, major challenges and limitations associated with the use of this mode of processing are also given due attention as an attempt to put into perspective the current position of continuous flow processing, either as an alternative or potential combinatory technology for batch processing.

**Comment:** I don't know if I have anything to add to the abstract. It is, in my opinion, a well-structured review explicating the advantages and the drawbacks of the continuous flow processing. This paper constitutes an excellent starting point for whoever would like to familiarize himself with this technique. Thus I highly recommend reading it, or at least the introduction of the article and of the different sub-chapters.

### High-Motility Visible Light-Driven Ag/AgCl Janus Micromotors

Wang, X.; Baraban, L.\*; Nguyen, A.; Ge, J.; Misko, V. R.; Tempere, J.; Nori, F.; Formanek, P.; Huang, T.; Cuniberti, G.; Fassbender, J.; Makarov, D. [Small 2018, 14 \(48\), e1803613.](#)



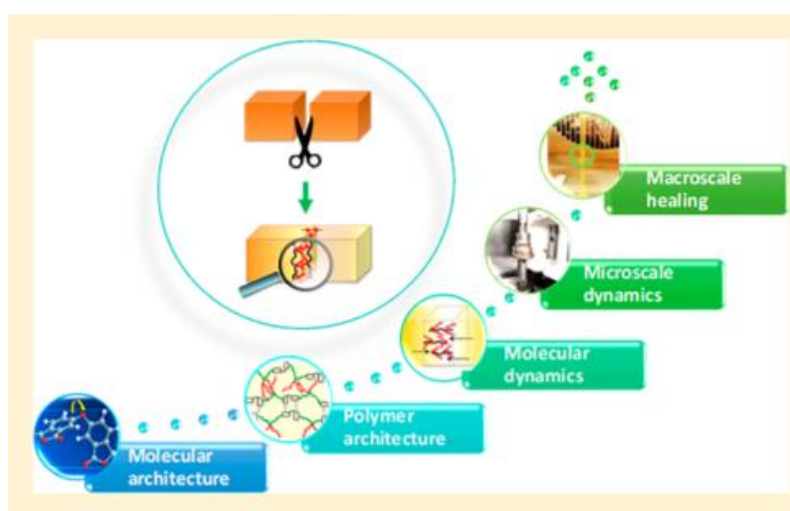
Visible light-driven nano/micromotors are promising candidates for biomedical and environmental applications. This study demonstrates blue light-driven Ag/AgCl-based spherical Janus micromotors, which couple plasmonic light absorption with the photochemical decomposition of AgCl. These micromotors reveal high motility in pure water, i.e., mean squared displacements (MSD) reaching  $800 \mu\text{m}^2$  within 8 s, which is  $100 \times$  higher compared to previous visible light-driven Janus micromotors and  $7 \times$  higher than reported ultraviolet (UV) light-driven AgCl micromotors. In addition to providing design rules to realize efficient Janus micromotors, the complex dynamics revealed by individual and assemblies of Janus motors is investigated experimentally and in simulations. The effect of suppressed rotational diffusion is focused on, compared to UV light-driven AgCl micromotors, as a reason for this remarkable increase of the MSD. Moreover, this study demonstrates the potential of using visible light-driven plasmonic Ag/AgCl-based Janus micromotors in human saliva, phosphate-buffered saline solution, the most common isotonic buffer that mimics the environment of human body fluids, and Rhodamine B solution, which is a typical polluted dye for demonstrations of photocatalytic environmental remediation. This new knowledge is useful for designing visible light driven nano/micromotors

based on the surface plasmon resonance effect and their applications in assays relevant for biomedical and ecological sciences.

**Comment:** Authors report here an efficient synthesis of light-driven Janus micromotors (AgCl/Ag layers over PS Microparticles) showing very high motility in pure water. Possible future bio-applications are pointed up but the particles are not propelled in non-diluted biological solutions and the motor produces  $\text{Ag}^{\circ}$ ,  $\text{Cl}^{\circ}$  and  $\text{O}_2^{\cdot-}$  with no concern about toxicity.

### Identifying the Role of Primary and Secondary Interactions on the Mechanical Properties and Healing of Densely Branched Polyimides

Susa, A.; Mordvinkin, A.; Saalwächter, K.; van der Zwaag, S.; Garcia, S. J.\* [Macromolecules 2018, 51, 8333.](#)



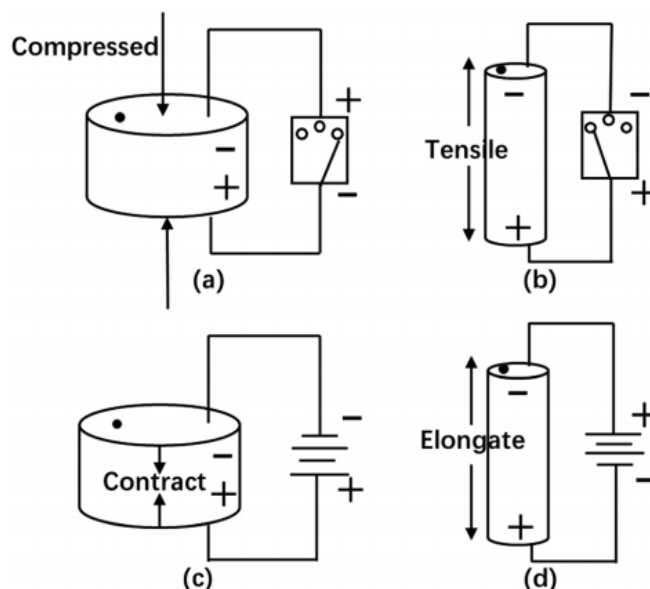
We present a systematic study of the role of the aromatic dianhydride structure on the self-healing behavior of dimer diamine-based polyimides. By means of solid-state NMR and rheology, we studied the molecular and microscale dynamics of four polyimides comprising the same aliphatic branched diamine yet with variable dianhydride rigidities and correlated these to their macroscopic healing kinetics measured by tensile testing. Following the two-step kinetics of the healing process, we were able to differentiate and quantify the extent of mechanical strength recovery in each of the healing stages separately. Moreover, the detailed rheology and solid-state NMR allowed us to shed light on the role of the aromatic interactions and branches on the mechanical properties and mechanical integrity during macroscopic healing. The study reveals the relevance and interplay of primary and secondary interactions in the development of non-cross-linked strong and healing polymers able to maintain mechanical integrity during healing.

**Comment:** The authors report here a kinetic study for the self-healing process in polyimides. This healing occurs in two steps: first, a quick interfacial interaction followed by much slower interaction diffusion. The role of aromatic residues is also discussed: they can crystallize leading to a drastic slowdown of healing kinetic.



## An Overview of Lead-Free Piezoelectric Materials and Devices

Wei, H.\*; Wang, H.; Xia, Y.; Cui, D.; Shi, Y.; Dong, M.; Liu, C.\*; Ding, T.\*; Zhang, J.; Ma, Y.; Wang, N.; Wang, Z.; Sun, Y.; Wei, R.\*; Guo, Z.\* [J. Mater. Chem. C 2018, 6, 12446–12467.](#)



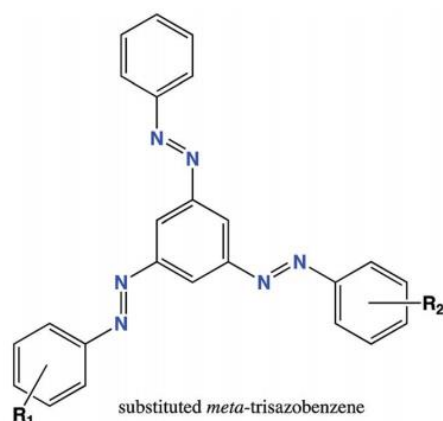
**Fig. 1** Schematic of the positive and inverse piezoelectric effects. (a) and (b) show the positive piezoelectric effect applied by a compressive and tensile force, respectively. (c) and (d) show an inverse piezoelectric effect which causes the piezoelectric material to contract and elongate, respectively.

Piezoelectric materials and devices have drawn extensive attention for energy harvesting due to their excellent electromechanical conversion properties. With increasing concerns about environmental problems in traditional lead-based piezoelectric materials, it is imperative to develop lead-free piezoelectric alternatives. This paper is intended to give **a brief review on the most recent advances** in both inorganic (with an emphasis on piezoelectric ceramics and ZnO nanostructures) and organic (*i.e.* polyvinylidene difluoride (PVDF) and its copolymers and their composites, and biopolymers) lead-free piezoelectric materials. State-of-the-art piezoelectric devices, namely, nanogenerators, sensors, and transducers, are also introduced with detailed examples. Finally, the challenges and perspectives of lead-free piezoelectric materials and devices are given.

**Comment:** In my opinion, the most intuitive way for a human to interactive with a machine is through the sense of touch (we could argue that interacting with a machine with our eyes could be more interesting, but we can all agree that in our current daily life, our sense of sight is rather passive). In this way, piezoelectric materials, and devices derived from them, will probably become even more common in the near future. This review discusses the state-of-art of piezoelectric materials, and perhaps some of us can find inspiration in the possible applications of piezoelectric devices the authors present.

### Computational Design of a Molecular Triple Photoswitch for Wavelength-Selective Control

Yang, C.; Slavov, C.; Wegner, H. A.; Wachtveitl, J.; Dreuw, A.\* [Chem. Sci. 2018, 9, 8665–8672.](#)

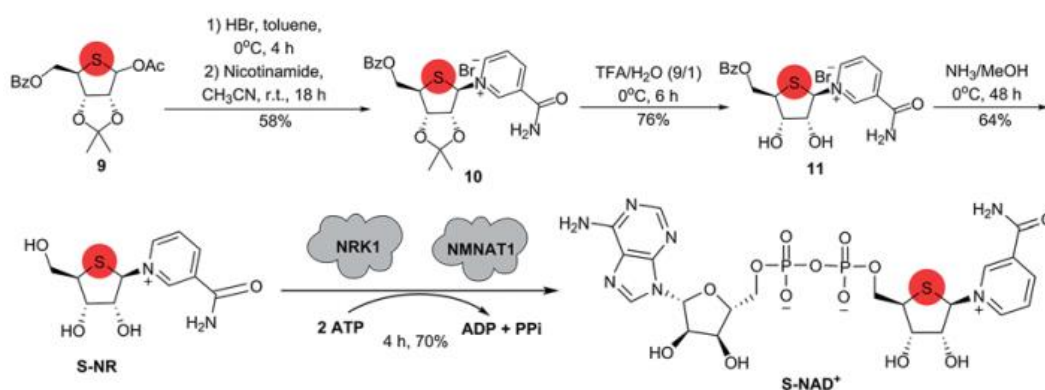


A small single molecule with multiple photoswitchable subunits, selectively and independently controllable by light of different wavelengths, is highly attractive for applications in multi-responsive materials and biological sciences. Herein, triple photoswitches are presented consisting of three independent azobenzene (AB) subunits that share a common central phenyl ring: the *meta*-trisazobenzenes (MTA). It is the unique meta-connectivity pattern leading to decoupling of all azo-subunits although they do overlap spatially. Based on this pattern, we design a triple MTA photoswitch, as proof-of-principle, with three different, electronically independent AB branches on the computer, which can be individually photo-excited to trigger ultra-fast  $E \rightarrow Z$  isomerization at the selected AB branch.

**Comment:** Azobenzene will again be part of the literature of the week, however in a slightly different type of work. Here, the authors computed (“designed *in silico*”) different structures of MTA (see the structure above) with different substituents on the aromatic rings. The calculations led to possible structures where the three branches could be isomerized independently; now, “all there is to do” is to synthesize it, and see if the theory is right.

### Facile Chemoenzymatic Synthesis of a Novel Stable Mimic of NAD<sup>+</sup>

Dai, Z.; Zhang, X.-N.; Nasertorabi, F.; Cheng, Q.; Pei, H.; Louie, S. G.; Stevens, R. C.\*; Zhang, Y.\* *Chem. Sci.* **2018**, *9*, 8337–8342.



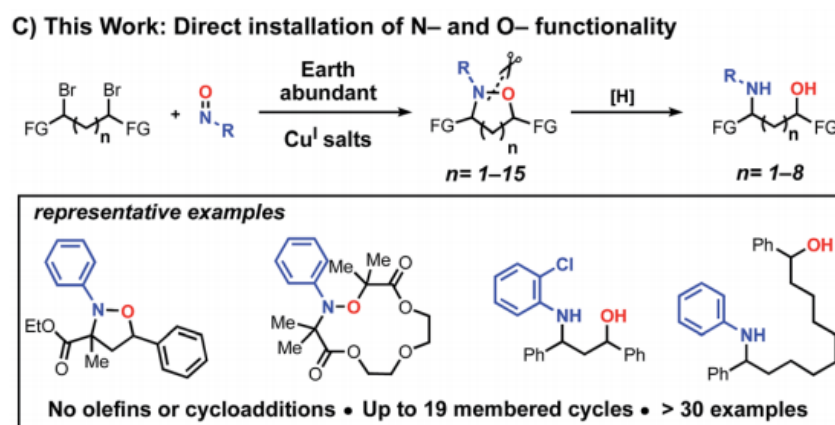
Nicotinamide adenine dinucleotide (NAD<sup>+</sup>) is an essential cofactor participating in a variety of important enzyme-catalyzed physiological and pathophysiological processes. Analogues of NAD<sup>+</sup> provide key and valuable agents for investigating NAD<sup>+</sup>-dependent enzymes. In this study, we report the preparation of a novel stable NAD<sup>+</sup> mimic, 4'-thioribose NAD<sup>+</sup> (S-NAD<sup>+</sup>), using a facile and efficient chemoenzymatic approach. Substrate activity assays indicated the resulting S-NAD<sup>+</sup> is chemically inert to human CD38 and sirtuin 2 enzymes, but capable of

participating in redox reactions in a manner similar to  $\text{NAD}^+$ . X-ray crystallographic analysis revealed binding of  $\text{S-NAD}^+$  to the active site of human CD38 and critical residues involved in leaving group activation and catalysis. By more closely mimicking  $\text{NAD}^+$  in geometry and electrostatics, the generated  $\text{S-NAD}^+$  offers a unique and important tool that can be extended to study enzymes utilizing  $\text{NAD}^+$ .

**Comment:**  $\text{NAD}^+$  is involved in redox processes in our body, and hence, the study of enzymatic processes involving this molecule are crucial to understand how the human machine works. However, as with many biological molecules, it may be complicated to isolate  $\text{NAD}^+$  in a sufficient quantity to study the enzymatic reactions systematically and quickly, hence the importance of synthesizing  $\text{NAD}^+$  analogues.

### Direct Introduction of Nitrogen and Oxygen Functionality with Spatial Control Using Copper Catalysis

Shaum, J. B.; Fisher, D. J.; Sroda, M. M.; Limon, L.; Read de Alaniz, J.\* [Chem. Sci. 2018, 9, 8748–8752](#).

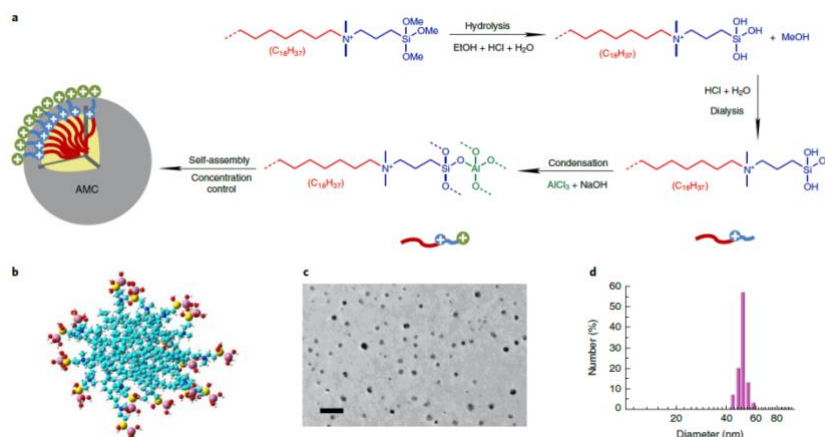


Synthetic chemists have spent considerable effort optimizing the synthesis of nitrogen and oxygen containing compounds through a number of methods; however, direct introduction of N- and O-functionality remains challenging. Presented herein is a general method to allow for the **simultaneous installation of N- and O-functionality** to construct unexplored N–O heterocyclic and amino-alcohol scaffolds. This transformation uses earth abundant copper salts to facilitate the formation of a carbon-centered radical and subsequent carbon–nitrogen bond formation. The intermediate aminoxyl radical is terminated by an intramolecularly appended carbon-centered radical. We have exploited this methodology to also access amino-alcohols with a range of aliphatic and aromatic linkers.

**Comment:** Introducing heteroatoms, especially nitrogen, in a molecule can be challenging; here, the authors present a way to introduce nitrogen and oxygen simultaneously in a chemical structure, and their separation can be modulated. Of course, there are limitations for the reactant, but overall, it presents several advantages: the catalysts are readily available, the yields are correct (on average, around 50%) and it is possible to predict the regioselectivity.

### Actinia-like Multifunctional Nanocoagulant for Single-step Removal of Water Contaminants

Liu, J.; Cheng, S.; Cao, N.; Geng, C.; He, C.; Shi, Q.; Xu, C.; Ni, J.; DuChanois, R.; Elimelech, M.; Zhao, H.; [Nat. Nanotechnol. 2018, ASAP](#).

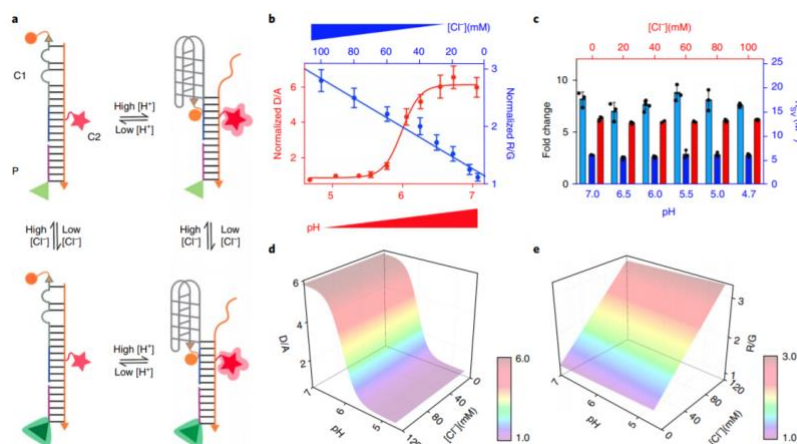


Current technologies for water purification are limited by their contaminant-specific removal capability, requiring multiple processes to meet water quality objectives. Here we show an innovative biomimetic micellar nanocoagulant that imitates the structure of Actinia, a marine predator that uses its tentacles to ensnare food, for the removal of an array of water contaminants with a single treatment step. The Actinia-like micellar nanocoagulant has a core–shell structure and readily disperses in water while maintaining a high stability against aggregation. To achieve effective coagulation, the nanocoagulant everts its configuration, similar to Actinia. The shell hydrolyses into ‘flocs’ and destabilizes and enmeshes colloidal particles while the core is exposed to water, like the extended tentacles of Actinia, and adsorbs the dissolved contaminants. The technology, with its ability to remove a broad spectrum of contaminants and produce high-quality water, has the potential to be a cost-effective replacement for current water treatment processes.

**Comment:** Inspired by the configuration of Actinia, scientist synthesized a biomimetic micellar nanocoagulant with a core–shell structure. It is simple but highly efficient when it comes to the water contaminant treatment.

### A DNA Nanomachine Chemically Resolves Lysosomes in Live Cells

Leung, K.; Chakraborty, K.; Saminathan, A.; Krishnan, Y.; [Nat. Nanotechnol. 2018, ASAP.](#)



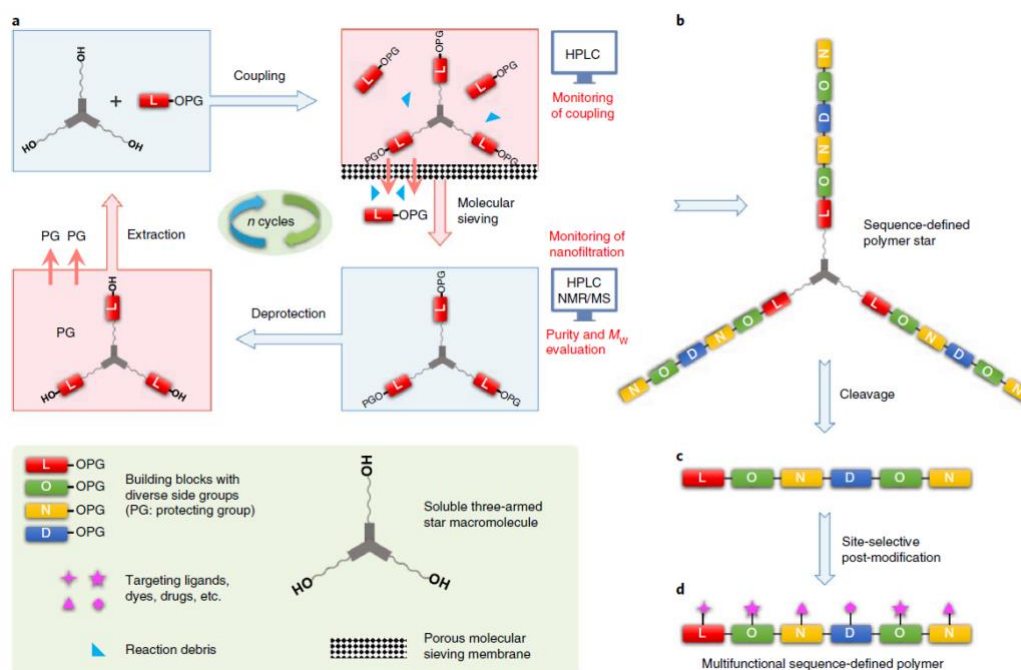


Lysosomes are multifunctional, subcellular organelles with roles in plasma membrane repair, autophagy, pathogen degradation and nutrient sensing. Dysfunctional lysosomes underlie Alzheimer's disease, Parkinson's disease and rare lysosomal storage diseases, but their contributions to these pathophysiology are unclear. Live imaging has revealed lysosome subpopulations with different physical characteristics including dynamics, morphology or cellular localization. Here, we chemically resolve lysosome subpopulations using a DNA-based combination reporter that quantitatively images pH and chloride simultaneously in the same lysosome while retaining single-lysosome information in live cells. We call this technology two-ion measurement or 2-IM. 2-IM of lysosomes in primary skin fibroblasts derived from healthy individuals shows two main lysosome populations, one of which is absent in primary cells derived from patients with Niemann–Pick disease. When patient cells are treated with relevant therapeutics, the second population re-emerges. Chemically resolving lysosomes by 2-IM could enable decoding the mechanistic underpinnings of lysosomal diseases, monitoring disease progression or evaluating therapeutic efficacy.

**Comment:** The scientists described a new technology to chemically resolve lysosome subpopulations in living cells. The rationale is that different subpopulations of lysosomes contain different ionic microenvironments that facilitate their distinct roles.

### Sequence-Defined Multifunctional Polyethers via Liquid-Phase Synthesis with Molecular Sieving

Dong, R.J.; Liu, R.Y.; Gaffney, R.J.; Schaepertoens, M.; Marchetti P.; Williams, C.M.; Chen, R.J.; Livingston, A.G. \* [Nat. Chem. 2018, ASAP.](#)



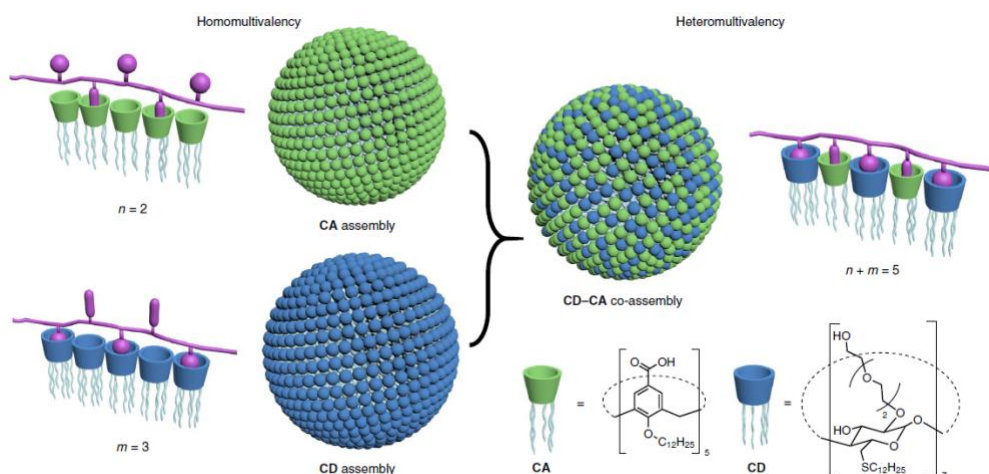
Synthetic chemists have devoted tremendous effort towards the production of precision synthetic polymers with defined sequences and specific functions. However, the creation of a general technology that enables precise control over monomer sequence, with efficient isolation of the target polymers, is highly challenging. Here, we report a robust strategy for the production of sequence-defined synthetic polymers through a combination of liquid-phase synthesis and selective molecular sieving. The polymer is assembled in solution with real-time monitoring to ensure couplings proceed to completion, on a three-armed star-shaped macromolecule to maximize

efficiency during the molecular sieving process. This approach is applied to the construction of sequence-defined polyethers, with side-arms at precisely defined locations that can undergo site-selective modification after polymerization. Using this versatile strategy, we have introduced structural and functional diversity into sequence-defined polyethers, unlocking their potential for real-life applications in nanotechnology, healthcare and information storage.

**Comment:** A new strategy, which is similar with solid phase peptide synthesis (SPPS), construct the news sequence-defined structural and functional polyethers in the liquid phase synthesis.

### Heteromultivalent Peptide Recognition by Co-Assembly of Cyclodextrin and Calixarene Amphiphiles Enables Inhibition of Amyloid Fibrillation

Xu, Z.; Jia, S.R.; Wang, W.; Yuan, Z.; Jan Ravoo, B, T; Guo, D.S.\* [Nat. Chem. 2018, ASAP.](#)

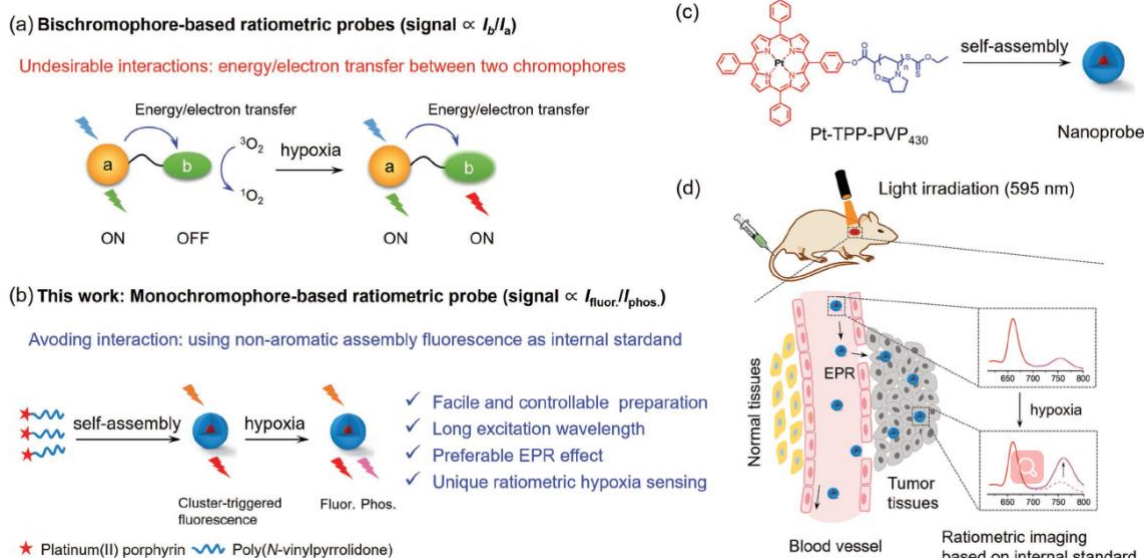


**Heteromultivalency**, which involves the simultaneous interactions of more than one type of ligand with more than one type of receptor, is ubiquitous in living systems and provides a powerful strategy to improve the binding efficiency of heterotopic species such as proteins and membranes. However, the design and development of artificial heteromultivalent receptors is still challenging owing to tedious synthesis processes and the need for precise control over the spatial arrangement of the binding sites. Here, we have designed a heteromultivalent platform by co-assembling cyclodextrin and calixarene amphiphiles, so that two orthogonal, non-covalent binding sites are distributed on the surface of the co-assembly. Binding with model peptides shows a synergistic effect of the two receptors, (hetero)multivalency and self-adaptability. The co-assembly shows promise for inhibition of the fibrillation of amyloid- $\beta$  peptides and the dissolution of amyloid- $\beta$  fibrils, substantially reducing amyloid cytotoxicity. This self-assembled heteromultivalency concept is easily amenable to other ensembles and targets, so that versatile biomedical applications can be envisaged.

**Comment:** This paper introduces aims to introduce the concept of heteromultivalent molecular recognition to artificial supramolecular systems. As they point out, it is and will be hard to achieve.

### Self-Assembly of a Monochromophore-Based Polymer Enables Unprecedented Ratiometric Tracing of Hypoxia

Wang, S.; Gu, Z.; Guo, Z. \*; Yan, C.; Yang, T.; Chen, Z.; Tian, H.; Zhu, W.\* [Adv. Mater. 2018, 1805735.](#)

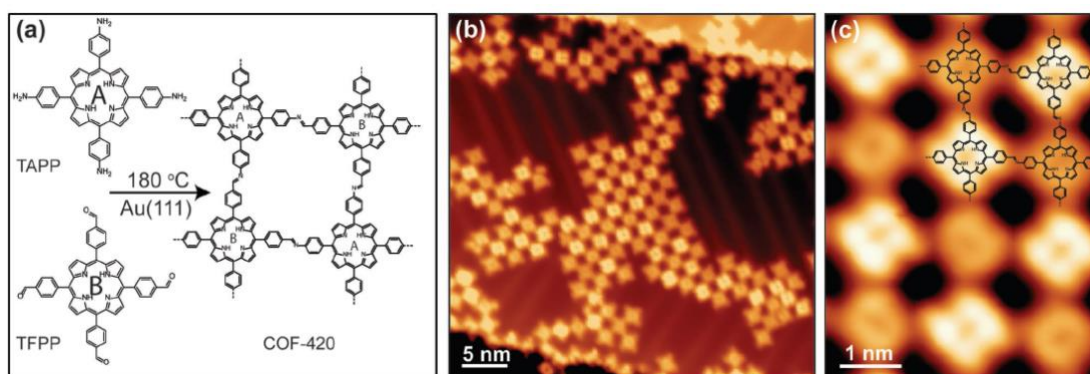


The accuracy of traditional bischromophore-based ratiometric probes is always compromised by undesirable energy/charge transferring interactions between the internal reference moiety and the sensing chromophore. In this regard, ratiometric sensing with a monochromophore system is highly desirable. Herein, an unprecedented monochromophore-based ratiometric probe, which consists of a hydrophilic backbone poly(N-vinylpyrrolidone) (PVP) and single chromophore of platinum(II) tetraphenylporphyrin (Pt-TPP) is reported. Combination of the specific assembled clustering-triggered fluorescent emission (oxygen-insensitive) with the original Pt-TPP phosphorescence (oxygen-sensitive) enables successful construction of a monochromophore-based ratiometric nanosensor for directly tracing hypoxia *in vivo*, along with the preferable facilitation of enhanced permeation and retention effect and long excitation wavelength. The unique ratiometric signals enable the direct observation from normoxic to hypoxic environment in both living A549 cells and a tumor-bearing mice model, providing a significant paradigm of a monochromophore-based dual-emissive system with the specific assembled cluster emission. The work satisfactorily demonstrates a valuable strategy for designing monochromophore-based dual-emissive materials, and validates its utility for *in vivo* ratiometric biological sensing without the common energy/charge interference in bischromophore-based system.

**Comment:** This article demonstrates a biological monochromophore sensor based on polymers without aromatic interaction, which could serve as ratiometric tracing of hypoxia. The magical aspect is that nanoparticles are known to accumulate at tumour sites by passive enhanced permeation and retention effect. All the important organs were monitored, only a small portion of the nanoparticles was found in the liver. There was almost no cytotoxicity even at a concentration up to  $6.4 \text{ mg mL}^{-1}$ .

### Local Electronic Structure of Molecular Heterojunctions in a Single-Layer 2D Covalent Organic Framework

Joshi, T.; Chen, C.; Li, H.; Diercks, C. S.; Wang, G.; Waller, P. J.; Li, H.\*; Bredas, J.-L.; Yaghi, O. M.\*; Crommie, M. F.\* [Adv. Mater. 2018, 1805941.](#)



The synthesis of a single-layer covalent organic framework (COF) with spatially modulated internal potentials provides new opportunities for manipulating the electronic structure of molecularly defined materials. Here, the fabrication and electronic characterization of COF-420: a single layer porphyrin-based square-lattice COF containing a periodic array of oriented, type II electronic heterojunctions is reported. In contrast to previous donor–acceptor COFs, COF-420 is constructed from building blocks that yield identical cores upon reticulation, but that are bridged by electrically asymmetric linkers supporting oriented electronic dipoles. Scanning tunneling spectroscopy reveals staggered gap (type II) band alignment between adjacent molecular cores in COF-420, in agreement with first-principles calculations. Hirshfeld charge analysis indicates that dipole fields from oriented imine linkages within COF-420 are the main cause of the staggered electronic structure in this square grid of atomically–precise heterojunctions.

**Comment:** Actually, it is not the first COF (anyway, they called this structure as COF) which exhibits these asymmetric configurations. But they did studied the electronic structure of this COF in sufficient detail.