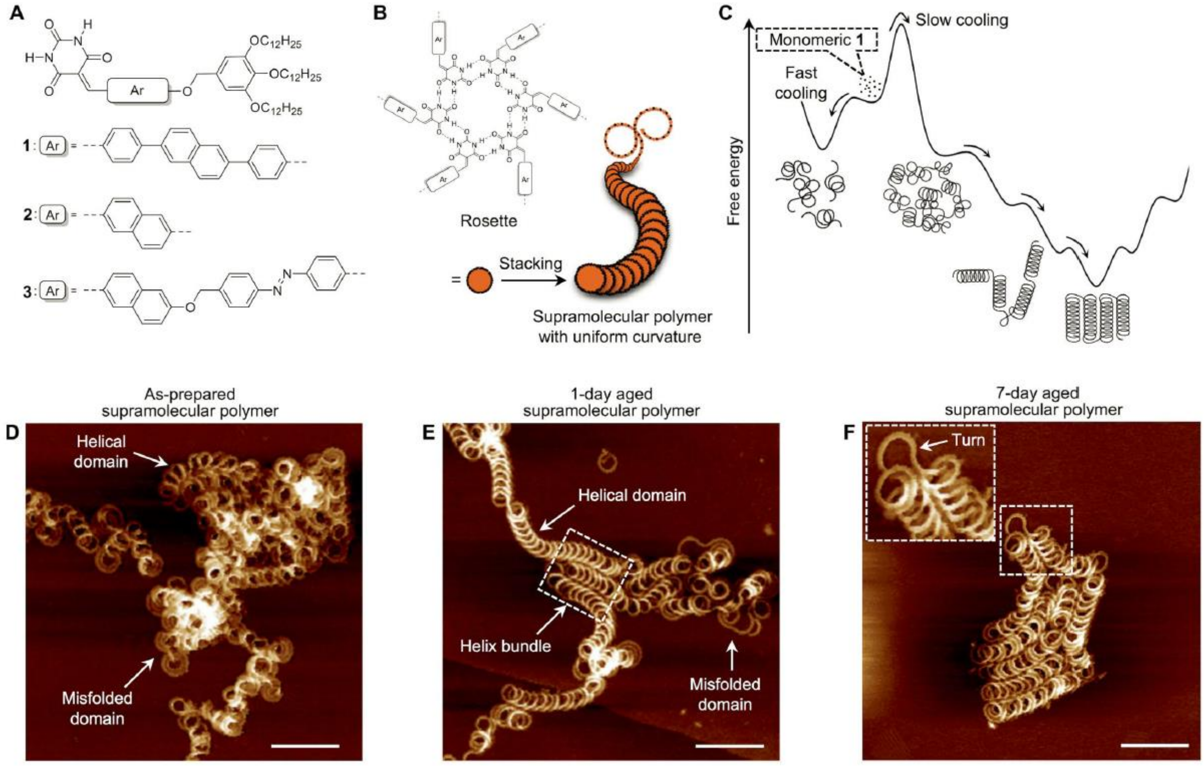
Self-folding of Supramolecular Polymers into Bioinspired Topology

Prabhu, D. D.; Aratsu, K.; Kitamoto, Y.; Ouchi, H.; Ohba, T.; Hollamby, M. J.; Shimizu, N.; Takagi, H.; Haruki, R.; Adachi, S.-i.; Yagai, S.* *Sci. Adv.* **2018**, *4:* eaat8466

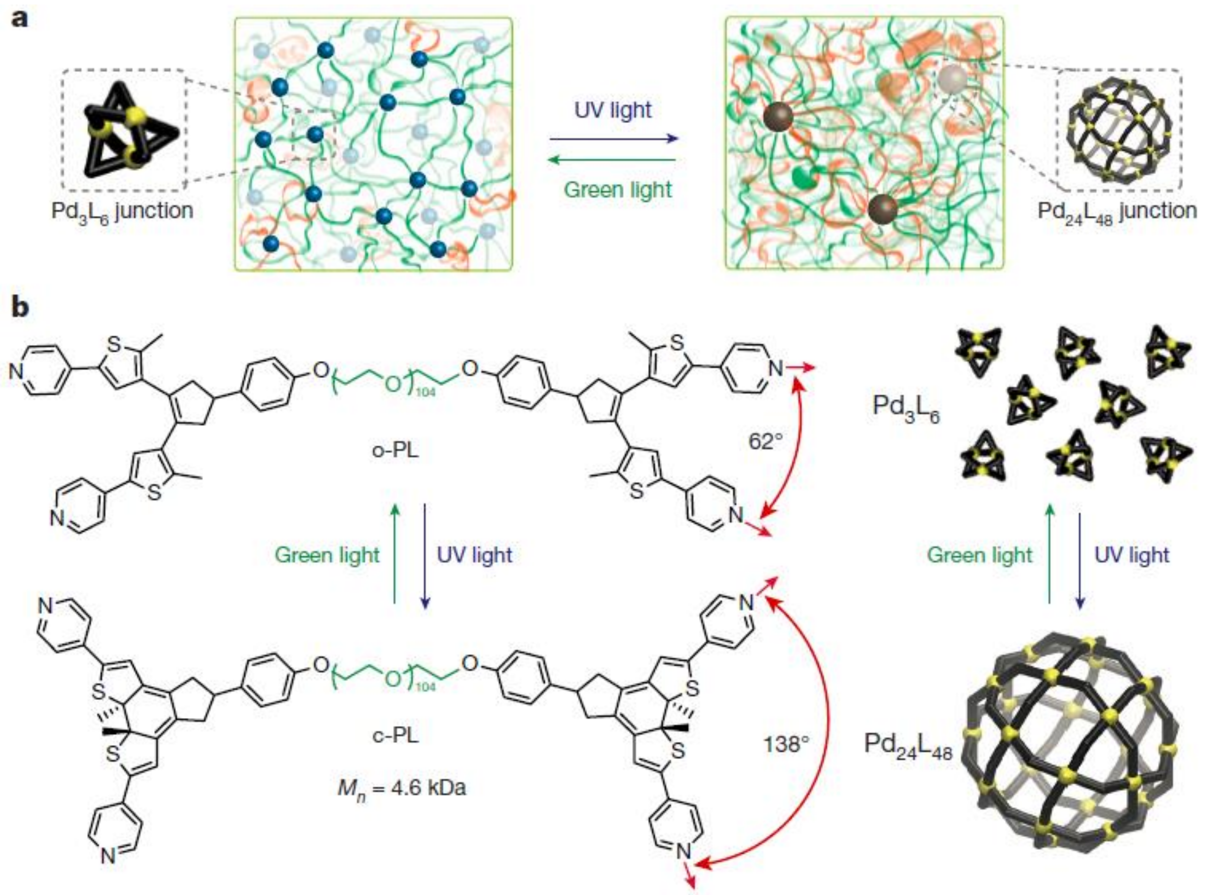


Folding one-dimensional polymer chains into well-defined topologies represents an important organization process for proteins, but replicating this process for supramolecular polymers remains a challenging task. We report supramolecular polymers that can fold into protein-like topologies. Our approach is based on curvature-forming supramolecular rosettes, which affords kinetic control over the extent of helical folding in the resulting supramolecular fibers by changing the cooling rate for polymerization. When using a slow cooling rate, we obtained misfolded fibers containing a minor amount of helical domains that folded on a time scale of days into unique topologies reminiscent of the protein tertiary structures. Thermodynamic analysis of fibers with varying degrees of folding revealed that the folding is accompanied by a large enthalpic gain. The self-folding proceeds via ordering of misfolded domains in the main chain using helical domains as templates, as fully misfolded fibers prepared by a fast cooling rate do not self-fold.

Comment: Regular self-fold of supramolecular polymer is rare and interesting. This work gave a detailed thermodynamic investigation of the folding process, and that is cool.

Photoswitching Topology in Polymer Networks with Metal-organic Cages as Crosslinks

Gu, Y.; Alt, E. A.; Wang, H.; Li, X.; Willard, A. P.; Johnson, J. A.* *Nature* **2018**, *560*, 65



Polymer networks can have a range of desirable properties such as mechanical strength, wide compositional diversity between different materials, permanent porosity, convenient processability and broad solvent compatibility[1,2]. Designing polymer networks from the bottom up with new structural motifs and chemical compositions can be used to impart dynamic features such as malleability or self-healing, or to allow the material to respond to environmental stimuli[3-8]. However, many existing systems exhibit only one operational state that is defined by the material's composition and topology[3-6]; or their responsiveness may be irreversible[7,9,10] and limited to a single network property[11,12] (such as stiffness). Here we use cooperative self-assembly as a design principle to prepare a material that can be switched between two topological states. By using networks of polymer-linked metal-organic cages in which the cages change shape and size on irradiation, we can reversibly switch the network topology with ultraviolet or green light. This photoswitching produces coherent changes in several network properties at once, including branch functionality, junction fluctuations, defect tolerance, shear modulus, stress-relaxation behaviour and self-healing. Topology-switching materials could prove useful in fields such as soft robotics and photo-actuators as well as providing model systems for fundamental polymer physics studies.

Comment: It's a nice work. It combined MOF and polymer to make functional network and that is really cool.

Spider Prey-Wrapping Silk is an α-Helical Coiled-Coil/β-Sheet Hybrid Nanofiber

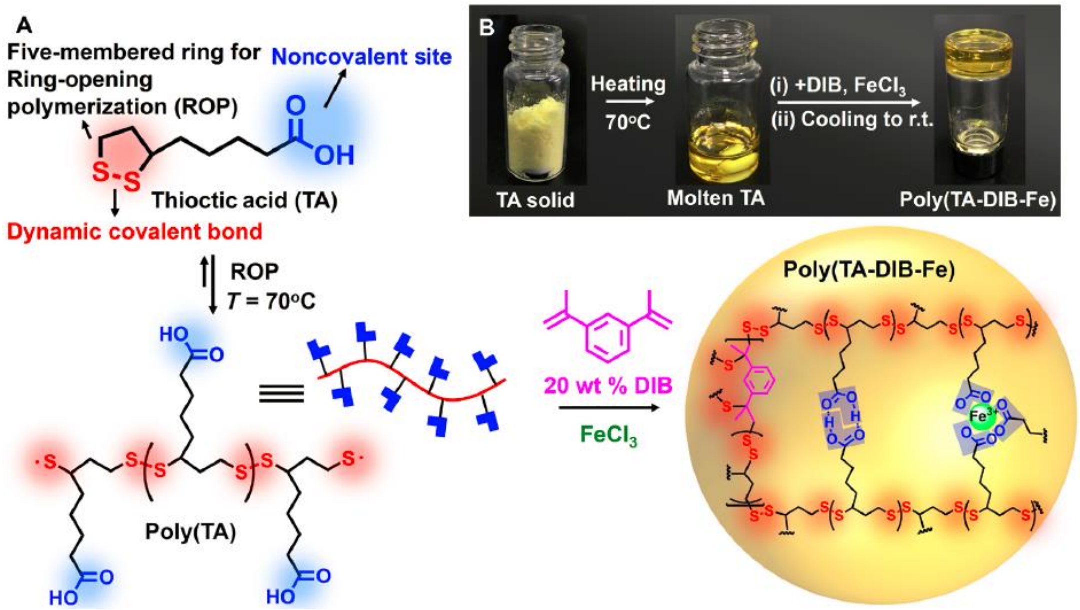
Addison, B.; Onofrei, D.; Stengel, D.; Blass, B.; Brenneman, B.; Ayon, J.; Holland, J. P.*
Chem. Commun., **2018**, Advance Article.

Solid-State NMR results on ^{13}**C-Ala/Ser and** ^{13}**C-Val** enriched *Argiope argentata* prey-wrapping silk show that native, freshly spun **aciniform silk nanofibers** are **α-helical** (~50% total) and **random-coil** (~35% total) **secondary structures**, with **minor β-sheet nanocrystalline domains** (~15% total). This is the most in-depth study to date characterizing the protein structural conformation of the toughest natural biopolymer: aciniform prey-wrapping silks.

Comment: This article might seem out of topic but it remains quite interesting. Indeed, besides the fact that the authors have captured wild spiders and used toothbrush to make them create a specific silk, they also highlighted the use of NMR to characterize secondary structures of proteins. Therefore, this approach could possibly be useful for the peptide team.

Exploring A Naturally Tailored Small Molecule for Stretchable, Self-healing, and Adhesive Supramolecular Polymers

Zhang, Q.; Shi, C. Y.; Qu, D. H.*; Long, Y. T.; Feringa, B. L.*; Tian, H.* *Sci. Adv.* **2018**, *4:* eaat8192

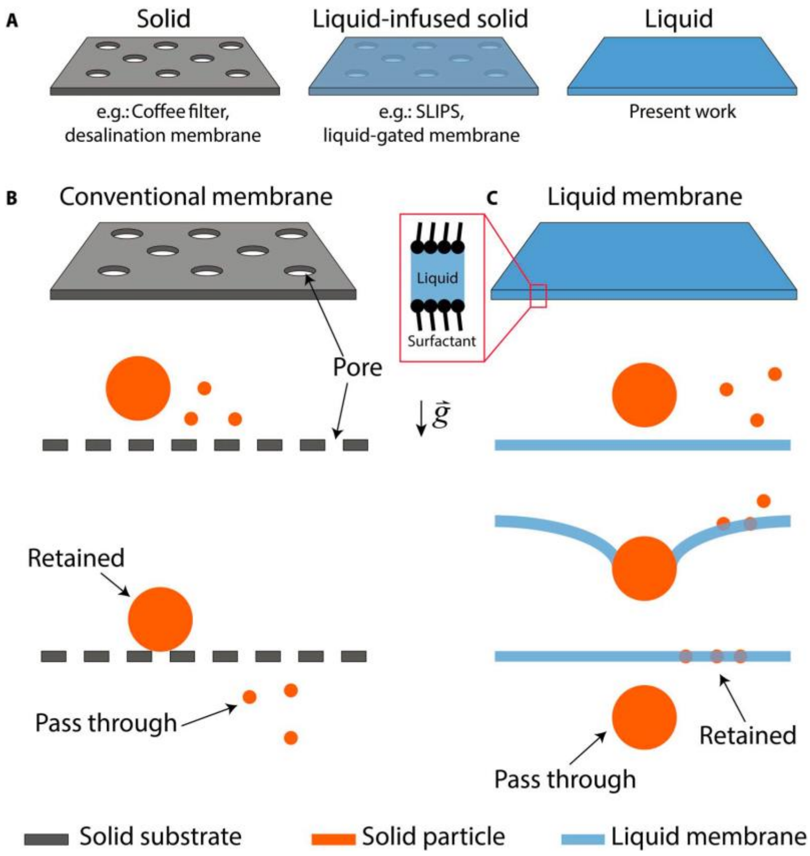


Polymeric materials with integrated functionalities are required to match their ever-expanding practical applications, but there is always a trade-off between complex material performances and synthetic simplification. A simple and effective synthesis route is reported to transform a small molecule of biological origin, thioctic acid, into a high-performance supramolecular polymeric material, which combines processability, ultrahigh stretchability, rapid self-healing ability, and reusable adhesivity to surfaces. The proposed one-step preparation process of this material involves the mixing of three commercially available feedstocks at mild temperature without any external solvent and a subsequent cooling process that resulted in a dynamic, high-density, and dry supramolecular polymeric network cross-linked by three different types of dynamic chemical bonds, whose cooperative effects in the network enable high performance of this supramolecular polymeric material.

Comment: One-step preparation of functional polymers from a small molecule is interesting.

Free-standing Liquid Membranes as Unusual Particle Separators

Stogin, B. B.; Gockowski, L.; Feldstein, H.; Claure, H.; Wang, J.; Wong, T. S.* *Sci. Adv.* **2018**, *4:* eaat3276

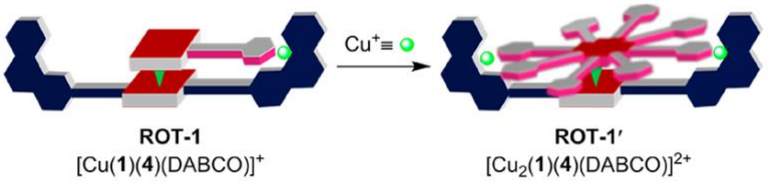


Separation of substances is central to many industrial and medical processes ranging from wastewater treatment and purification to medical diagnostics. Conventional solid-based membranes allow particles below a critical size to pass through a membrane pore while inhibiting the passage of particles larger than that critical size; membranes that are capable of showing reversed behavior, that is, the passage of large particles and inhibition of small ones, are unusual in conventional engineering applications. Inspired by endocytosis and the self-healing properties of liquids, we show that free-standing membranes composed entirely of liquid can be designed to retain particles smaller than a critical size given the particle inertial properties. We further demonstrate that these membranes can be used for previously unachievable applications, including serving as particle barriers that allow macroscopic device access through the membrane (for example, open surgery) or as selective membranes inhibiting gas/vapor passage while allowing solids to pass through them (for example, waste/odor management).

Comment: This work is interesting in that it sounds like a common phenomenon that is ignored by ordinary people, but the authors pay a attention and that means something.

Rotating Catalysts Are Superior: Suppressing Product Inhibition by Anchimeric Assistance in Four-Component Catalytic Machinery

Biswas, P. K.; Saha, S.; Paululat, T.; Schmittel, M.* *J. Am. Chem. Soc.* **2018**, *140*, 9038-9041.

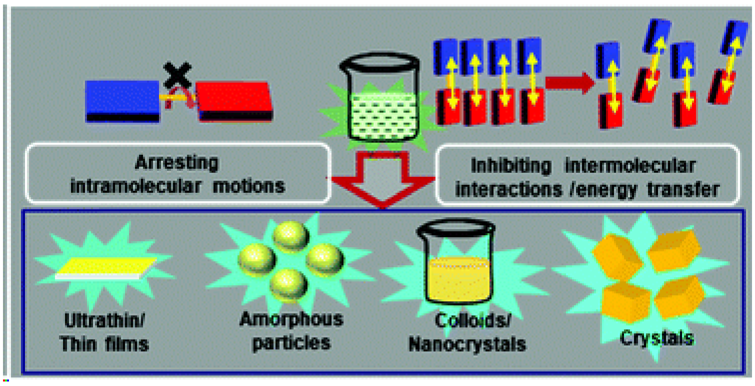


Three distinct four-component supramolecular nanorotors, prepared by varying the rotator’s structure and keeping all other components constant, exhibit rotational frequencies that differ by almost 2 orders of magnitude. When the rotors were used as catalyst for two click reactions, the product yield correlated with the speed of the machine, e.g., 20% at 0.50 kHz, 44% at 20 kHz and 62% at 42 kHz. The kinetic effect on the product yield is attributed to the ability of the rotating catalysts to displace the product more efficiently from the active site at higher speed (anchimeric assistance). This mechanistic hypothesis was convincingly corroborated by a linear correlation between product yield and product liberation.

Comment: The authors show a nice application of molecular rotors. In this example, they designed a rotor for purposes of catalysis and show that there is a clear correlation between the rotator’s speed and the catalytic activity. The experiments suggest that this correlation is linked to the ability to reduce product inhibition at higher rotation speeds through displacement of the reaction products. In my opinion, the important message here is that **you don’t need to control the motion to be able to use it**.

Enhancement of Fluorescence Efficiency from Molecules to Materials and the Critical Role of Molecular Assembly

Srujana, P.; Sudhakar, P.; Radhakrishnan, T. P.* *J. Mater. Chem. C* **2018**, *6*, 9314–9329.



Molecules exhibiting enhanced fluorescence emission in the aggregated/solid state are of immense interest in various functional materials applications. While most traditional fluorophores suffer fluorescence quenching upon aggregation, select molecules show fluorescence efficiency enhancement from the molecular to the materials state. An overview of these systems and the popular 'aggregation-induced emission' phenomenon is presented, followed by a critical appraisal of the related models largely focused on intramolecular structural motions. The enhanced fluorescence of crystals, nanocrystals, ultrathin films and amorphous particles of the family of diaminodicyanoquinodimethanes is discussed subsequently. Fluorescence switching accompanying amorphous–crystalline transformations in these materials is described; insights gained into two-step nucleation, crystallinity as a tool for the hierarchical assembly of molecular materials, and the new domain of functional molecular phase change materials, are highlighted. An emerging model that emphasizes the relevance of 'specifically oriented aggregation' in molecular assemblies and intra/intermolecular effects, with consequences for new materials designs is discussed in the final part.

Comment: For those interested in AIEgens, this review presents the basics of the models used to explain the enhancement of fluorescence due to restricted intramolecular motions. It focuses mainly on diaminodicyanoquinodimethanes, but it may inspire some of you for other molecules.

The Scientists Who Publish a Paper Every Five Days

Ioannidis, J. P. A.; Klavans, R.; Boyack, K. W. *Nature* **2018**, *561*, 167.

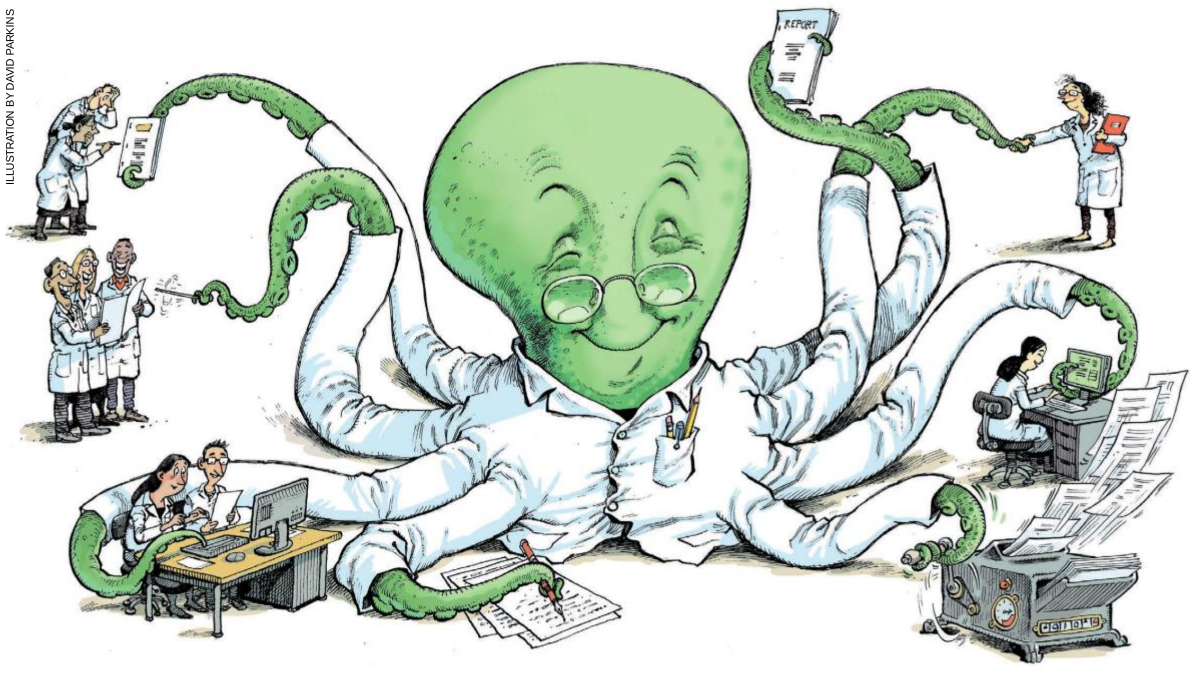


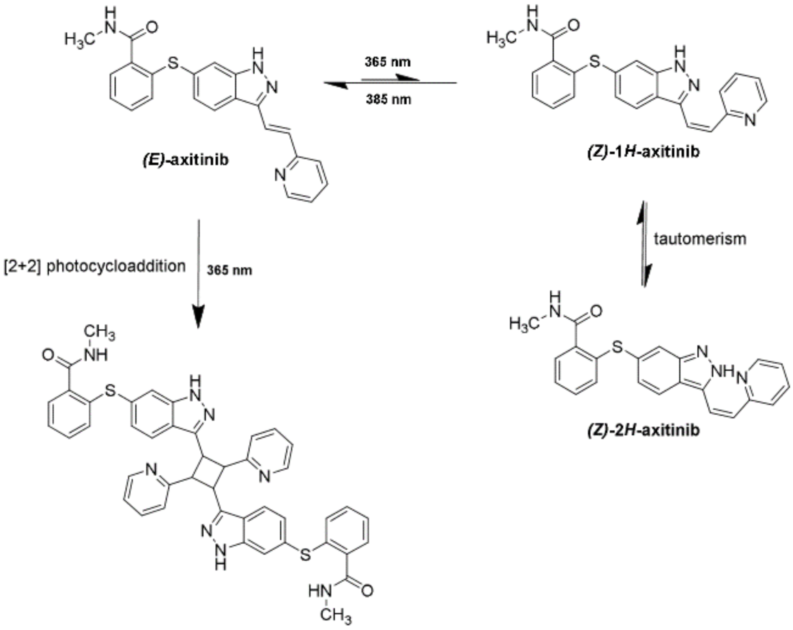
ILLUSTRATION BY DAVID PARKINS

Authorship is the coin of scholarship — and some researchers are minting a lot. We searched Scopus for **authors who had published more than 72 papers (the equivalent of one paper every 5 days)** in any one calendar year between 2000 and 2016, a figure that many would consider implausibly prolific. **We found more than 9,000 individuals**, and made every effort to count only 'full papers' — articles, conference papers, substantive comments and reviews — not editorials, letters to the editor and the like. We hoped that this could be a useful exercise in understanding **what scientific authorship means**.

Comment: I really could not help but submitting this paper, which is not a "paper" *per se* but rather a comment. But still, a study was made, and conclusions were drawn: sounds very scientific to me! But on a serious note, it is absolutely brilliant; not the paper but the supporting information, which happens to contain the answers of such "hyper-prolific" authors to questions *close* to: **Have you read all those papers?** I like it and it was close to become one of my favorite papers! Because we all have a list of our favorite papers, don't we?

Axitinib - A Photoswitchable Approved Tyrosine Kinase Inhibitor

Peifer, C.*; Schmidt, D.; Rodat, T.; Heintze, L.; Weber, J.; Horbert, R.; Girreser, U.; Raeker, T.; Bussmann, L; Kriegs, M.; Hartke, B. *ChemMedChem* **2018**, *Just Accepted.*

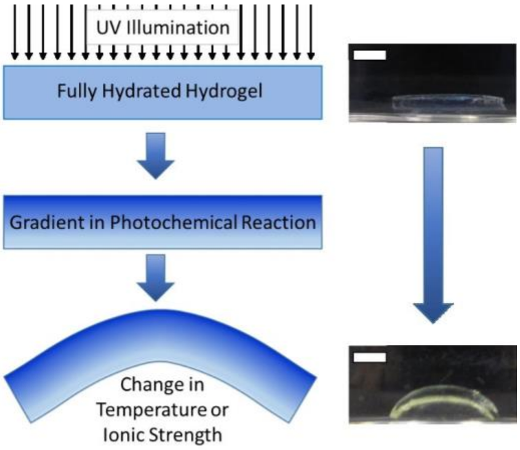


Axitinib is an **approved drug targeting** tyrosine kinases including the vascular endothelial growth factor receptor 2 (**VEGFR2**) and is licensed for second-line therapy of renal cell carcinoma. Interestingly, axitinib contains a stilbene-like double bond allowing for **E/Z isomerization**. In this study, we investigated the photoinduced E/Z isomerization of axitinib to explore if its inhibitory effect can be turned "on" and "off", triggered by light. Compared to the E-isomer, the absorption of the Z-isomer is red-shifted indicating reversible photoswitching properties. When both isolated isomers were measured in a commercialy available profiling under ambient light, no differences of biological activities could be determined. However, under controlled light conditions we could demonstrate that (Z) axitinib is 43 times less active compared to the (E) isomer in an VEGFR2 assays. Furthermore, we proved that kinase activity in HUVEC assays is reduced by (E)-axitinib, but only weakly affected by (Z) axitinib. By irradiating (Z) axitinib in vitro with UV light (385 nm) it is possible to switch it almost quantitatively to the (E)-isomer and to completely restore the biological activity of (E) axitinib. However, vice versa switching the biological activity "off" from (Z)- to (E)-axitinib was not possible in aqueous solution due to a competing irreversible [2+2]-photocycloaddition yielding a biologically inactive axitinib-dimer.

Comment: First, an easy-to-understand process occurs upon E/Z photoisomerization of axitinib. Then, the Z isomer is 43 times less active compared to its E isomer because that conformation lacks the proper fit within the targeted VEGFR2 binding pocket. Finally, and unfortunately, this drug's inhibitory activity cannot be switched on and off in aqueous solution because of the formation of an inactive by-product. However, the authors do point out that photoisomerization can be a mean of enhancing commercially available drugs which contain an important amount of the inactive isomer.

3D Shape Change of Multi-Responsive Hydrogels Based on a Light-Programmed Gradient in Volume Phase Transition

Jiang, Z.; Sanchez, R. J. P.; Blakey, I.; Whittaker, A. K.* *Chem. Commun.*, **2018**, Advance Article.

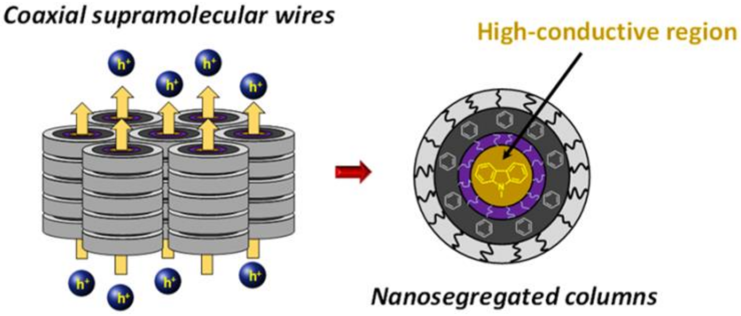


We present a new **multi-responsive hydrogel** based on **oligo(ethylene glycol) methacrylate** (OEGMA) and **incorporating** the **photosensitive monomer 4-acetoxystyrene** (AOST). **Light irradiation** creates a **gradient in the volume phase transition temperature** (VPTT) across the hydrogel, resulting in **stimuli-responsive 3D deformations**, with a largest achievable bending angle of 354°. The gradient hydrogels exhibited controllable, reversible and repeatable 3D deformations driven by changes in temperature or ionic strength. Multiple complex shape changes were achieved through patterned illumination.

Comment: This article presents an unusual approach to create a responsive material. We could draw inspiration from this work for our own systems. However, I think it is important to notice that there is no reversibility in the contraction of this gel. Therefore, once the irradiation is done, we cannot call the remaining polymer: "responsive".

Making Coaxial Wires Out of Janus Dendrimers for Efficient Charge Transport

Iguarbe, V.; Concellón, A.; Termine, R.; Golemme, A.*; Barberá, J.*; Serrano, J. L.* *ACS Macro Lett.* **2018**, *7*, 1138−1143.

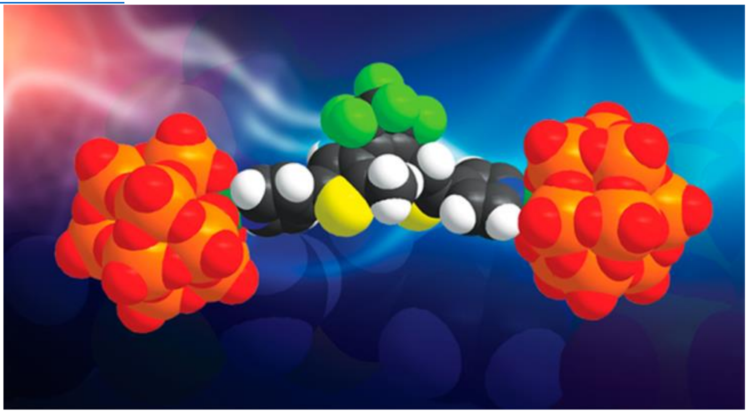


Highly conductive coaxial supramolecular wires are prepared by using a new family of Janus dendrimers that combines two rigid aromatic parts and two flexible aliphatic parts. The two external regions consist of a promesogenic block based on a third generation Percec-type dendron with four terminal dodecyloxy alkyl chains, whereas the two internal regions are formed by one, two, or three carbazole units bearing flexible spacers. These functional Janus dendrimers self-organize in columnar liquid crystal phases with a strong coaxial segregation within each column. Interestingly, the charge mobility studies revealed that these Janus dendrimers display semiconductor properties with hole mobility values up to 0.5 $cm^2 V^{-1} s^{-1}$, depending on the packing within the columns which can be tuned by the number of carbazole functional units. The high hole mobility values measured in these materials are among the highest values reported for columnar liquid crystals.

Comment: The authors synthesized a new family of dendrimers to obtain materials that combine the good luminescent and charge-transport properties of the carbazole unit with the columnar organization of the dendron.

Visible-Light-Driven "On"/"Off" Photochromism of a Polyoxometalate Diarylethene Coordination Complex

Xu, J.; Volfova, H.; Mulder, R. J.; Goerigk, L.; Bryant, G.; Riedle, E.; Ritchie, C.* *J. Am. Chem. Soc.* **2018**, *140*, 10482-10487.

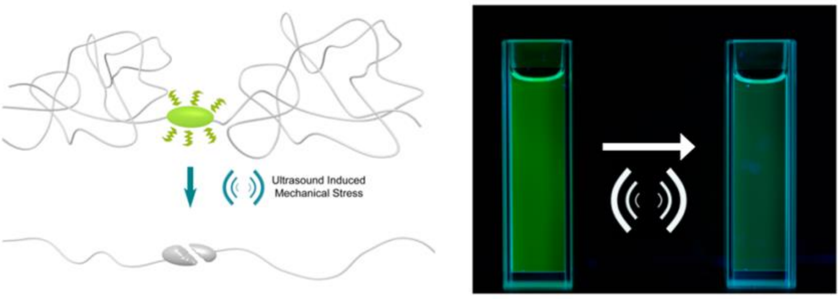


Herein **we report the first photochromic polyoxometalate (POM)-based diarylethene (DAE) coordination complex**, prepared by ligation of two cobalt(III)-incorporated borotungstates $[B^{III}W^{VI}{}_{11}O_{39}Co^{III}]^{6-}$ with theditopic pyridyl-containing diarylethene ($C_{25}H_{16}N_2F_6S_2$). The solution-state composition, structure, and stability of the assembly were probed using 1H and 19F nuclear magnetic resonance spectroscopy (NMR), electrospray ionization quadrupolar time-of-flight mass spectrometry (ESI-QTOFMS), ultraviolet−visible spectroscopy (UV−vis), and smallangle X-ray scattering (SAXS), revealing that the complex selforganizes to adopt a molecular dumbbell structure due to electrostatic and steric considerations. This conformation is a prerequisite for the photocyclization reaction. **The assembly was found to be switchable** between two states using visible light due to the perturbation of the DAE electronic structure on coordination to the POM. We present photophysical data, including the reaction quantum efficiency of the molecular switch in both directions measured using a custom-built quantum yield determination setup in addition to fatigue resistance on prolonged irradiation.

Comment: This paper describes the formation of a coordination complex between polyoxometalate and diarylethene. It appears to be a promising way to improve the photochromic efficiency of diarylethene derivatives.

Mechanochemical Fluorescence Switching in Polymers Containing Dithiomaleimide Moieties

Karman, M.; Verde-Sesto, E.; Weder, C.*; Simon, J. C.* *ACS Macro Lett.* **2018**, *7*, 1099−1104.

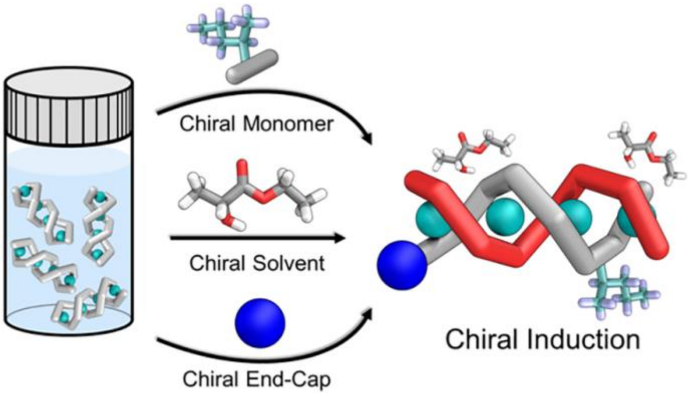


Polymers that display useful mechanochemical responses, such as changes of their fluorescence characteristics, are attracting great interest. Here, we introduce the fluorescent dithiomaleimide (DTM) motif as a mechanofluorophore and report the mechanoresponse of two polymer types containing this motif. Poly(methyl acrylate) (PMA) and poly(ε-caprolactone)s (PCL) featuring one DTM moiety in the center of each chain (PMA-DTM and PCL-DTM) were synthesized by controlled radical and coordination−insertion ring-opening polymerizations using bifunctional DTM-containing initiators. Upon ultrasonic treatment of PMA-DTM or PCLDTM of sufficiently high initial molecular weight, both the molecular weight and the fluorescence intensity decreased with similar kinetics, while no significant fluorescence changes were observed for DTM-free reference polymers. The results show that the DTM motif can serve as a mechanophore that displays a mechanically induced fluorescence turn-off.

Comment: Here are described two mechanoresponsive materials in which the application of a mechanical stress induces a change in their fluorescence properties.

Unraveling Mechanisms of Chiral Induction in Double-Helical Metallopolymers

Greenfield, J. L.; Evans, E. W.; Di Nuzzo, D.; Di Antonio, M.; Friend, R. H.*; Nitschke, J. R.* *J. Am. Chem. Soc.* **2018**, *140*, 10344-10353.

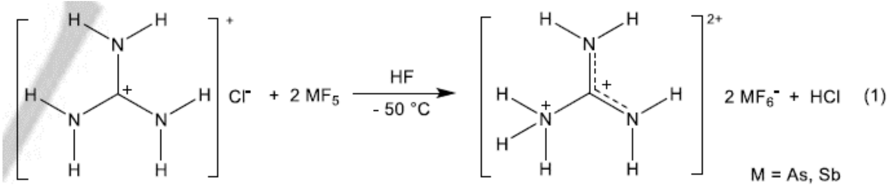


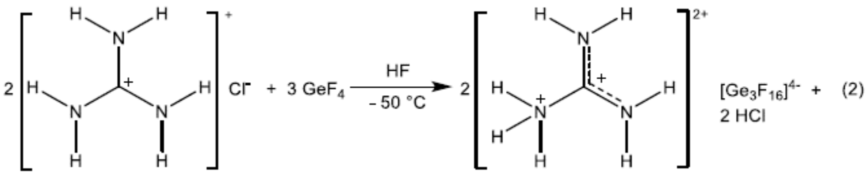
Self-assembled helical polymers hold great promise as new functional materials, where helical handedness controls useful properties such as circularly polarized light emission or electron spin. The technique of subcomponent self-assembly can generate helical polymers from readily prepared monomers. Here we present three distinct strategies for chiral induction in double-helical metallopolymers prepared via subcomponent self-assembly: (1) employing an enantiopure monomer, (2) polymerization in a chiral solvent, (3) using an enantiopure initiating group. Kinetic and thermodynamic models were developed to describe the polymer growth mechanisms and quantify the strength of chiral induction, respectively. We found the degree of chiral induction to vary as a function of polymer length. Ordered, rod-like aggregates more than 70 nm long were also observed in the solid state. Our findings provide a basis to choose the most suitable method of chiral induction based on length, regiochemical, and stereochemical requirements, allowing stereochemical control to be established in easily accessible ways.

Comment: This paper provides design rules to obtain chiral supramolecular polymers. The authors explore three different methods of chirality induction and provide us with the pros and cons of these approaches. I wonder if the authors have tried to use mixtures of chiral and achiral solvents to control the handedness of their helical polymers.

The Diprotonation of Guanidine in Superacidic Solutions

Morgenstein, Y.; Zischka, F.; Kornath, A.* *Chem. Eur. J.* **2018**, *Just Accepted.*



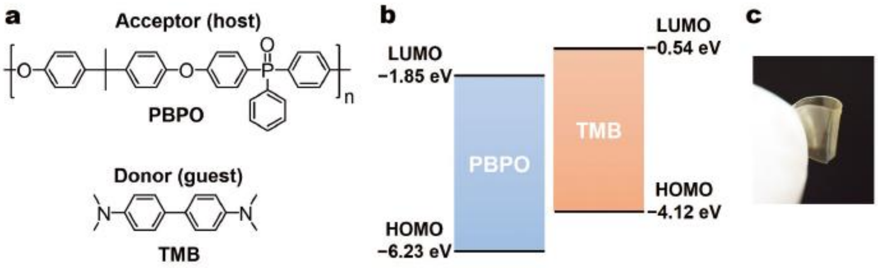


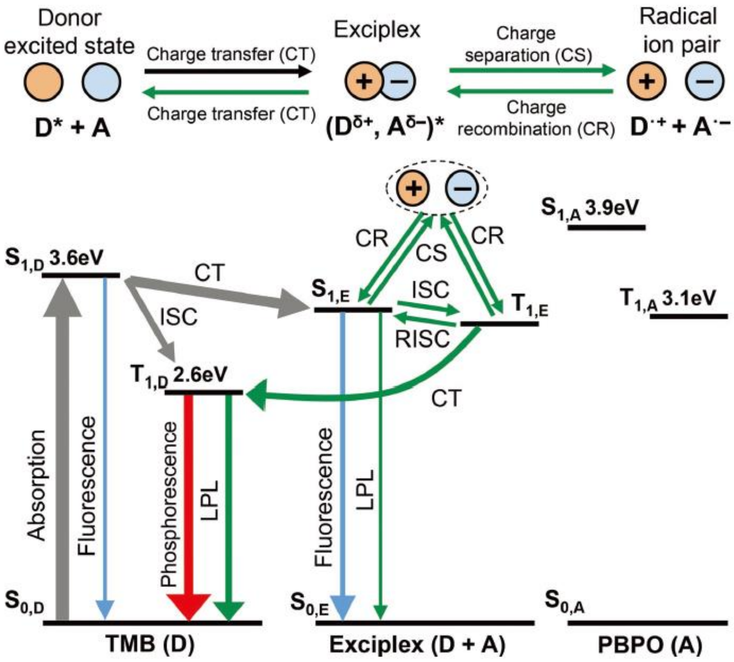
Guanidinium chloride reacts with the superacidic solutions HF/MF$_5$ (M = As, Sb) at a molar ratio of one to two under formation of the diprotonated guanidinium salts [C(NH$_2$)$_2$(NH$_3$)][AsF$_6$]$_2$ (1) and [C(NH$_2$)$_2$(NH$_3$)][SbF$_6$]$_2$ (3). The compounds were characterized by infrared and Raman spectroscopy. Furthermore, single crystal X-ray structure analysis of the guanidinium(2+) salts [C(NH$_2$)$_2$(NH$_3$)][SbF$_6$]$_2$·HF (5), [C(NH$_2$)$_2$(NH$_3$)]$_2$[Ge$_3$F$_{16}$]·HF (6) and [C(NH$_2$)$_2$(NH$_3$)]$_2$[Ge$_3$F$_{16}$]·2HF (7) and the guanidinium(1+) salt [C(NH$_2$)$_3$][SbF$_6$] (4) are reported. The discussion of the experimental data is supported by quantum chemical calculations of the [C(NH$_2$)$_2$(NH$_3$)]$^{2+}$ cation and the [C(NH$_2$)$_3$]$^{+}$ cation in order to investigate the modification of the resonance stabilization over the protonation process at the PBE1PBE/6−311G++(3df,3pd) level of theory. The planar CN3 skeleton of the guanidinium(2+) has two C N bonds in the range of 1.286(4) to 1.293(4) Å and one C N bond with 1.453(4) Å, which can be explained with a decreased resonance stabilization compared to the guanidinium(1+) cation.

Comment: The nitrogen analog of carbonic acid (guanidine) has been isolated for the first time as a diprotonated salt in superacidic media. This is quite remarkable knowing that the monoprotonated species is a very stable cation. By the way, did you know guanidine was first synthesized in **1861**? This is the same year in which **Frederick G. Hopkins** (Nobel Prize in Medicine) was born and **William Wrigley, Jr.** (the American chewing gum industrialist).

Organic Long-Persistent Luminescence from a Flexible and Transparent Doped Polymer

Lin, Z.; Li, J.; Kabe, R. *; Nishimura, N.; Jinnai, K.; Adachi, C.* *Adv. Mater.* **2018**, 1803713.



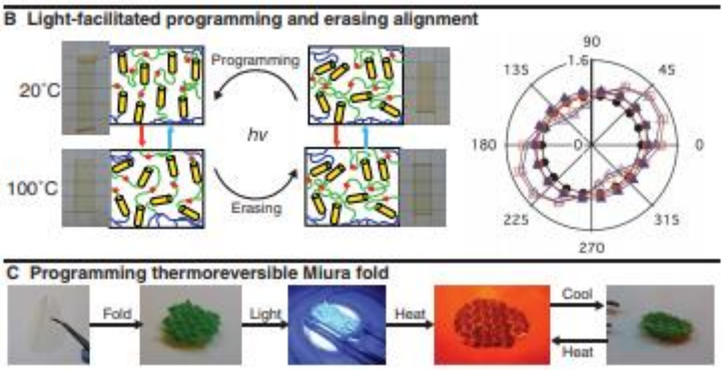


Long-persistent luminescence (LPL) materials have a wide range of applications, such as in architectural decorations, safety signs, watch dials, and glow-in-the-dark toys. Present LPL materials based on inorganics must be processed into powders and blended with polymer matrices before use. However, micropowders of inorganic LPL materials show poor compatibility with common polymers, limiting the mechanical properties and transparency of the composites. Here, a polymer-based organic LPL (OLPL) system that is flexible, transparent, and solution processable is reported. Following low-power excitation at room temperature, this polymer-based OLPL system exhibits LPL after phosphorescence from the donor.

Comment: To me, it is an amazing piece of research: First because I do not understand well about photoluminescence mechanism but mainly since this work demonstrates a polymer-based organic long-persistent luminescence system, which exhibits good mechanical flexibility and deformability. However, **the soul of this paper is the explanation of OLPL**, which mainly originates from the triplet state of the donor molecule, and is followed by a charge separation process. If you are also interested in the LPL or phosphorescence, read it and you will get something useful.

A Readily Programmable, Fully Reversible Shape-Switching Material

McBride, M. K.; Martinez, A. M.; Cox, L.; Alim, M.; Childress, K.; Beiswinger, M.; Podgorski, M.; Worrell, B. T.; Killgore, J.; Bowman, C. N. *Sci. Adv.* **2018**, *4*, ASAP.

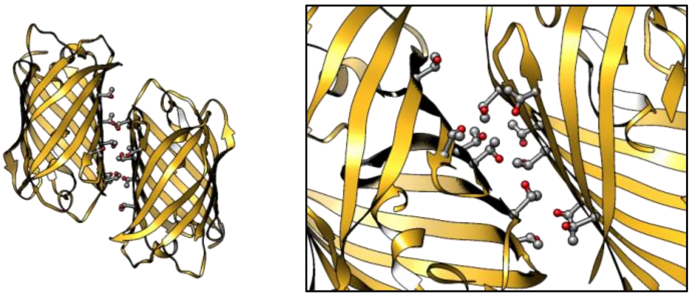


Liquid crystalline (LC) elastomers (LCEs) enable large-scale reversible shape changes in polymeric materials; however, they require intensive, irreversible programming approaches in order to facilitate controllable actuation. We have implemented **photoinduced dynamic covalent chemistry** (DCC) that chemically anneals the LCE toward an applied equilibrium only when and where the light-activated DCC is on. By using light as the stimulus that enables programming, the dynamic bond exchange is orthogonal to LC phase behavior, enabling the LCE to be annealed in any LC phase or in the isotropic phase with various manifestations of this capability explored here. In a photopolymerizable LCE network, we report the synthesis, characterization, and **exploitation of readily shape-programmable DCC functional LCEs** to create predictable, complex, and fully reversible shape changes, thus enabling the literal square peg to fit into a round hole.

Comment: Programmable (by light, heating and stretching) shape-changing material based on liquid crystalline elastomers with dynamic covalent bonds. They added radical-mediated addition-fragmentation chain transfer functionalities not for the chain extension control but as dynamic covalent function.

A Threonine Zipper That Mediates Protein-Protein Interactions: Structure and Prediction

Oi, C.; Treado, J. D.; Levine, Z. A.; Lim, C. S.; Knecht, K. M.; Xiong, Y.; O'Hern, C. S.; Regan, L.* *Protein Sci.* **2018**, *Just Accepted.*

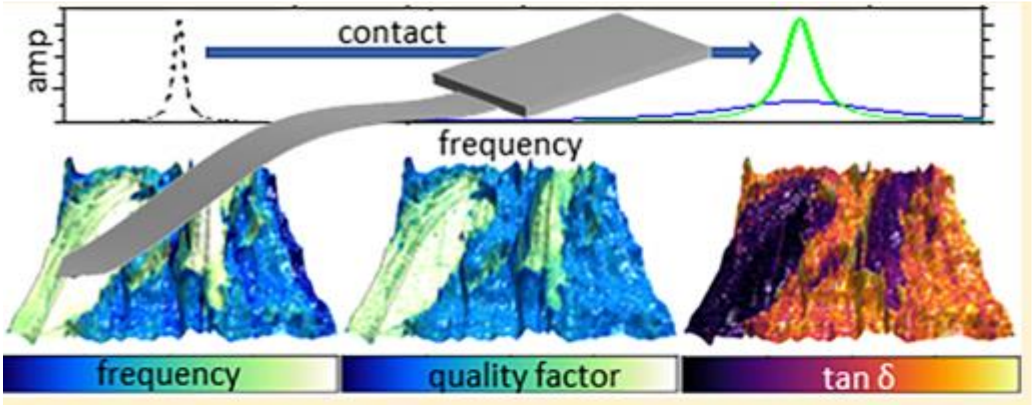


We present the structure of an engineered **protein-protein interface** between **two beta barrel proteins**, which is mediated by interactions between threonine (Thr) residues. This **Thr zipper** structure suggests that the protein interface is stabilized by close-packing of the Thr residues, with only one inter-monomer hydrogen bond (H-bond) between two of the Thr residues. This Thr-rich interface provides a unique opportunity to study the behavior of Thr in the context of many other Thr residues. In previous work, we have shown that the side chain ($\chi 1$) dihedral angles of interface and core Thr residues can be predicted with high accuracy using **a hard sphere plus stereochemical constraint (HS) model**. Here, we demonstrate that in the Thr-rich local environment of the Thr zipper structure, we are able to predict the $\chi 1$ dihedral angles of most of the Thr residues. Some, however, are not well predicted by the HS model. We therefore employed explicitly solvated **molecular dynamics (MD) simulations** to further investigate the side chain conformations of these residues. The MD simulations illustrate the role that transient H-bonding to water, in combination with steric constraints, play in determining the behavior of these Thr side chains.

Comment: This is a short investigation on a new protein-protein interaction (PPI) interface. The authors used both X-ray crystallography and two computational methods (HS and MD) to determine the structural basis of this newly (serendipitously) discovered Thr interface (also called a zipper) in between two beta barrels. By the way, PPIs are very critical in modern drug discovery and represent one of the most sought-after targets to disrupt. Also, you might've already heard about leucine zippers which are ubiquitous PPIs both in nature "and in the literature".

Contact Resonance Force Microscopy for Viscoelastic Property Measurements: From Fundamentals to State-of-the-Art Applications

Killgore, J.; DelRio, F. *Macromolecules* **2018**, *ASAP.*

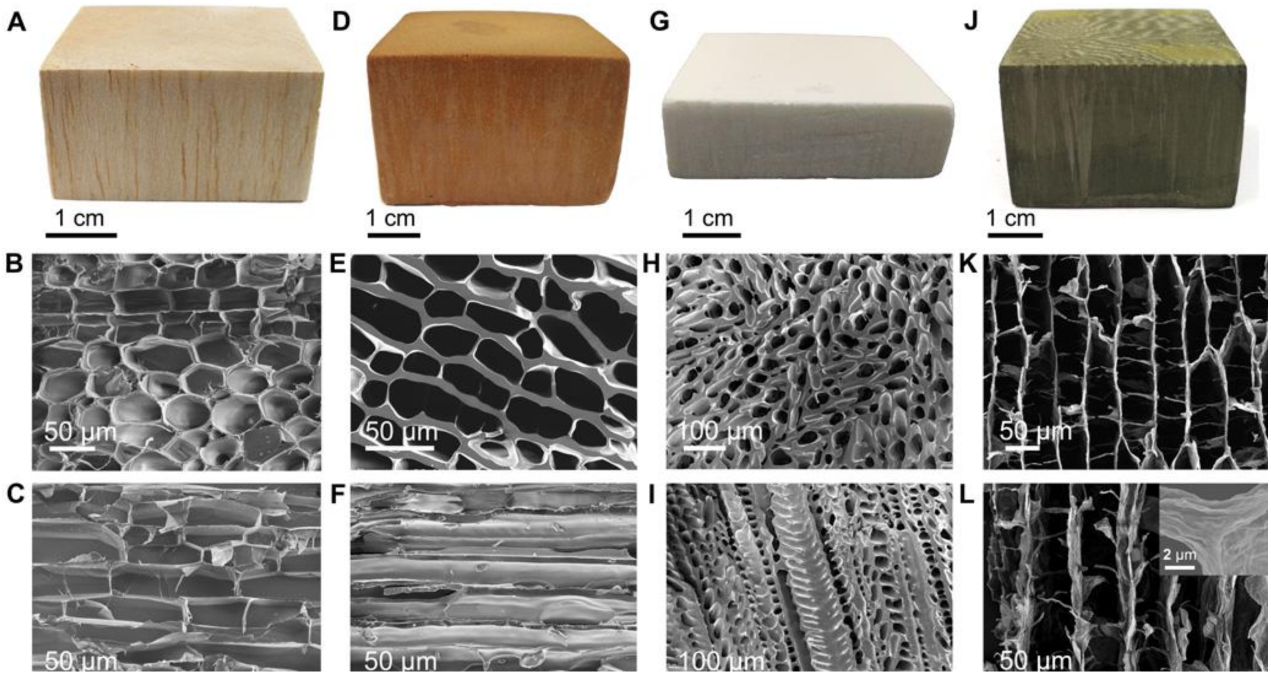


Contact resonance force microscopy (CRFM) is an atomic force microscopy (AFM) method that evolvedfrom a curiosity about the detection of ultrasonic vibrationswith an AFM cantilever and an unaddressed need tocharacterize the mechanical properties of stiffer materials(elastic modulus >50 GPa). The method has matured to allownear-surface and subsurface elastic property measurements ofsingle crystals, thin films, nanomaterials, composites, andother advanced materials. More recently, CRFM has beenextended to viscoelastic property measurements, where the CR frequency and CR quality factor are utilized to quantitatively assess properties such as storage modulus, loss modulus, andloss tangent. In this Perspective, we trace the evolution of CRFM from initial discovery to elastic property measurements to viscoelastic property measurements. The techniques for extending single-point property measurements to **two-dimensional property maps** are then described in terms of their operational characteristics, demonstrated on calibration materials, and validated via comparisons to other viscoelastic measurement tools. The focus of the discussion then shifts to viscoelastic CRFM in nonambient conditions to highlight the challenges and developments related to thermomechanical analyses and liquid operation. The current state-of-the-art and best practices in data acquisition and analyses for viscoelastic CRFM are elucidated via a step-by-step demonstration on a wood −polymer composite. Finally, we conclude with a discussion of potential polymer science application areas that are poised to benefit from the recent advances in the ambient and nonambient CRFM methodologies. Altogether, we feel that the recent addition of CRFM to commercially available AFMs together with guides that clearly define state-of-the-art and best practices will accelerate its acceptance and adoption in polymer science via viscoelastic property measurements at unprecedented length and time scales

Comment: A current review that should be interesting for those who would like to go deeper into AFM applications. The authors briefly discuss the possibility to use contact resonance force microscopy to measure storage and loss modulii and create the map of mechanical parameters of viscoelastic materials.

Bioinspired Polymeric Woods

Yu, Z.-L.*; Yang, N.*; Zhou, L.-C.; Ma, Z.-Y.; Zhu, Y.-B.; Lu, Y.-Y.; Qin, B.; Xing, W.-Y.; Ma, T.; Li, S.-C.; Gao, H.-L.; Wu, H.-A.; Yu, S.-H. *Sci. Adv.* **2018**, *4*, eaat7223.

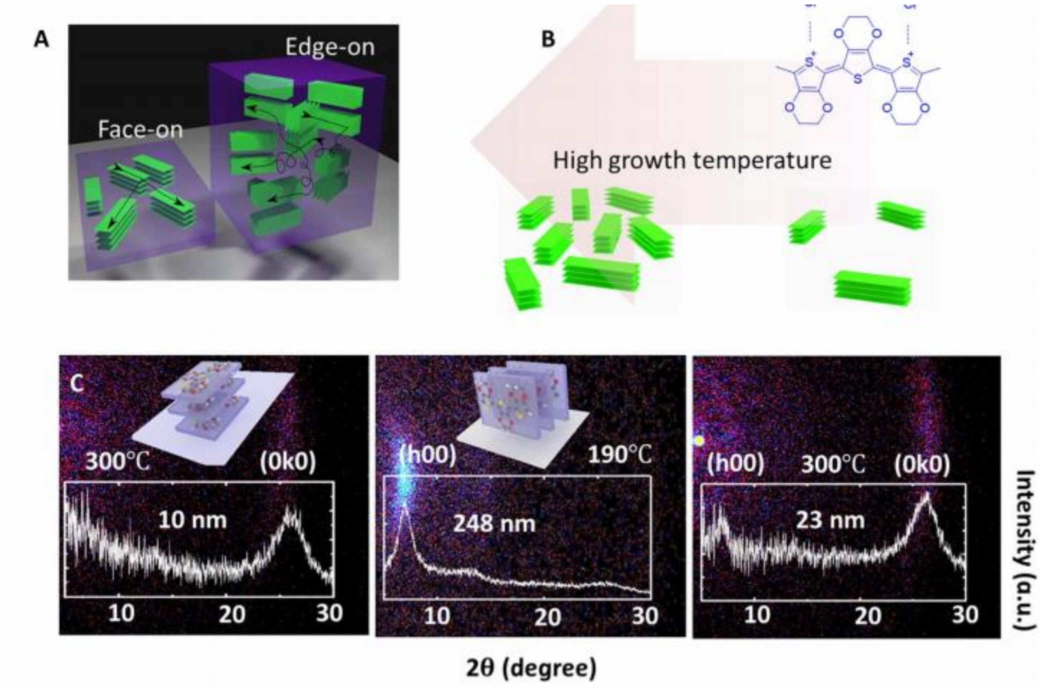


Woods provide bioinspiration for engineering materials due to their superior mechanical performance. We demonstrate a novel strategy for large-scale fabrication of a family of bioinspired polymeric woods with similar polyphenol matrix materials, wood-like cellular microstructures, and outstanding comprehensive performance by a self-assembly and thermocuring process of traditional resins. In contrast to natural woods, polymeric woods demonstrate comparable mechanical properties (a compressive yield strength of up to 45 MPa), preferable corrosion resistance to acid with no decrease in mechanical properties, and much better thermal insulation (as low as ~21 mW m^{-1} K^{-1}) and fire retardancy. These bioinspired polymeric woods even stand out from other engineering materials such as cellular ceramic materials and aerogel-like materials in terms of specific strength and thermal insulation properties. The present strategy provides a new possibility for mass production of a series of high-performance biomimetic engineering materials with hierarchical cellular microstructures and remarkable multifunctionality.

Comment: They proposed an "artificial wood" composite synthesized using commercially available materials (starting solution included water soluble thermoset resins, chitosan, and acetic acid). The obtained materials have good mechanical performances.

High electrical conductivity and carrier mobility in oCVD PEDOT thin films by engineered crystallization and acid treatment

Wang, X.; Zhang, X.; Sun, L.; Lee, D.; Lee, S.; Wang, M.; Zhao, J.; Shao-Horn, Y.; Dincă, M.; Palacios, T.; Gleason, K. K. *Sci. Adv.* **2018**, *4*, eaat5780.

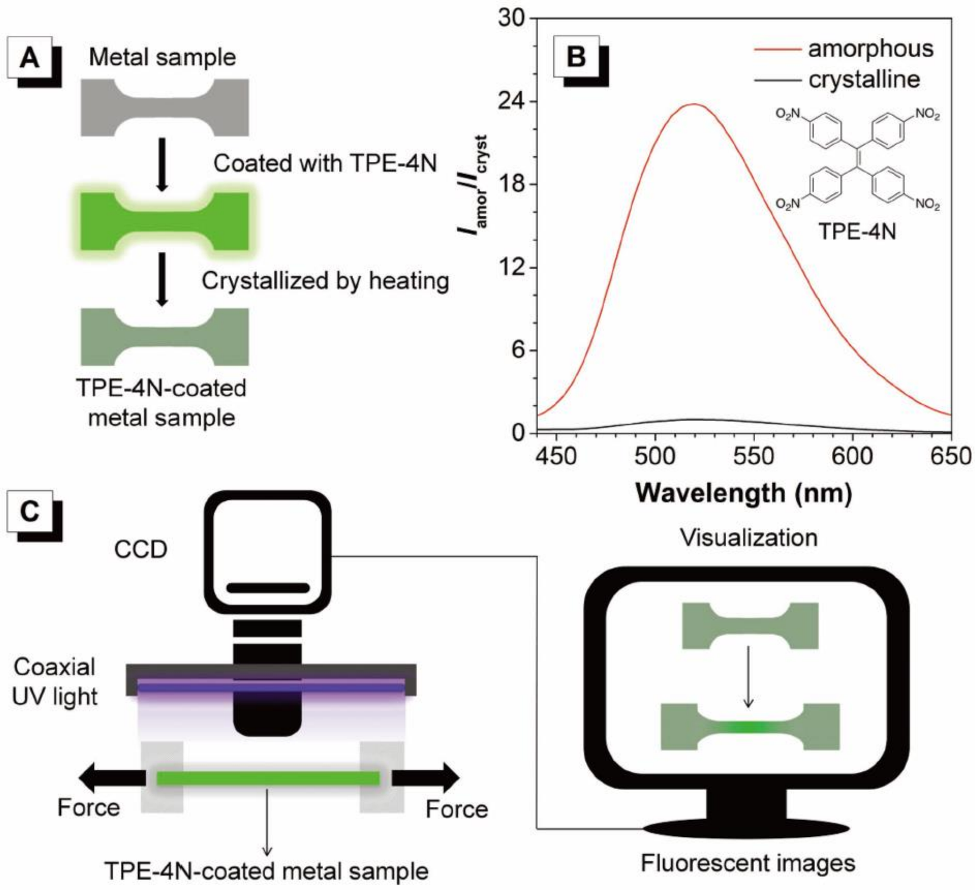


Air-stable, lightweight, and electrically conductive polymers are highly desired as the electrodes for next-generation electronic devices. However, the low electrical conductivity and low carrier mobility of polymers are the key bottlenecks that limit their adoption. We demonstrate that the key to addressing these limitations is to molecularly engineer the crystallization and morphology of polymers. We use oxidative chemical vapor deposition (oCVD) and hydrobromic acid treatment as an effective tool to achieve such engineering for conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT). We demonstrate PEDOT thin films with a record-high electrical conductivity of 6259 S/cm and a remarkably high carrier mobility of 18.45 $cm^2 V^{-1} s^{-1}$ by inducing a crystallite-configuration transition using oCVD. Subsequent theoretical modeling reveals a metallic nature and an effective reduction of the carrier transport energy barrier between crystallized domains in these thin films. To validate this metallic nature, we successfully fabricate PEDOT-Si Schottky diode arrays operating at 13.56MHz for radio frequency identification(RFID)readers, demonstrating wafer-scale fabrication compatible with conventional complementary metal-oxide semiconductor (CMOS) technology. The oCVD PEDOT thin films with ultrahigh electrical conductivity and high carrier mobility show great promise for novel high-speed organic electronics with low energy consumption and better charge carrier transport.

Comment: Highly conductive thin films have been proposed. I enjoyed the clear theoretical explanations.

Dynamic Visualization of Stress/Strain Distribution and Fatigue Crack Propagation by an Organic Mechanoresponsive AIE Luminogen

Qiu, Z.; Zhao, W.; Cao, M.; Wang, Y.; Lam, J. W. Y.; Zhang, Z.*; Chen, X.; Tang, B. Z.* *Adv. Mater.* **2018**, 1800629.

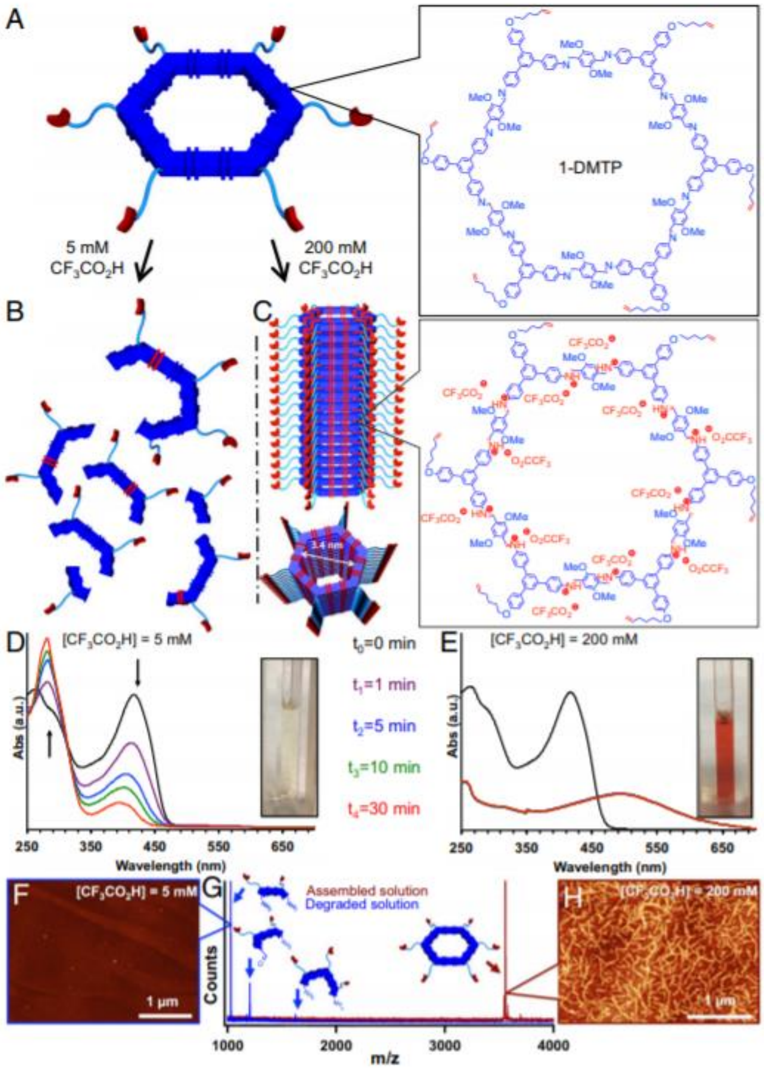


Stress exists ubiquitously and is critically important for the manufacturing industry. Due to the ultrasensitive mechanoresponse of the emission of 1,1,2,2,-tetrakis(4-nitrophenyl)ethane (TPE-4N), a luminogen with aggregation-induced emission characteristics, the visualization of stress/strain distributions on metal specimens with a pure organic fluorescent material is achieved. Such a fluorescence mapping method enjoys the merits of simple setup, real-time, full-field, on-site, and direct visualization. Surface analysis shows that TPE-4N can form a nonfluorescent, crystalline uniform film on the metal surface, which cracks into fluorescent amorphous fragments upon mechanical force. Therefore, the invisible information of the stress/strain distribution of the metal specimens are transformed to visible fluorescent signals, which generally matches well but provides more details than software simulation. Remarkably, fatigue crack propagation in stainless steel and aluminum alloy can be observed and predicted clearly, further demonstrating the ultrasensitivity and practicability of TPE-4N.

Comment: It looks very simple. Actually, this paper is mainly based on their previous research (DOI: 10.1038/s41467-018-05476-y). The interesting point is that the TPE core shows no fluorescence when substituted with enough nitrophenyl moieties due to intersystem crossing. In this research, they utilized this special mechanoresponsive property to monitor the fracture of a material.

High aspect ratio nanotubes assembled from macrocyclic iminium salts

Sun, C.; Shen, M.; Anton, C.; Austin. E.; Liu, X.; Boris, H.; Nathan, F.; Mark, H.; Michael, B.; Monica, O.; Dichtel, W.; *Proc. Nat. Acad. Sci. USA. 2018, 115, 8883.*



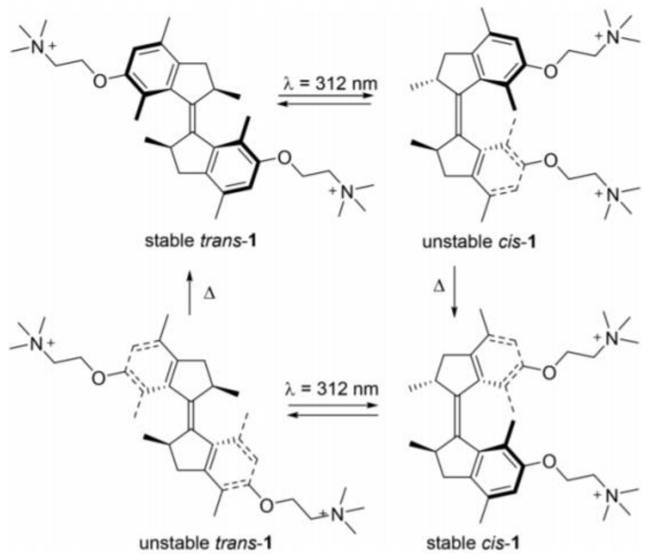
One-dimensional nanostructures such as carbon nanotubes and actin filaments rely on strong and directional interactions to stabilize their high aspect ratio shapes. This requirement has precluded making isolated, long, thin organic nanotubes by stacking molecular macrocycles, as their noncovalent stacking interactionsare generally too weak. Here we report high aspect ratio (>103), lyotropic nanotubes of stacked, macrocyclic, iminium salts, which are formed by protonation of the corresponding imine-linked macrocycles. Iminium ion formation establishes cohesive interactions that, in organic solvent (tetrahydrofuran), are two orders of magnitude stronger than the neutral macrocycles, as explained by physical arguments and demonstrated by molecular dynamics simulations. Nanotube formation stabilizes the iminium ions, which otherwise rapidly hydrolyze, and is reversed and restored upon addition of bases and acids. Acids generated by irradiating a photoacid generator or sonicating chlorinated solvents also induced nanotube assembly, allowing these nanostructures to be coupled to diverse stimuli, and, once assembled, they can be fixed permanently by cross-linking their pendant alkenes. As large macrocyclic chromonic liquid crystals, these iminium salts are easily accessible through a modular design and provide a means to rationally synthesize structures that mimic the morphology and rheology of carbon nanotubes and biological tubules.

Comment: By using the bottom-up strategy, the isolated hexagonal imine-linked MCs bearing alkyl solubilizing groups can assembled into nanotubes. This paper provides synthetic routes to functional nanotubes with accessible interiors which could have huge potential applications.

Molecular Motors in Aqueous Environment

Lubbe, A.; Böhmer, C.; Tosi, F.; Szymanski, W.; Feringa, B.* *J. Org. Chem. 2018.ASAP.*

Scheme 1. Structure and Four-Step Rotation Cycle of Proposed Water-Soluble Motor 1 (counterions omitted for clarity)

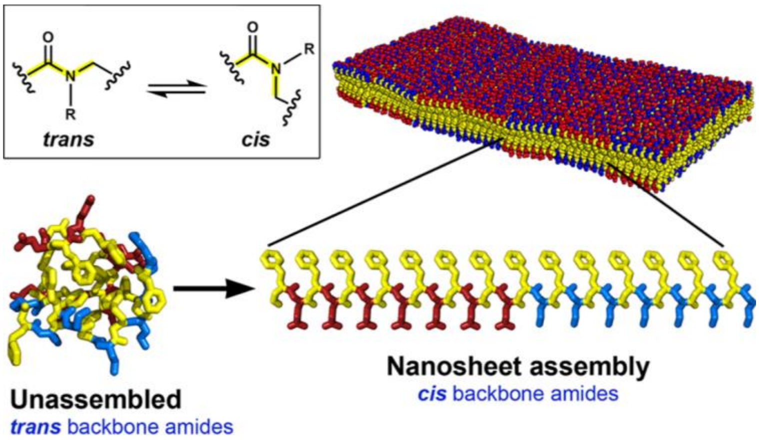


Molecular motors are Nature’s solution for (supra)molecular transport and muscle functioning and are involved in most forms of directional motion at the cellular level. Their synthetic counterparts have also found a myriad of applications, ranging from molecular machines and smart materials to catalysis and anion transport. Although light-driven rotary molecular motors are likely to be suitable for use in an artificial cell, as well as in bionanotechnology, thus far they are not readily applied under physiological conditions. This results mainly from their inherently aromatic core structure, which makes them insoluble in aqueous solution.Here, the study of the dynamic behavior of these motors in biologically relevant media is described. Two molecular motors were equipped with solubilizing substituents and studied in aqueous solutions. Additionally, the behavior of a previously reported molecular motor was studied in micelles, as a model system for the biologically relevant confined environment. Design principles were established for molecular motors in these media, and insights are given into pH-dependent behavior. The work presented herein may provide a basis for the application of the remarkable properties of molecular motors in more advanced biohybrid systems.

Comment: Quaternary ammonium salt is a useful solubilizing substituent, which was easily appended to a molecular motor. Such water-soluble molecular motors are proposed to be extremely useful in several areas of biological sciences. This paper may provide insights about the preparation and applications of molecular motors.

Evidence for cis Amide Bonds in Peptoid Nanosheets

Hudson, B. C.; Battigelli, A.; Connolly, M. D.; Edison, J.; Spencer, R. K.; Whitelam, S.; Zuckermann, R. N.*; Paravastu, A. K.* *J. Phys. Chem. Lett.* **2018**, *9*, 2574.

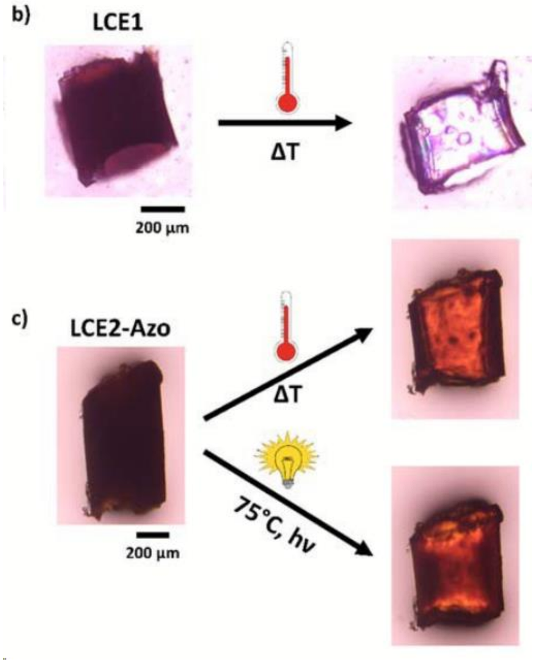


Peptoid nanosheets are supramolecular protein-mimetic materials that form from amphiphilic polypeptoids with aromatic and ionic side chains. Nanosheets have been studied at the nanometer scale, but the molecular structure has been difficult to probe. **We report the use of ^{13}C–^{13}C dipolar recoupling solid-state NMR measurements to reveal the configuration of backbone amide bonds selected by ^{13}C isotopic labeling of adjacent α-carbons.** Measurements on the same molecules in the amorphous state and in nanosheets revealed that amide bonds in the center of the amino block of peptoid $(NaeNpe)_7$–$(NceNpe)_7$ (B28) favor the *trans* configuration in the amorphous state and the *cis* configuration in the nanosheet. This unexpected result contrasts with previous NMR and theoretical studies of short solvated peptoids. Furthermore, examination of the amide bond at the junction of the two charged blocks within B28 revealed a mixture of both *cis* and *trans*configurational states, consistent with the previously predicted brickwork-like intermolecular organization.

Comment: Many of you have certainly already been in the situation of having an NMR where the cis/trans isomers of an amide made everything look awful. Well, it appears that making our lives difficult is not the only use of such an isomerism. That being said, although the study is sound, you might not be overwhelmed by the paper.

Actuating Thermo- and Photo-Responsive Tubes from Liquid Crystalline Elastomers

Braun, L. B.; Hessberger, T.; Pütz, E.; Müller, C.; Giesselmann, F.; Serra, C. A.; Zentel, R.* *J. Mater. Chem. C* **2018**, *6*, 9093–9101.



Large (many mm long) closed tubes from liquid crystalline (LC)-elastomers can be prepared in a microfluidic setup by photopolymerization of an LC-monomer mixture. In these tubes, the director of the LC-phase is oriented parallel to their long axes as proven by X-ray measurements, thus leading to shortening at the transition to the isotropic phase while their walls become thicker simultaneously. The process of tube preparation relies on an appropriate choice of 3 immiscible phases in the microfluidic setup (continuous, LC-monomer and inner phase) as well as their interfacial tensions. Water can be used as the inner phase in combination with a selective detergent (an amphiphilic block copolymer from PNIPAM and the LC-polymer) to reduce the LC/water surface tension. In this way, long actuating (up to 50%) tubes can be prepared either from a thermotropic LC-elastomer or from an azo-containing LC-elastomer with the latter being both thermo- and photo-responsive. By irradiation of individual tubes consisting of the azo-system with white (*trans–cis*) or red light (*cis–trans*), actuations of up to 29% can be achieved. The contraction (shortening) of the tubes thereby requires about 10 seconds, while the photochemical reisomerization needs about 230 seconds. This sets the time frame for the tubes' photochemical actuation.

Comment: Here, the main advance is a technical one: the liquid crystalline material is aligned in a microfluidic setup. It could allow for a large-scale preparation of monocrystalline LC tubes. One of the author (C. Serra) works at the ICS, so it is also interesting to keep in touch with what the other teams are doing (by the way, L. Biniek is also author of one of the articles addressing the same issue).