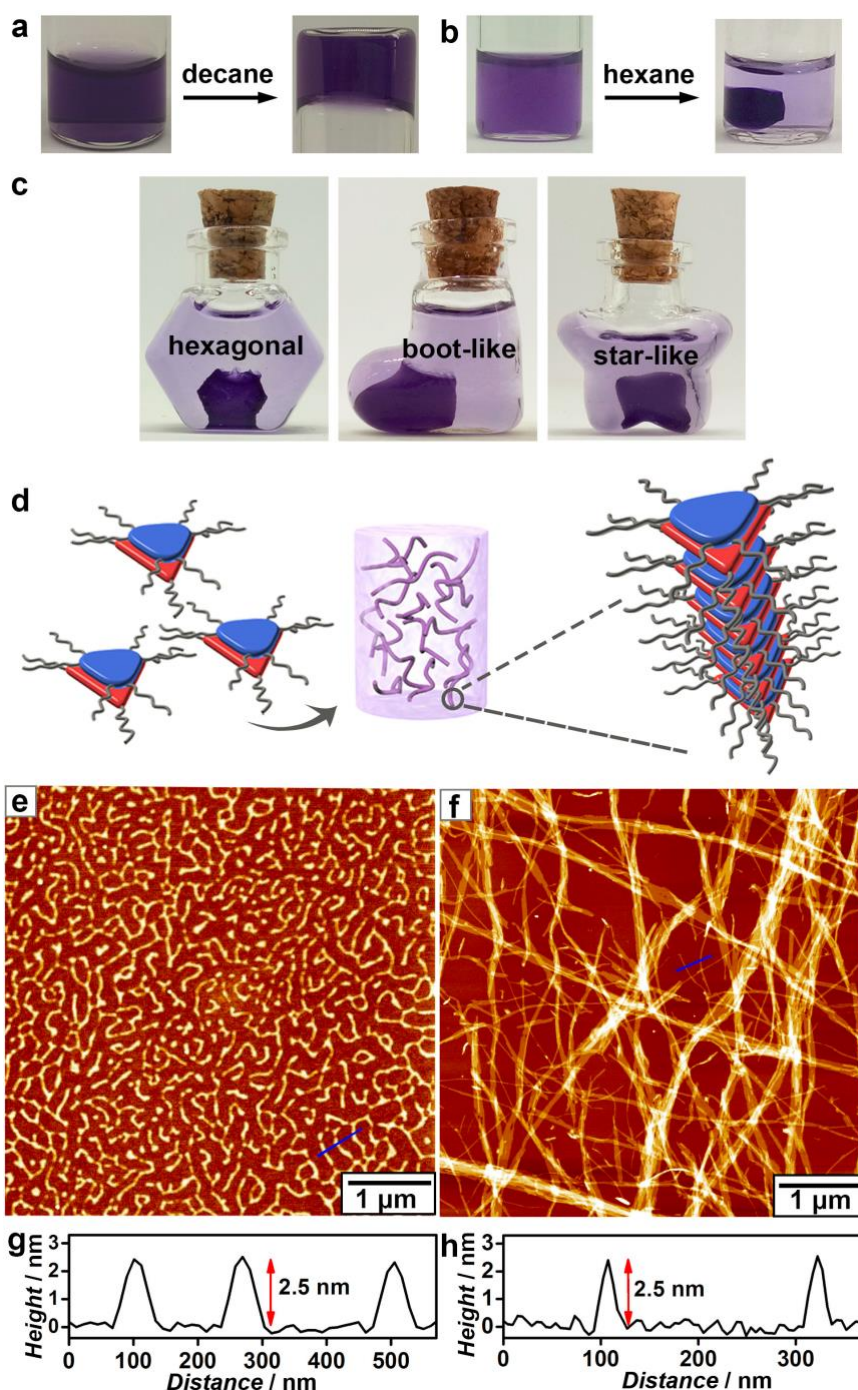


# Multi-Responsive Supramolecular Gels Based on Charge Transfer Interactions

Chen, L.; Chengshuo, S.; Jiucheng, N.; Huibin, Q.\* *Chem. Asian J.* **2018**, *Accepted Article*



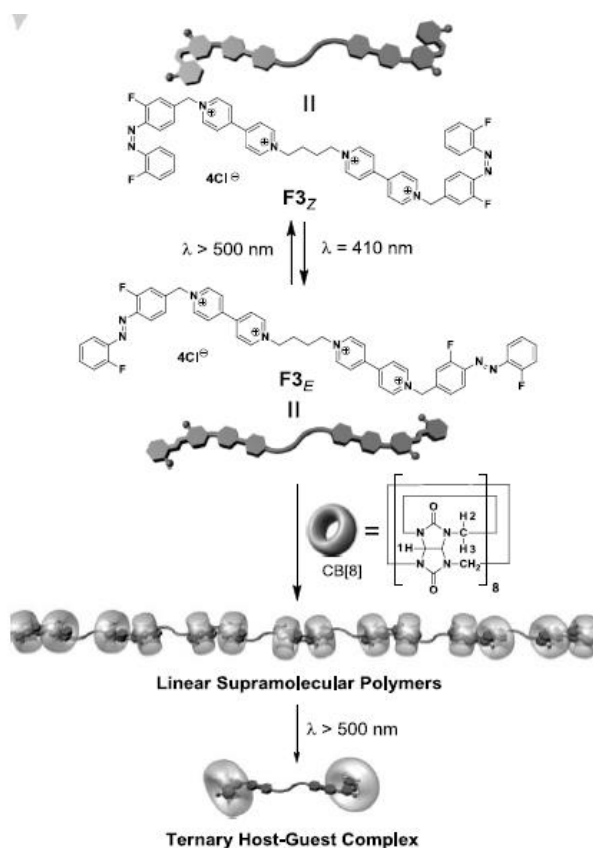
We report the co-assembly of aromatic donor (D) and acceptor (A) molecules into purple sponge-like supramolecular gels through susceptible charge transfer interactions with the aid of solvophobic interactions. The gel remained intact with the addition of up to 23 % (v/v) of nonpolar good solvents, such as toluene and xylene, but dissociated in the presence of <2 % (v/v) of polar solvents, such as tetrahydrofuran, ethyl acetate, and alcohols, with highly distinguishable changes of color. Notably, the gel dissolved within 1 min and the solution turned blue when 0.1 % (v/v) of

methanol was added. The response to trifluoroacetic acid was extremely sensitive (i.e., the gel vanished immediately in the presence of 2 equivalents of trifluoroacetic acid), and the subsequent addition of trimethylamine could recover the purple gel. The multiple and visible response thus render the D–A gels as a potential detector for sensing complex chemical environments.

**Comment:** It's an interesting work: the sponge-like gels can be used as a colored sensor.

### Tunable Water-Soluble Supramolecular Polymers via Visible Light Regulated Host-Guest Interactions

Kang-Da, Z.; Ting-Ting, J.; Xiao-He, Z.; Yong-Fei, Y.; Tian-Guang, Z.\*; Jiecheng, C.; Li-Juan, L.\*; Li-Chun, K.\* [Chem. Asian J. 2018, Accepted Article](#)



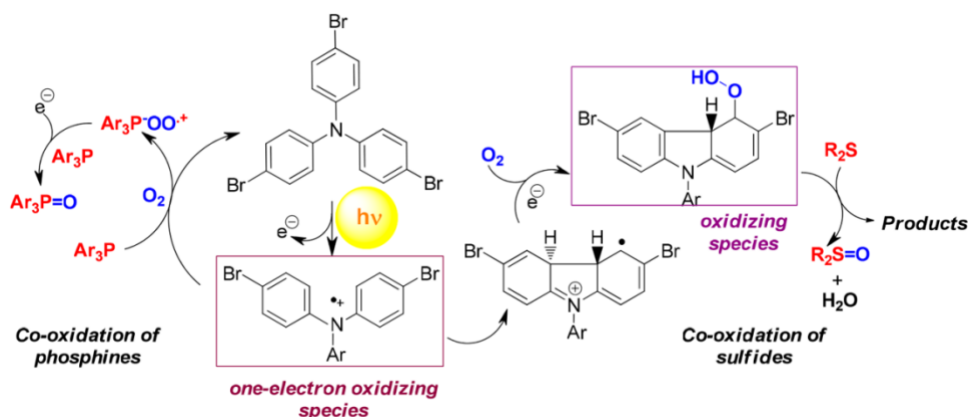
The development of artificial self-assembling systems with dynamic photo-regulation features in aqueous solutions has drawn great attention owing to the potential applications in fabricating elaborate biological materials. Here we demonstrate the fabrication of water-soluble cucurbit[8]uril (CB[8])-mediated supramolecular polymers by connecting the fluorinated azobenzene (FAB) containing monomer through host-enhanced multiple charge-transfer interactions. The formation of the supramolecular polymers could be regulated through the visible-light-induced E/Z photoisomerization of the FAB units, which determines the encapsulation behaviour between CB[8] macrocycle and the monomers.

**Comment:** The use of the visible-light induced E to Z-isomerization of azobenzene to depolymerize guest-host supramolecular polymers is very interesting.

## Photochemical Co-oxidation of Sulfides and Phosphines with Tris(*p*-bromophenyl)amine. A Mechanistic Study

Bonesi, S. M.\*; Protti, S.; Albini, A. *J. Org. Chem.* 2018, ASAP.

### BEGINNING

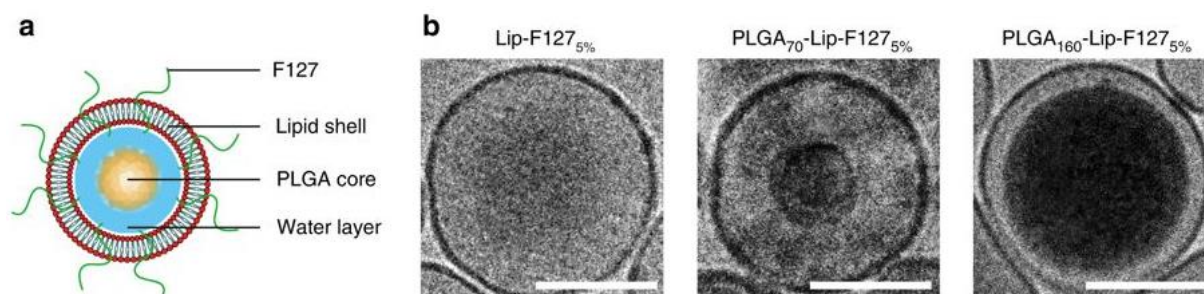


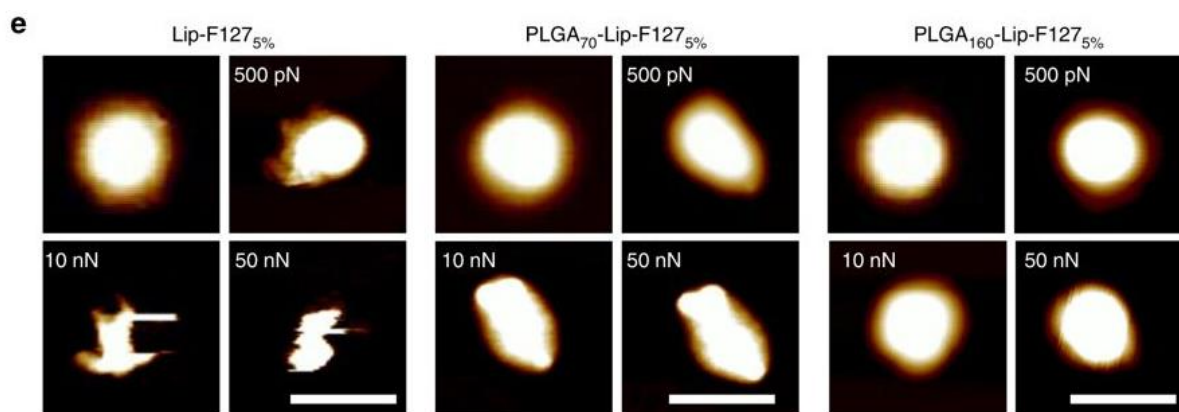
The photochemistry of tris(*p*-bromophenyl)amine was investigated in a nitrogen- and oxygen-flushed solution under laser flash photolysis conditions. The detected intermediates were the corresponding amine radical cation (“Magic Blue”) and the *N*-phenyl-4a,4b-dihydrocarbazole radical cation that, under an oxygen atmosphere, is converted to the corresponding hydroperoxyl radical. The role of the last species was supported by the smooth co-oxidation of sulfides to sulfoxides. On the other hand, co-oxidation of nucleophilic triarylphosphines to triarylphosphine oxides arose from an electron transfer between the photogenerated “Magic Blue” and phosphine that prevented the amine cyclization. In this case, intermediate  $\text{Ar}_3\text{P}^+\text{OO}^\bullet$  was found to play a key role in phosphine oxide formation.

**Comment:** This research gives insights to the single-electron-transfer based oxidation processes occurring between the so-called Magic Blue and triarylamine, which also highlights the possible use of triarylamine in photocatalysis.

## Rapid Transport of Deformation-tuned Nanoparticles Across Biological Hydrogels and Cellular Barriers

Yu, M.; Xu, L.; Tian, F.; Su, Q.; Zheng, N.; Yang, Y.; Wang, J.; Wang, A.; Zhu, C.; Guo, S.; Zhang, X.; Gan, Y.\*; Shi, X.\*; Gao, H.\* *Nat. Commun.* 2018, 9, 2607.



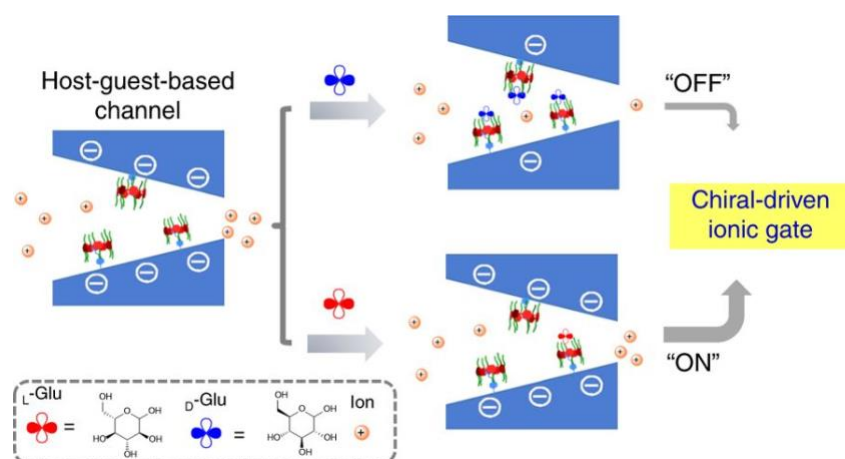


To optimally penetrate biological hydrogels such as mucus and the tumor interstitial matrix, nanoparticles (NPs) require physicochemical properties that would typically preclude cellular uptake, resulting in inefficient drug delivery. Here, we demonstrate that (poly(lactic-co-glycolic acid) (PLGA) core)-(lipid shell) NPs with moderate rigidity display enhanced diffusivity through mucus compared with some synthetic mucus penetration particles (MPPs), achieving a mucosal and tumor penetrating capability superior to that of both their soft and hard counterparts. Orally administered **semi-elastic NPs** efficiently overcome multiple intestinal barriers, and result in increased bioavailability of doxorubicin (Dox) (up to 8 fold) compared to Dox solution. Molecular dynamics simulations and super-resolution microscopy reveal that the semi-elastic NPs deform into ellipsoids, which enables rotation-facilitated penetration. In contrast, rigid NPs cannot deform, and overly soft NPs are impeded by interactions with the hydrogel network. Modifying particle rigidity may improve the efficacy of NP-based drugs, and can be applicable to other barriers.

**Comment:** One important problem of NPs(Au, SiO<sub>2</sub>...)-based drug delivery system is the clearance of these NPs from the circulatory system of the human body. Normally, NPs with different sizes will get accumulated in the kidney, spleen or liver, and can hardly be fully removed. It would be very interesting to test if these semi-elastic NPs could have better clearance properties.

### A biomimetic Chiral-driven Ionic Gate Constructed by Pillar[6]arene-based Host-guest Systems

Sun, Y.; Zhang, F.; Quan, J.; Zhu, F.; Hong, W.; Ma, J.; Pang, H.; Sun, Y.; Tian, D.; Li, H.\*  
[Nat. Commun. 2018, 9, 2617.](#)



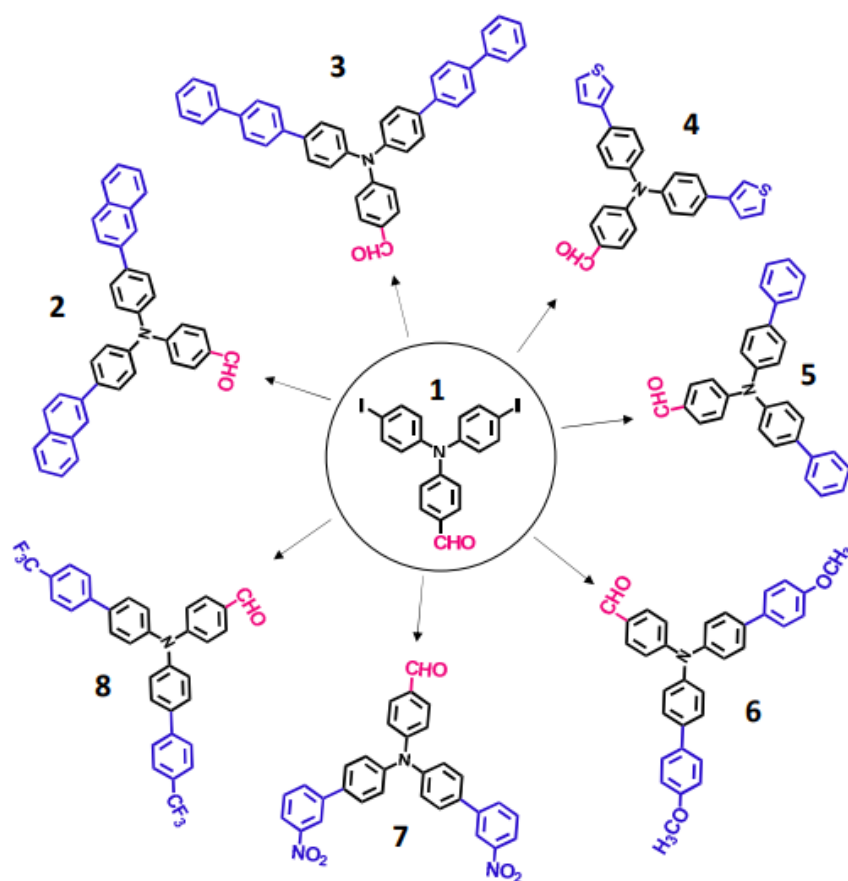


Inspired by glucose-sensitive ion channels, herein we describe a biomimetic glucose-enantiomer-driven ion gate via the introduction of the chiral pillar[6]arene-based host–guest systems into the artificial nanochannels. The chiral nanochannels show a high chiral-driven ionic gate for glucose enantiomers and can be switched “off” by D-glucose and be switched “on” by L-glucose. Remarkably, the chiral nanochannel also exhibited a good reversibility toward glucose enantiomers. Further research indicates that the switching behaviors differed due to the differences in binding strength between chiral pillar[6]arene and glucose enantiomers, which can lead to the different surface charge within nanochannel. Given these promising results, the studies of chiral-driven ion gates may not only give interesting insight for the research of biological and pathological processes caused by glucose-sensitive ion channels, but also help to understand the origin of the high stereoselectivity in life systems

**Comment:** It seems that the photo-control based on the azobenzene did not work for this system. I had similar ideas when I was working on the host-guest systems & nanopore collaboration project. But it's a pity that we did not have solid-state nanopores with well-defined sizes at that time. Actually, the synthesis and assembly are not difficult.

### Unsymmetrical Starburst Triarylamines: Synthesis, Properties, and Characteristics of OFETs

Dheepika, R.; Sonalin, S.; Imran, P. M.; Nagarajan, S.\* *J. Mater. Chem. C* **2018**, *6*, 6916–6919.



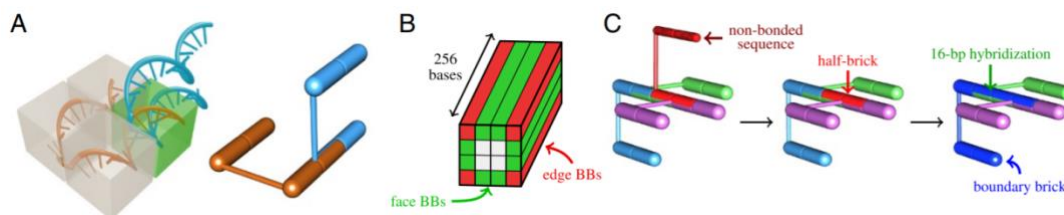
**Scheme 1** Synthetic route for the preparation of compounds **1** to **8**.

Functionalized triarylamines were constructed through Suzuki coupling for organic field effect transistor (OFET) applications. **Easy solution processable OFETs yielded a good field effect mobility of up to  $15 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .** The ON/OFF ratio had a magnitude of  $10^7$ , enabling the molecules to be promising electronic materials.

**Comment:** I am not an expert in triaryl amines so I cannot really say that the results presented are outstanding, but I think that their **systematic study of the structure/properties relationship** is interesting to take a look at, even if TAAs are not your main interest.

### Direct Observation and Rational design of Nucleation Behavior in Addressable Self-assembly

Sajfutdinow, M.; Jacobs, W. M.; Reinhardt, A.; Schneider, C.; Smith, D. M.\* [\*Proc. Nat. Acad. Sci. USA\* \*\*2018\*\*, \*26\*, 5877-5886.](#)

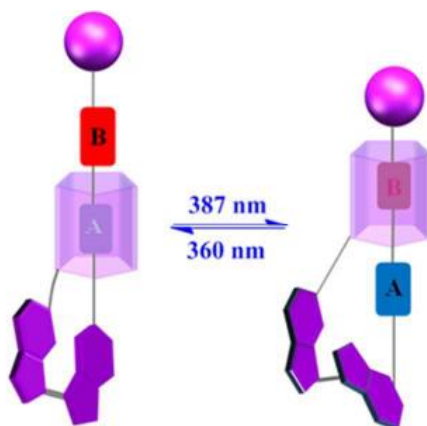


To optimize a self-assembly reaction, it is essential to understand the factors that govern its pathway. Here, we examine the influence of nucleation pathways in a model system for addressable, multicomponent self-assembly based on a prototypical “DNA brick” structure. By combining temperature-dependent dynamic light scattering and atomic force microscopy with coarse-grained simulations, we show how subtle changes in the nucleation pathway profoundly affect the yield of the correctly formed structures. In particular, we can increase the range of conditions over which self-assembly occurs by using stable multisubunit clusters that lower the nucleation barrier for assembling subunits in the interior of the structure. Consequently, modifying only a small portion of a structure is sufficient to optimize its assembly. Due to the generality of our coarse-grained model and the excellent agreement that we find with our experimental results, the design principles reported here are likely to apply generically to addressable, multicomponent self-assembly.

**Comment:** This paper proposed a detailed investigation of the self-assembly process through a series of detailed calculations. It could help us to understand how to rationally design an optimum monomer and then use it to construct clusters or even bigger assemblies.

### A Light-Driven Molecular Machine Based on Stiff Stilbene

Wang, Y.; Tian, Y.; Chen, Y., Z.; Niu, L. Y.; Wu, L., Z.; Tung, C. H.; Yang, Q. Z.\*; Boulatov, R. [\*Chem. Commun.\* \*\*2018\*\*, ASAP.](#)

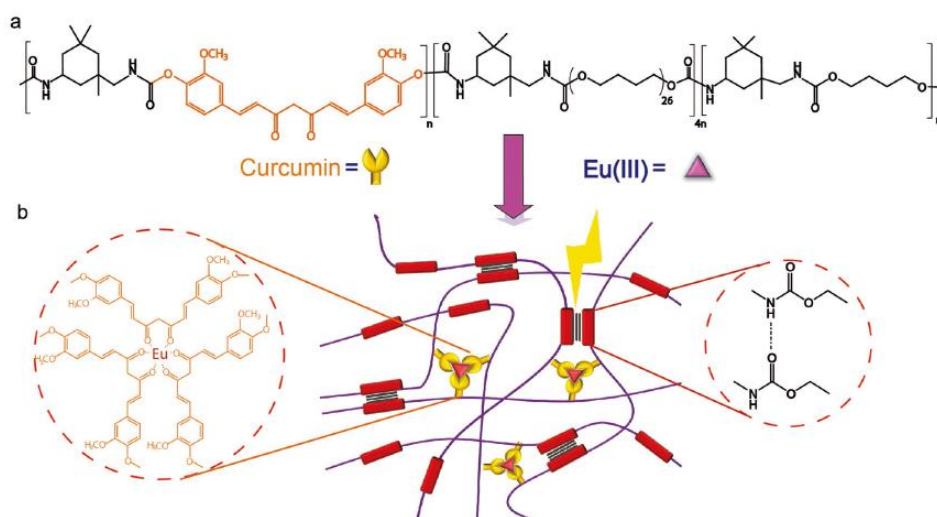


We report a new molecular design for **optically triggered nm-scale translation of a submolecular component** relative to another. We used a **rotaxane-like molecule** terminated at one end with **stiff stilbene** that served both as a chromophore to trigger the translation of the pillar[5]arene “wheel” and as a stopper to prevent its dethreading.

**Comment:** The molecular motor presented in this article possesses a simple but clever design. Unfortunately, the contraction remains restricted to the nanoscopic scale. It could be interesting to integrate it into a polymer in order to obtain a system quite similar to what has [been recently published in our team](#), but optically triggered.

### An Elastic Autonomous Self-Healing Capacitive Sensor Based on a Dynamic Dual Crosslinked Chemical System

Zhang, Q.; Niu, S.; Wang, L.; Lopez, J.; Chen, S.; Cai, Y.; Du, R.; Liu, Y.; Lai, J.; Liu, L.; Li, C.; Yan, X.; Liu, C.; Tok, J. B.; Jia, X.\*; Bao, Z.\* [Adv. Mater. 2018. 180145.](#)



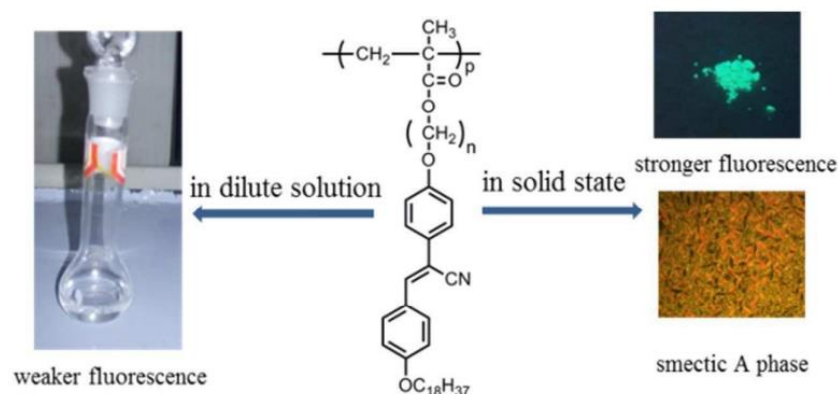
Adopting self-healing, robust, and stretchable materials is a promising method to enable next-generation wearable electronic devices, touch screens, and soft robotics. Both elasticity and self-healing are important qualities for substrate materials as they comprise the majority of device components. However, most autonomous self-healing materials reported to date have poor elastic properties, i.e., they possess only modest mechanical strength and recoverability. Here, a substrate material designed is reported based on **a combination of dynamic metal-coordinated bonds** ( $\beta$ -diketone–europium interaction) and **hydrogen bonds** together in a multiphase separated network. Importantly, this material is able to undergo self-healing and exhibits excellent elasticity. The polymer network forms a microphase-separated structure and exhibits a high stress at break ( $\approx 1.8$  MPa) and high fracture strain ( $\approx 900\%$ ). Additionally, it is observed that the substrate can achieve up to 98% self-healing efficiency after 48 h at 25 °C, without the need of any external stimuli. A stretchable and self-healable dielectric layer is fabricated with a dual-dynamic bonding polymer system and self-healable conductive layers are created using polymer as a matrix for a silver composite. These materials are employed to prepare capacitive sensors to demonstrate a stretchable and self-healable touch pad.

**Comment:** Nowadays, e-wear and e-skin are promising subjects and attract increasing attention due to the urgent demand for soft robotics and wearable devices. This paper demonstrates a

multifunctional material, which exhibits robust, self-healing and stretchable properties by introducing dynamic metal-coordinated and hydrogen bonds. We also could take account of this combination of multi non-covalent bonds in our following designs of polymers based on motors.

### Preparation and Properties of Side Chain Liquid Crystalline Polymers with Aggregation-Induced Emission Enhancement Characteristics

Yuan, Y.; Li, J.; He, L.; Liu, Y.\*; Zhang, H.\* [\*J. Mater. Chem. C\* \*\*2018\*\*, \*6\*, 7119–7127.](#)

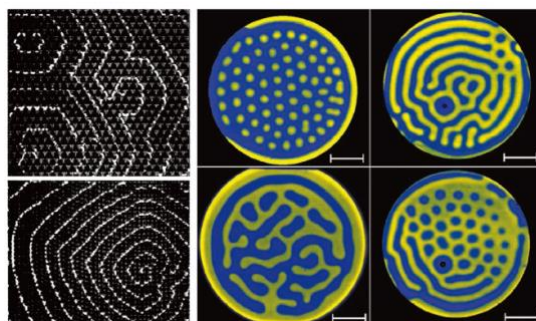


In this article, novel side chain liquid crystalline polymers (SCLCPs) based on cyanostilbene were synthesized to obtain **luminescent liquid crystalline materials**. The fluorescent luminescence behavior and liquid crystallinity of SCLCPs were evaluated and characterized by differential scanning calorimetry (DSC), polarized optical microscopy (POM), X-ray diffraction (XRD), ultraviolet spectroscopy (UV) and photoluminescence (PL) measurements. Testing results showed that all polymers exhibited good thermo-stability and stable double-layer smectic A phase below the clearing point temperature. The liquid crystalline properties of polymers were affected by the spacer length. The clearing point temperature ( $T_i$ ) of SCLCPs decreased with increasing spacer length. All polymers were weakly emissive in good solvent but emitted stronger fluorescence in the aggregation state, showing **aggregation-induced emission enhancement (AIEE) behavior**. The fluorescent luminescence behavior of polymers was closely linked with chemical structure and the fluorescence quantum yield of polymers in solid phase, which increased with increasing spacer length.

**Comment:** The study of the material is complete and logical, going from the monomers to the polymers obtained. Their techniques of characterization may interest the ones who are working on liquid crystals or fluorescent molecules.

### Under Diffusion Control: From Structuring Matter to Directional Motions

Cera, L.; Schalley, C. A.\* [\*Adv. Mater.\* \*\*2018\*\*, 1707029.](#)



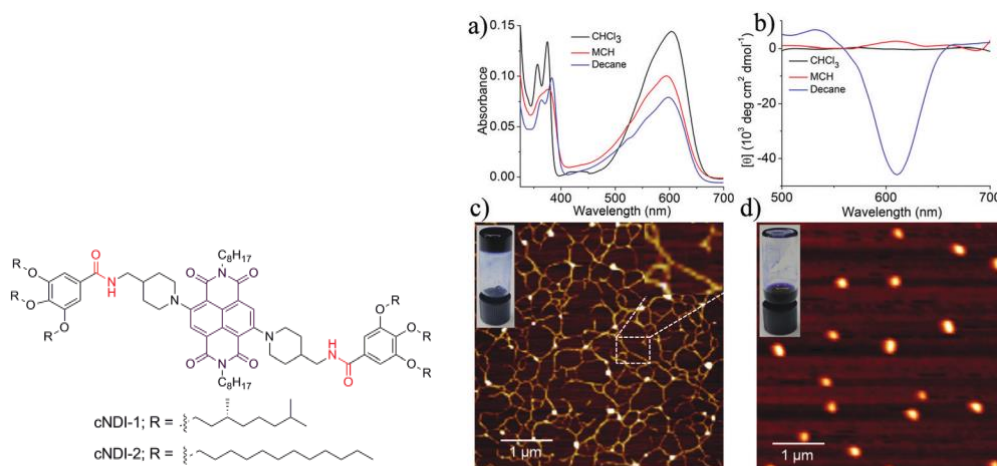


Self-organization in synthetic chemical systems is quickly developing into a powerful strategy for designing new functional materials. As self-organization requires the system to exist far from thermodynamic equilibrium, chemists have begun to go beyond the classical equilibrium self-assembly that is often applied in bottom-up supramolecular synthesis, and to learn about the surprising and unpredicted emergent properties of chemical systems that are characterized by a higher level of complexity and extended reactivity networks. The present review focuses on self-organization in reaction diffusion systems. Selected examples show how the emergence of complex morphogenesis is feasible in synthetic systems leading to hierarchically and nanostructured matter. Starting from well-investigated oscillating reactions, recent developments extend diffusion-limited reactivity to supramolecular systems. The concept of dynamic instability is introduced and illustrated as an additional tool for the design of smart materials and actuators, with emphasis on the realization of motion even at the macroscopic scale. The formation of spatio-temporal patterns along diffusive chemical gradients is exploited as the main channel to realize symmetry breaking and therefore anisotropic and directional mechanical transformations. Finally, the interaction between external perturbations and chemical gradients is explored to give mechanistic insights in the design of materials responsive to external stimuli.

**Comment:** This paper is a very interesting review, it starts from the self-organization and introduces lots of representative non-equilibrium systems. This paper contains many unfamiliar concepts, such as chemical wave, reaction diffusion system and so on. If you are interested in dissipation system, read it.

### Solvent Dependent Pathway Complexity and Seeded Supramolecular Polymerization

Ghosh, G.; Ghosh, S.\* [\*Chem. Commun.\* \*\*2018\*\*, \*54\*, 5720.](#)

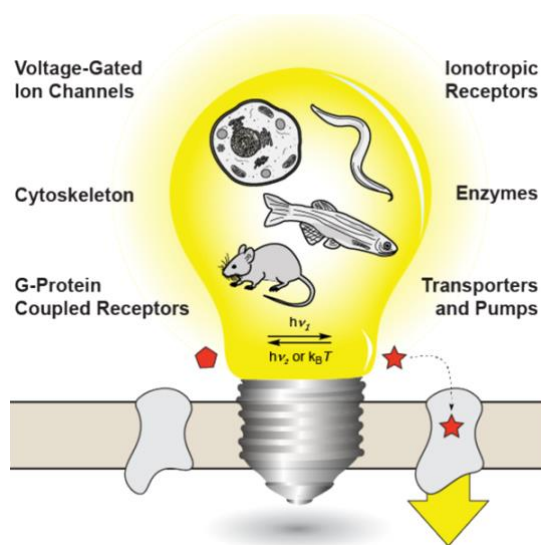


**cNDI-1 exhibits an off-pathway aggregate in cyclic hydrocarbon (MCH) but produces a helical supramolecular polymer in linear alkane (decane) by well-defined J-aggregation.** Effective solvent- assisted nucleation in linear alkanes due to shape matching with the peripheral alkyl chains of a monomer is responsible for the pathway complexity. Seed, produced by sonication induced fragmentation of the fibers in decane, could initiate supramolecular polymerization of the off-pathway aggregate in MCH generating controllable helical nanostructures. The chiral seed of cNDI-1 was also successfully employed for the synthesis of a helical supramolecular polymer from the off-pathway aggregate of achiral cNDI-2

**Comment:** Nothing really new here: supramolecular aggregation depends on solvents. But there is some novelty in that one could overcome the energetic barrier leading to one or the other polymer by the seeding of one of the structures. That is interesting and would have ended up higher if some structural rational would come in place, even if it would be only some computational models at the B3LYP level. But what you get here is pure phenomenology which feels like a curse on today's research.

### In Vivo Photopharmacology

Hüll, K.; Morstein, J.; Trauner, D.\* [Chem. Rev. 2018, ASAP.](#)

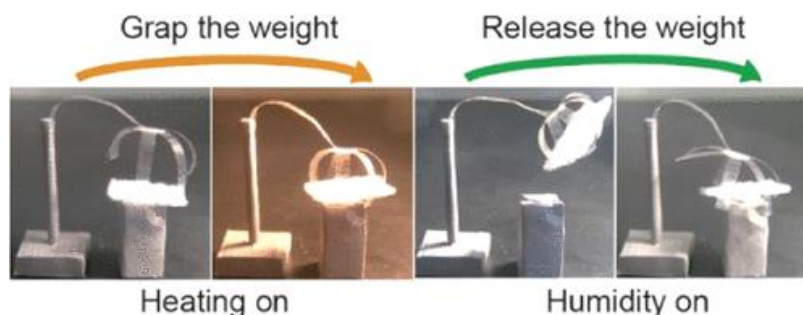


Synthetic photoswitches have been known for many years, but their usefulness in biology, pharmacology, and medicine has only recently been systematically explored. Over the past decade photopharmacology has grown into a vibrant field. As the photophysical, pharmacodynamic, and pharmacokinetic properties of photoswitches, such as azobenzenes, have become established, they have been applied to a wide range of biological targets. These include transmembrane proteins (ion channels, transporters, G protein-coupled receptors, receptor-linked enzymes), soluble proteins (kinases, proteases, factors involved in epigenetic regulation), lipid membranes, and nucleic acids. In this review, **we provide an overview of photopharmacology using synthetic switches that have been applied in vivo**, i.e., in living cells and organisms. **We discuss the scope and limitations of this approach to study biological function** and the challenges it faces in translational medicine. The relationships between synthetic photoswitches, natural chromophores used in optogenetics, and caged ligands are addressed.

**Comment:** Oh yeah, a review on photopharmacology. It has to have crossed your mind: the idea of molecular motors regulating “things” in a living organism and maybe this will offer a picture of where this could lead to. I can but strongly recommend it mainly because of the lead author Dirk Trauner, author as well of what I consider a great description of the contrast between biology and material science and so on: “**Biology is not linear**”. Meaning that in biology you do not need 100% conversion, but just enough to push the system in one direction. As such, azobenzenes are perfectly fine even if they are awful switches.

### Multi-Responsive Kinematics and Robotics of Surface-Patterned Polymer Film

Liang, S.; Qiu, X.; Yuan, J.; Huang, W.; Du, X.; Zang, L.\* [\*Appl. Mater. Interfaces\*, \*\*2018\*\*, \*10\*, 19123-19132](#)

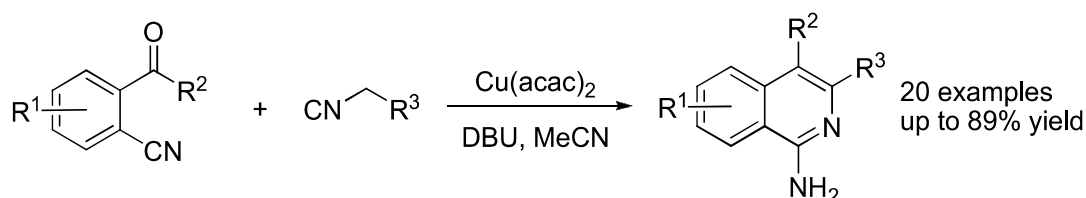


Soft robots, sensors and energy harvesters require materials that are capable of converting external stimuli to visible deformations, and especially shape-programmable deformations are desired. Herein, we develop a polymer film that can reversibly respond to humidity, heating and acetone vapors with generation of shape-programmable large deformations. Polyvinylidene fluoride (PVDF) film, capable of providing acetone responsiveness, is designed with microchannel patterns on its one side by using templates, and the microchannels-patterned side is then treated with hygroscopic 3-aminopropyltriethoxysilane (APTES) to give humidity/heating-responsive elements. The APTES-modified microchannels lead to anisotropic flexural modulus and hygroscopicity in the film, resulting in the shape-programmed kinematics depending on the orientations of surface microchannels. As the microchannels align at oblique/right angles with respect to the long axis of the film strips, the coiling/curling motions can be generated in response to the stimuli, and the better motion performances are found in humidity- and heating-driven systems. This material utilized in self-adaptive soft robots exhibits prominent toughness, powerful strength and long endurance for converting humidity and heating to mechanical works including transportation of lightweight objects, automatic sensing cap and mimicking crawling in nature. We thus believe that this material with shape-programmable multi-sensing capability might be suitable for soft machines and robotics.

**Comment:** Really cool example of soft robot devices with funny experiments. The fact that motion mechanisms are discussed with illustration is a real plus for the article.

### Copper-Catalyzed Cyclization of 2-Cyanobenzaldehydes and 2-isocyanoacetates: an Efficient Strategy for the Synthesis of Substituted 1-Aminoisoquinolines

Bao, W.; Wang, J. Q.; Xu, X. T.; Zhang, B. H.; Liu, W. T.; Lei, L. S.; Liang, H.; Zhang, K.; Wang, S. H.\* [\*Chem. Commun.\* \*\*2018\*\*, ASAP](#).



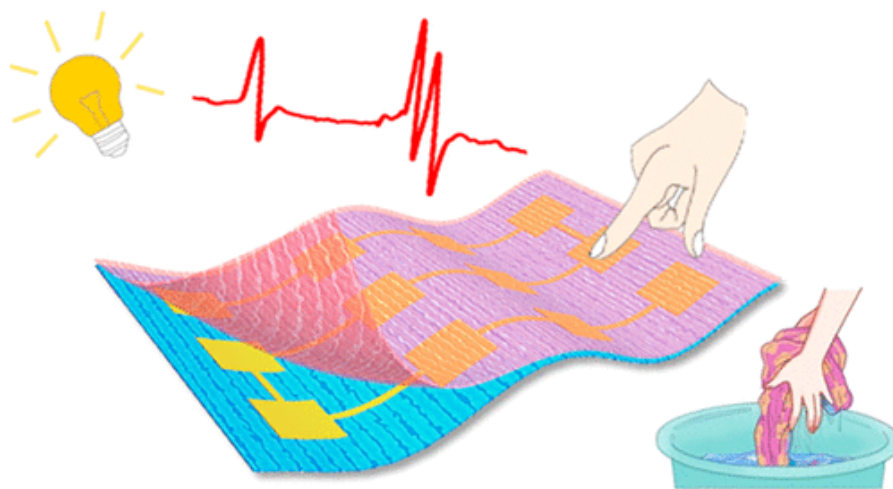
A  $\text{Cu}(\text{acac})_2$ -catalyzed cyclization reaction of 2-cyanobenzaldehydes with 2-isocyanoacetates has been successfully developed providing an efficient strategy for the synthesis of substituted 1-aminoisoquinoline. The reaction proceeds smoothly under mild conditions

with **high efficiency**, and might provide an alternative strategy for the synthesis of 1-aminoisoquinoline containing molecules.

**Comment:** This relatively short paper should be added to the growing list of articles to keep in mind when one would like to develop a new synthetic pathway. The authors tested their novel approach on around twenty compounds, in order to prove its efficiency. Even though the reaction may seem easy to perform (mild conditions and high efficiency), one must not forget that one or two other steps have to be performed beforehand to obtain the starting ketone/aldehyde.

### Screen-Printed Washable Electronic Textiles as Self-Powered Touch/Gesture Tribo-Sensor for Intelligent Human-Machine Interaction

Cao, R.; Pu, X.; Du, X.; Yang, W.; Wang, J.\*; Guo, H.\*; Zhao, S.; Yuan, Z.; Zhang, C.; Li, C.\*; Wang, Z. L. *ACS nano* **2018**, *12*, 5190-5196



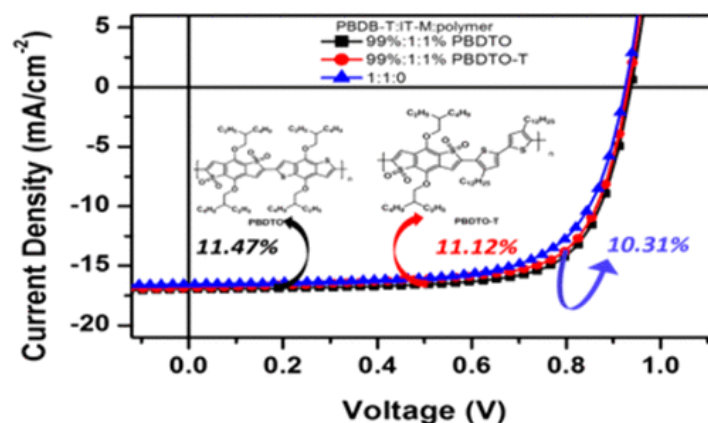
Multi-functional electronic textile (E-textile) with embedded electric circuits holds great application prospect for future wearable electronics. However, most of the E-textiles still have critical challenges, including air permeability, satisfactory washability and massive fabrication. In this work, we fabricate a washable E-textile that addresses all of the concerns and show its application as a self-powered triboelectric gesture textile for intelligent human-machine interface. Utilizing conductive carbon nanotubes (CNTs) and screen-printing technology, this kind of E-textile embraces high conductivity (0.2 kΩ/sq), high air permeability (88.2 mm/s) and can be manufactured on common fabric at large scale. Taking advantage of the interaction between the CNTs and the fabrics, the electrode shows excellent stability under harsh mechanical deformation and even after washing. Moreover, based on single electrode mode triboelectric nanogenerator and electrode pattern design, our E-textile exhibits high sensitive touch/gesture sensing performance, has potential applications for human-machine interfacing.

**Comment:** This article captured my attention because of its applicability, regrettably it is written in bad English. An elaborative study is performed on the stability and characteristics of the CNT ink on nylon, which shows very good results. However, the washing tests are weak: the stability of the ink is studied after immersion into water for several hours, but in absence of soaps or centrifugation etc. This is disappointing because the major improvement they wanted to demonstrate was its washability.

### Highly Efficient Non-Fullerene Organic Solar Cells Using 4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-Based Polymers as Additives



Lei, T.; Peng, R.; Fan, X.; Wei, Q.; Liu, Z.; Guan, Q.; Song, W.; Hong, L.; Huang, J.; Yang, R., Ge, Z.\* [\*Macromolecules\*, 2018, 51, 4032-4039](#)

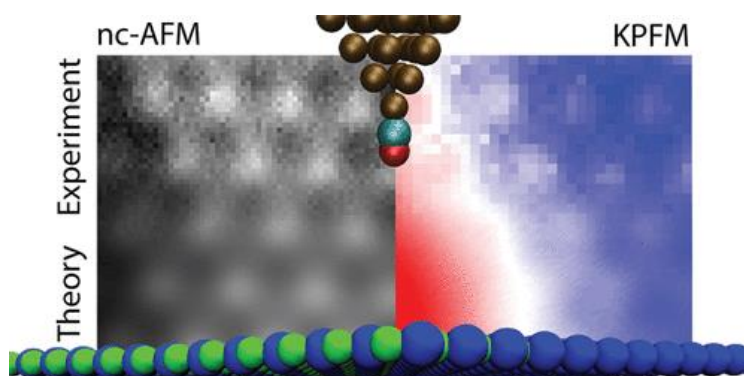


Electron acceptor units play an important role in the design of donor–acceptor (D–A) type polymers for efficient organic solar cells (OSCs). In this report, with the oxidation of the thiophene moiety, the electron-rich 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (BDT) unit was tuned into electron-deficient 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']-dithiophene 1,1,5,5-tetraoxide (BDTO) unit. Two novel polymers of PBDO and PBDO-T based on BDT unit were synthesized and employed as additives in efficient non-fullerene OSCs with the active layer consist of PBDB-T and IT-M. With doping 1% PBDO or PBDO-T, the power conversion efficiency (PCE) of the prepared OSCs increased from 10.31% to 11.47% or 11.12%, respectively. These two polymers can afford cascaded energy levels and smooth the surface of the active layer, which are beneficial for better carrier transportation and separation. Our results open a new avenue to construct electron acceptor backbone in the design of D–A type polymers for OSCs.

**Comment:** I often had the occasion to hear questions about error-bars in some chemistry presentations and I think this is the exact field in which these should be always indicated. The article did not persuaded me to believe the presented results (even more with almost same-looking AFM images) and **I would be glad to discuss it a bit with someone.**

### Elemental Identification by Combining Atomic Force Microscopy and Kelvin Probe Force Microscopy

Schulz, F.; Ritala, J.; Krejci, O.; Seitsonen, A.P.; Foster, A. S. and Liljeroth, P.\* [\*ACS nano\* 2018, 12, 5274-5283](#)

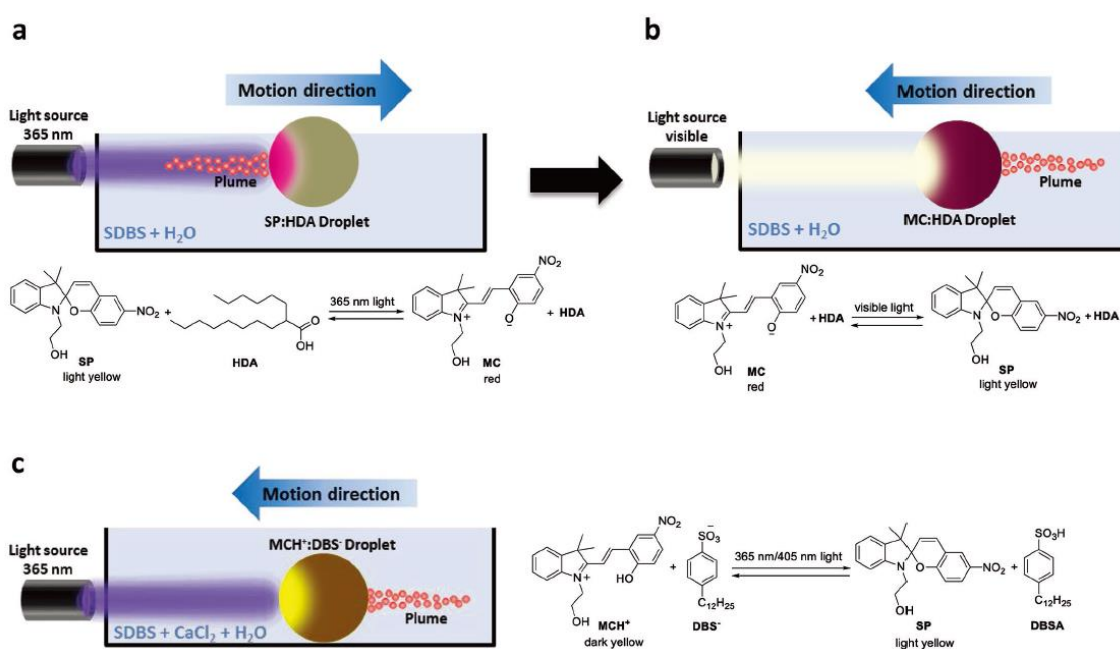


There are currently no experimental techniques that combine atomic resolution imaging with elemental sensitivity and chemical fingerprinting on single molecules. The advent of using molecular-modified tips in non-contact atomic force microscopy (nc-AFM) has made it possible to image (planar) molecules with atomic resolution. However, the mechanisms responsible for elemental contrast with passivated tips are not fully understood. Here, we investigate elemental contrast by carrying out both nc-AFM and Kelvin probe force microscopy (KPFM) experiments on epitaxial monolayer hexagonal boron nitride (hBN) on Ir(111). The hBN overlayer is inert and the in-plane bonds connecting nearest-neighbor boron and nitrogen atoms possess strong covalent character and a bond-length of only  $\sim 1.45$  Å. Nevertheless, constant-height maps of both the frequency shift  $\Delta f$  and the local contact potential difference (LCPD) exhibit striking sublattice asymmetry. We match the different atomic sites with the observed contrast by comparison with nc-AFM image simulations based on the density functional theory (DFT)-optimized hBN/Ir(111) geometry, which yields detailed information on the origin of the atomic-scale contrast.

**Comment:** An article on the state of the art in atomic force microscopy that expands the limits of elemental identification.

### Moving Droplets in 3D Using Light

Xiao, Y.; Zarghami, S.; Wagner, K.; Wagner, P.; Gordon, K. C.; Florea, L.; Diamond, D.; Officer, D. L.\* [\*Adv. Mater.\* \*\*2018\*\*, 1801821.](#)



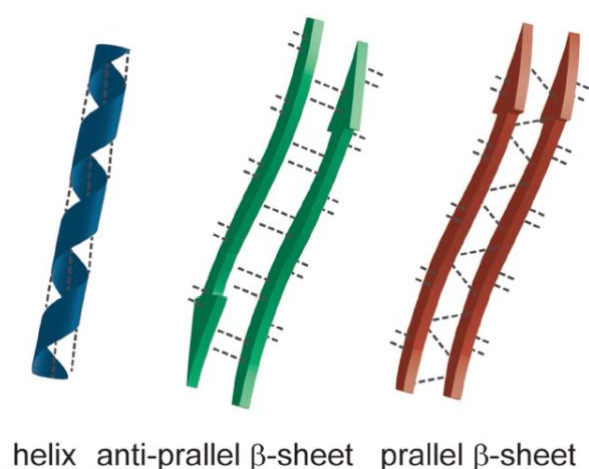
The emulation of the complex cellular and bacterial vesicles used to transport materials through fluids has the potential to add revolutionary capabilities to fluidic platforms. Although a number of artificial motile vesicles or microdroplets have been demonstrated previously, control over their movement in liquid in 3D has not been achieved. **Here it is shown that by adding a chemical “fuel,” a photoactive material, to the droplet, it can be moved in any direction (3D) in water using simple light sources without the need for additives in the water.** The droplets can be made up of a range of solvents and move with speeds as high as 10.4 mm s<sup>-1</sup> toward or away from the irradiation source as a result of a light-induced isothermal change in interfacial tension (Marangoni flow). It is further demonstrated that more complex functions can be accomplished by

merging a photoactive droplet with a droplet carrying a “cargo” and moving the new larger droplet to a “reactor” droplet where the cargo undergoes a chemical reaction. The control and versatility of this light-activated, motile droplet system will open up new possibilities for fluidic chemical transport and applications.

**Comment:** The authors demonstrated that a droplet formed by photoisomerizable spiropyrans and an organic acid can be propelled by light. And that the direction of motion could be precisely controlled by adjusting the position of light source. This kind of macroscopic motion driven by light also could transport special cargo to affect a chemical reaction. Such macroscopic machines resemble real machines which can perform work. We could consider that use of a motor to drive a droplet.

### Tailor-Made Functional Peptide Self-Assembling Nanostructures

Amit, M.; Yuran, S.; Gazit, E.\*; Reches, M.\*; Ashkenasy, N.\* [\*Adv. Mater.\* \*\*2018\*\*, 1707083.](#)

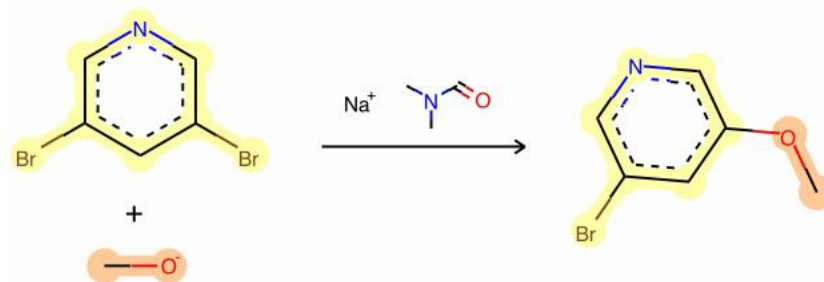


Noncovalent interactions are the main driving force in the folding of proteins into a 3D functional structure. Motivated by the wish to reveal the mechanisms of the associated self-assembly processes, scientists are focusing on studying self-assembly processes of short protein segments (peptides). While this research has led to major advances in the understanding of biological and pathological process, only in recent years has the applicative potential of the resulting self-assembled peptide assemblies started to be explored. Here, major advances in the development of biomimetic supramolecular peptide assemblies as **coatings, gels, and as electroactive materials**, are highlighted. The guiding lines for the design of helical peptides,  $\beta$  strand peptides, as well as surface binding monolayer-forming peptides that can be utilized for a specific function are highlighted. Examples of their applications in diverse immerging applications in, e.g., ecology, biomedicine, and electronics, are described. Taking into account that, in addition to extraordinary design flexibility, these materials are naturally biocompatible and ecologically friendly, and their production is cost effective, the emergence of devices incorporating these biomimetic materials in the market is envisioned in the near future.

**Comment:** This review described some characteristic examples of self-assemblies consisting of peptides. It gives us a general understanding about peptide structure and their diverse applications. **If you are interested in self-assemblies of peptide, read it.**

### “Found in Translation”: Predicting Outcomes of Complex Organic Chemistry Reactions Using Neural Sequence-to-Sequence Models

Schwaller, P.\*; Gaudin, T.; Lányi, D.; Bekas, C.; Laino, T. *Chem. Sci.* **2018**, *9*, 6091–6098.

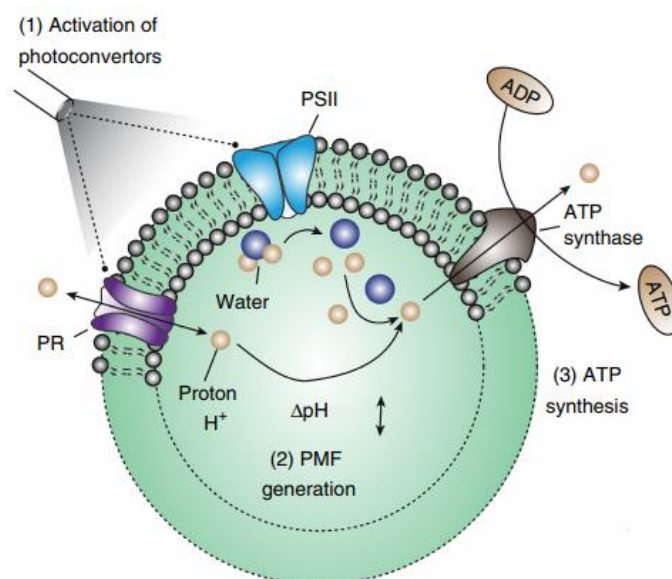


There is an intuitive analogy of an organic chemist's understanding of a compound and a language speaker's understanding of a word. Based on this analogy, it is possible to introduce the basic concepts and analyze potential impacts of linguistic analysis to the world of organic chemistry. In this work, we cast the reaction prediction task as a translation problem by introducing a template-free sequence-to-sequence model, trained end-to-end and fully data-driven. We propose a tokenization, which is arbitrarily extensible with reaction information. Using an attention-based model borrowed from human language translation, **we improve the state-of-the-art solutions in reaction prediction on the top-1 accuracy by achieving 80.3%** without relying on auxiliary knowledge, such as reaction templates or explicit atomic features. Also, a top-1 accuracy of 65.4% is reached on a larger and noisier dataset.

**Comment:** Even if some of us are convinced that the intuition of an organist chemist will never be replaced, we cannot deny that computers and algorithms are getting better and better at our job...

### Photosynthetic Artificial Organelles Sustain and Control ATP-Dependent Reactions in a Protocellular System

Lee, K. Y.; Park, S.-J.; Lee, K. A.; Kim, S.-H.; Kim, H.; Meroz, Y.; Mahadevan, L.; Jung, K.-H.\*; Ahn, T. K.\*; Parker, K. K.\*; Shin K.\* *Nat. Biotechnol.* **2018**, *36*, 530–535.



Inside cells, complex metabolic reactions are distributed across the modular compartments of organelles. Reactions in organelles have been recapitulated in vitro by reconstituting functional

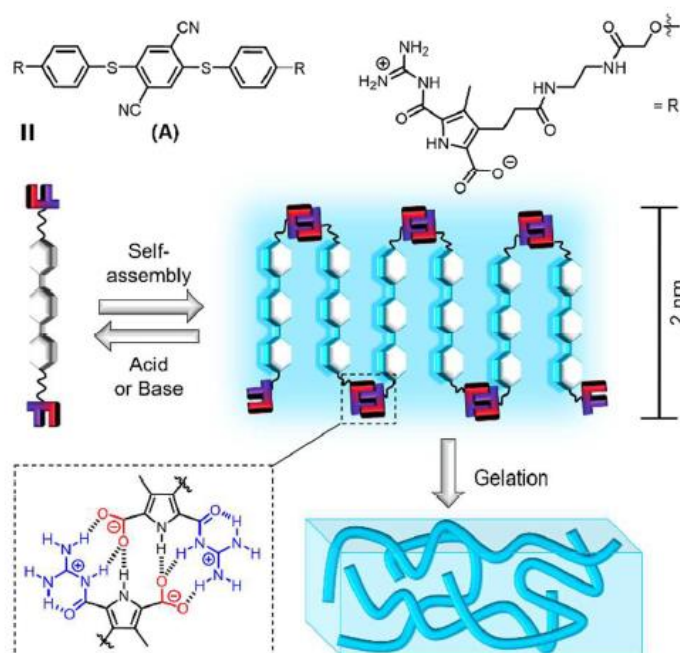


protein machineries into membrane systems. However, maintaining and controlling these reactions is challenging. Here **we designed, built, and tested a switchable, light-harvesting organelle that provides both a sustainable energy source and a means of directing intravesicular reactions**. An ATP (ATP) synthase and two photoconverters (plant-derived photosystem II and bacteria-derived proteorhodopsin) enable ATP synthesis. Independent optical activation of the two photoconverters allows dynamic control of ATP synthesis: red light facilitates and green light impedes ATP synthesis. We encapsulated the photosynthetic organelles in a giant vesicle to form a protocellular system and demonstrated optical control of two ATP-dependent reactions, carbon fixation and actin polymerization, with the latter altering outer vesicle morphology. Switchable photosynthetic organelles may enable the development of biomimetic vesicle systems with regulatory networks that exhibit homeostasis and complex cellular behaviors.

**Comment:** This paper may be far from our field of expertise, and, hence, not so easy to understand at first glance. However, I believe it represents a huge step towards “**new**” **living systems**, because they managed to combine different machineries from different species.

### A Dual pH-Responsive Supramolecular Gelator with Aggregation-Induced Emission Properties

Externbrink, M.; Riebe, S.; Schmuck, C.\*; Voskuhl, J.\* [\*Soft Matter\*. \*\*2018\*\*, \*14\*, 6166–6170.](#)

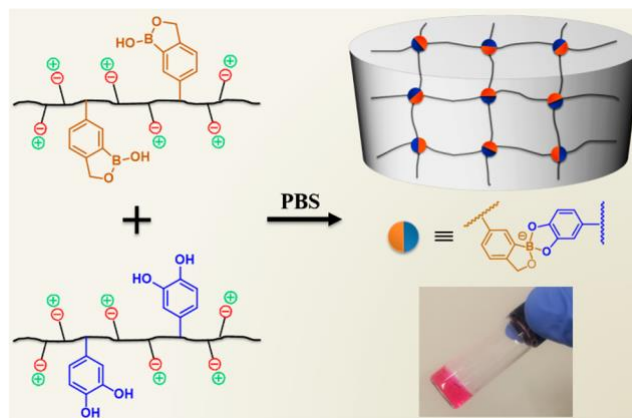


Functionalizing AIE-active aromatic thioethers with self-complementary zwitterionic binding sites leads to a dual pH-responsive supramolecular organogelator with aggregation-induced emission (AIE) properties. The self-assembled fibrillar gel network is highly fluorescent ( $\lambda_{em} = 490$  nm), whereas the addition of both acid and base leads to the sol state with a loss of emission. Moreover, the gel was found to be thermo- and mechanoresponsive.

**Comment:** Description of a self-assembled fluorescent system with interesting mechanic properties.

## Bioinspired Self-Healing Hydrogel Based on Benzoxaborole-Catechol Dynamic Covalent Chemistry for 3D Cell Encapsulation

Chen, Y.; Diaz-Dussan, D.; Wu, D.; Wang, W.; Peng, Y.; Benozir Asha, A.; Hall, D. G.; Ishihara, K.; Narain, R.\* [\*ACS Macro Lett.\* \*\*2018\*\*, \*7\*, 904–908.](#)

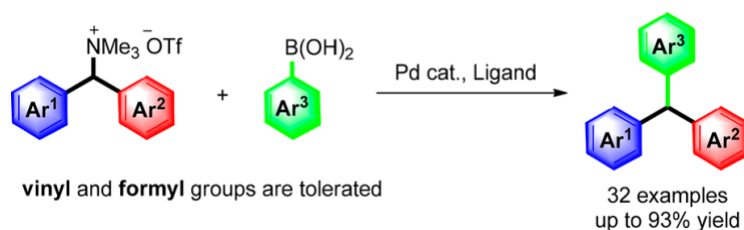


Boronic ester, one typical example of dynamic covalent bonds, has presented great potential to prepare selfhealing hydrogels. However, most of currently reported hydrogels based on boronic esters are formed at pH > 8, which impeded their further use in physiological conditions. In this study, we designed two kinds of zwitterionic copolymers with benzoxaborole and catechol pendant groups, respectively. Owing to the lower pKa value of benzoxaborole (7.2), gelation can happen easily at pH 7.4 PBS after mixing these two copolymers due to efficient formation of benzoxaborole-catechol complexations. The resulting hydrogels exhibited excellent self-healing property as well as dual pH/sugar responsiveness due to the dynamic nature of boronic ester. Moreover, benefiting from the cell membrane bioinspired 2-methacryloyloxyethyl phosphorylcholine (MPC)-based polymeric matrix, the hydrogel was further investigated for 3D cell encapsulation. The combination of biocompatible zwitterionic polymers with dynamic benzoxaborole-catechol complexation makes the hydrogels a promising platform for diversepotential bioapplications like drug delivery and tissue engineering.

**Comment:** An interesting way to obtain self-healing material.

## Synthesis of Triarylmethanes via Palladium-Catalyzed Suzuki Coupling of Trimethylammonium Salts and Arylboronic Acids

Zhang, Z. M.; Wang, H.; Qiu, N. L.; Kong, Y. J.; Zeng, W. J.; Zhang, Y. Q.; Zhao, J. F.\* [\*J. Org. Chem.\* \*\*2018\*\*, ASAP.](#)



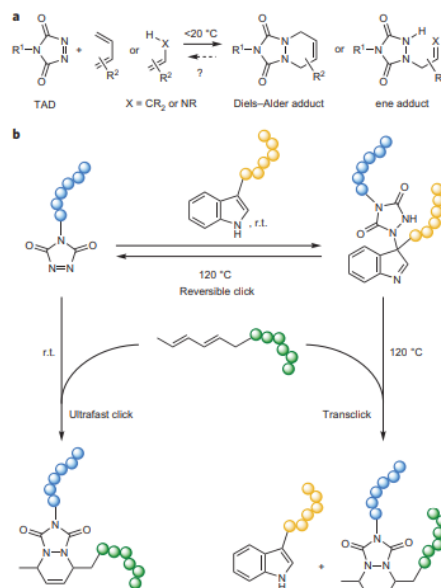
An efficient palladium-catalyzed Suzuki coupling of 1,1-diarylmethyl-trimethylammonium triflates with arylboronic acids is reported. This reaction offers a novel approach to triarylmethane derivatives in good to excellent yields with the palladium-catalyzed C–N bond cleavage as the key

feature. Broad substrate scope regarding both reaction partners are observed. Moreover, reactive functional groups such as vinyl and formyl groups are conserved in this transformation.

**Comment:** This paper may represent a useful alternative to our current approach towards the synthesis the triarylmethane.

### Triazolinediones Enable Ultrafast and Reversible Click Chemistry for the Design of Dynamic Polymer Systems

Billiet, S.; De Bruycker, K.; Driessen, F.; Goossens, H.; Van Speybroeck, V.; Winne, J. M.\*; Du Prez, F. E.\* [\*Nat. Chem.\* \*\*2014\*\*, \*6\*, 815.](#)

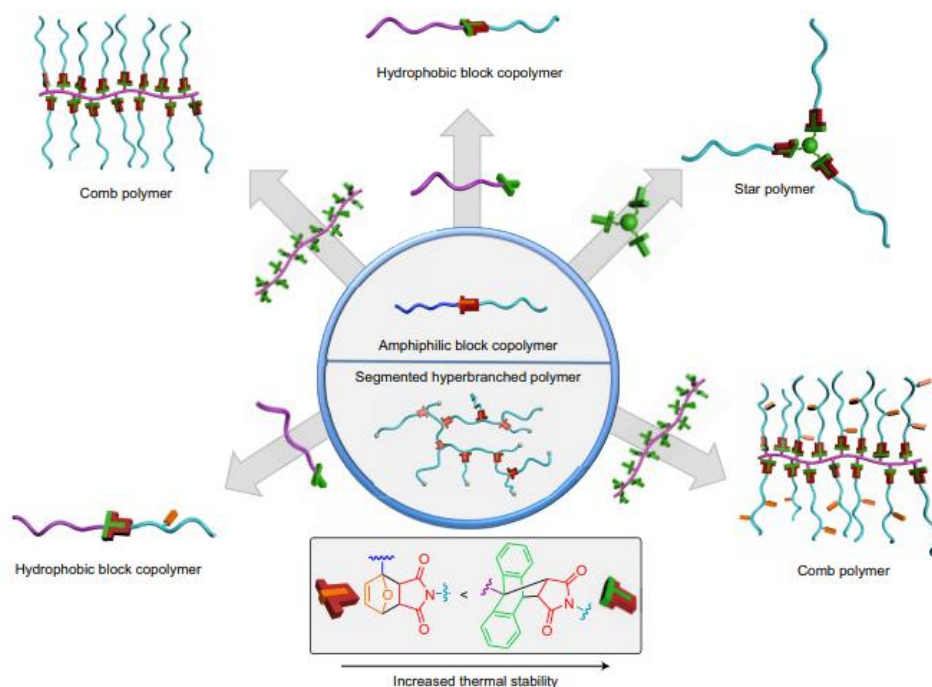


With its focus on synthetic reactions that are highly specific and reliable, ‘click’ chemistry has become a valuable tool for many scientific research areas and applications. Combining the modular, covalently bonded nature of click-chemistry linkages with an ability to reverse these linkages and reuse the constituent reactants in another click reaction, however, is a feature that is not found in most click reactions. Here we show that triazolinedione compounds can be used in click-chemistry applications. We present examples of simple and ultrafast macromolecular functionalization, polymer–polymer linking and polymer crosslinking under ambient conditions without the need for a catalyst. Moreover, when triazolinediones are combined with indole reaction partners, the reverse reaction can also be induced at elevated temperatures, and the triazolinedione reacted with a different reaction partner, reversibly or irreversibly dependent on its exact nature. We have used this ‘transclick’ reaction to introduce thermoreversible links into polyurethane and polymethacrylate materials, which allows dynamic polymer-network healing, reshaping and recycling.

**Comment:** The paper presents a new and irreversible click reaction *via* the formation of a new Diels–Alder adduct. Also, this paper gives me some ideas on the design and production of molecular systems with unique, modular and tunable dynamic properties.

### Macromolecular Metamorphosis via Stimulus-Induced Transformations of Polymer Architecture

Sun, H.; Kabb, C. P.; Dai, Y.; Hill, M. R.; Ghiviriga, I.; Bapat, A. P.; Sumerlin, B. S.\* [\*Nat. Chem\* \*\*2017\*\* \*9\*, 817.](#)



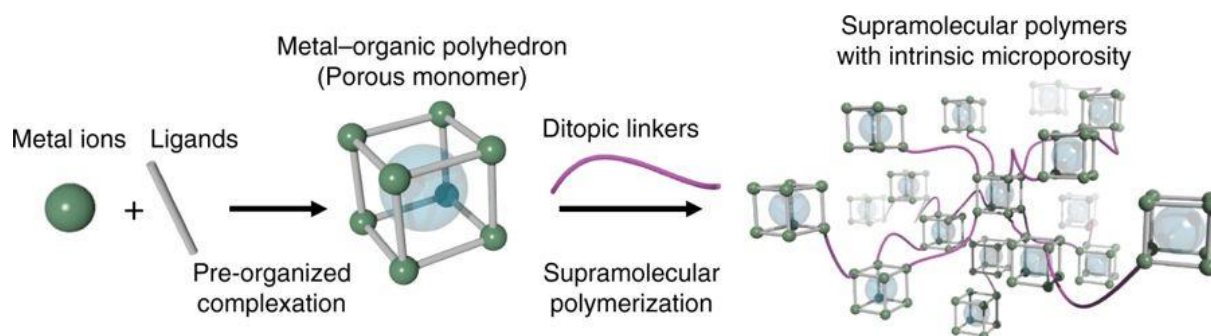
Macromolecular architecture plays a pivotal role in determining the properties of polymers. When designing polymers for specific applications, it is not only the size of a macromolecule that must be considered, but also its **shape**. In most cases, the topology of a polymer is a static feature that is **inalterable once synthesized**. **Using reversible-covalent chemistry to prompt the disconnection of chemical bonds and the formation of new linkages in situ, we report polymers that undergo dramatic topological transformations via a process we term macromolecular metamorphosis.** Utilizing this technique, a linear amphiphilic block copolymer or hyperbranched polymer undergoes ‘metamorphosis’ into comb, star and hydrophobic block copolymer architectures. This approach was extended to include a macroscopic gel which transitioned from a densely and covalently crosslinked network to one with larger distances between the covalent crosslinks when heated. These architectural transformations present an entirely new approach to ‘smart’ materials.

**Comment:** This paper shows several examples of macromolecular metamorphosis, a robust method to alter macromolecular architecture and might serve as foundation for the design and investigation of dynamic polymers.

### Self-assembly of Metal–organic Polyhedra into Supramolecular Polymers with Intrinsic Microporosity

Carné-Sánchez, A.; Craig, G. A.; Larpent, P.; Hirose, T.; Higuchi, M.; Kitagawa, S.; Matsuda, K.; Urayama, K.; Furukawa, S.\* [\*Nat. Commun.\* \*\*2018\*\*, \*9\*, 2506.](#)



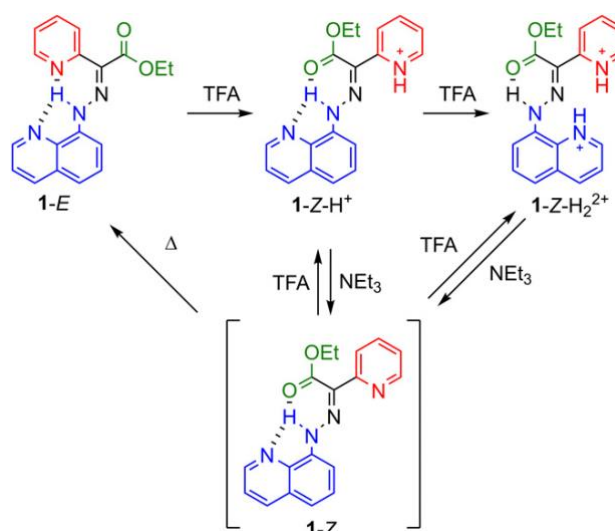


Designed porosity in coordination materials often relies on highly ordered crystalline networks, which provide stability upon solvent removal. However, the requirement for crystallinity often impedes control of higher degrees of morphological versatility, or materials processing. Herein, we describe a supramolecular approach to the synthesis of amorphous polymer materials with controlled microporosity. The strategy entails the use of robust metal-organic polyhedra (MOPs) as porous monomers in the supramolecular polymerization reaction. Detailed analysis of the reaction mechanism of the MOPs with imidazole-based linkers revealed the polymerization to consist of three separate stages: nucleation, elongation, and cross-linking. By controlling the self-assembly pathways, we successfully tuned the resulting macroscopic form of the polymers, from spherical colloidal particles to colloidal gels with hierarchical porosity. The resulting materials display distinct microporous properties arising from the internal cavity of the MOPs. This synthetic approach could lead to the fabrication of soft, flexible materials with permanent porosity.

**Comment:** Although the gel was formed based on supramolecular interactions which may produce gels with adjustable shapes, the authors did not show the benefits from non-covalent bonds like self-healing or easy recycling properties.

### New Molecular Switch Architectures

Harrisa, J. D.; Morana, M. J.; Aprahamiana, I. \* *Proc. Nat. Acad. Sci. USA.* **2018**, *ASAP*.



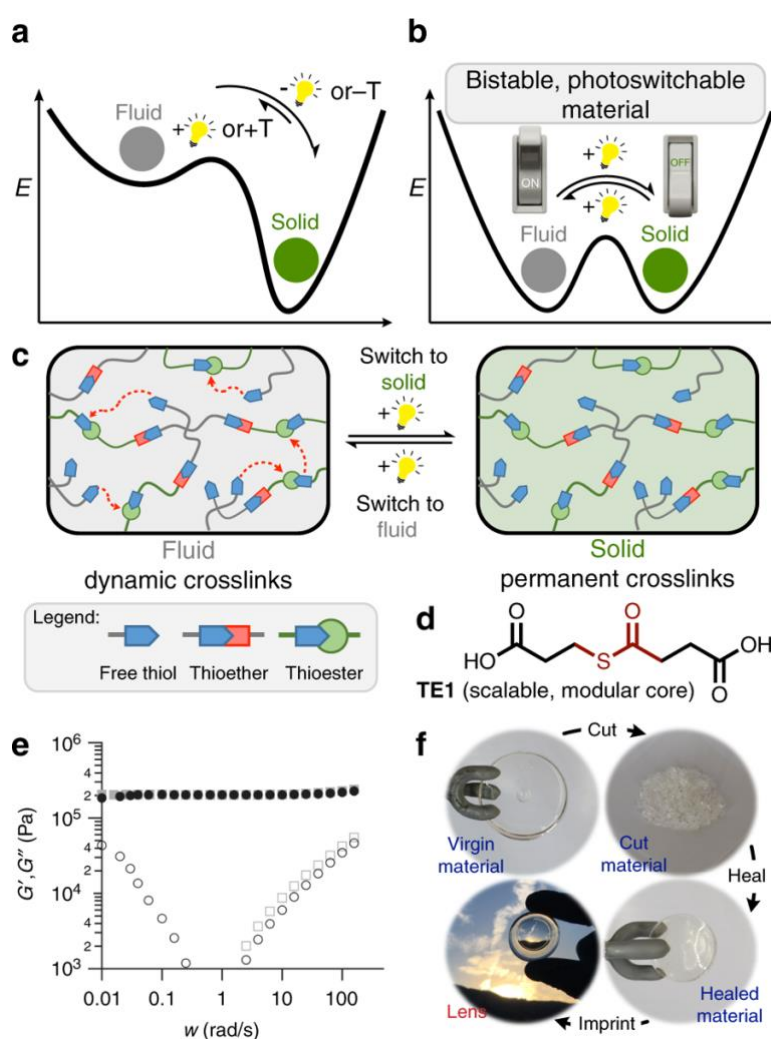
In this paper we elaborate on recently developed molecular switch architectures and how these new systems can help with the realization of new functions and advancement of artificial molecular machines. Progress in chemically and photoinduced switches and motors is summarized and

contextualized such that the reader may gain an appreciation for the novel tools that have come about in the past decade. Many of these systems offer distinct advantages over commonly employed switches, including improved fidelity, addressability, and robustness. Thus, this paper serves as a jumping-off point for researchers seeking new switching motifs for specific applications, or ones that address the limitations of presently available systems.

**Comment:** The authors make a review of the recently developed molecular-switch architectures which enrich the library of artificial molecular machines. What about using these chemical responsive architectures to construct polymers such as hydrazone-based polymers.

### Bistable and Photoswitchable States of Matter

Worrell, B. T.; McBride, M. K.; Lyon, G. B.; Cox, L. M.; Wang, C.; Mavila, S.; Lim, C.-H.; Coley, H. M.; Musgrave, C. B.; Ding, Y.; Bowman, C. N.\* [Nat. Commun. 2018, 9, 2804.](#)



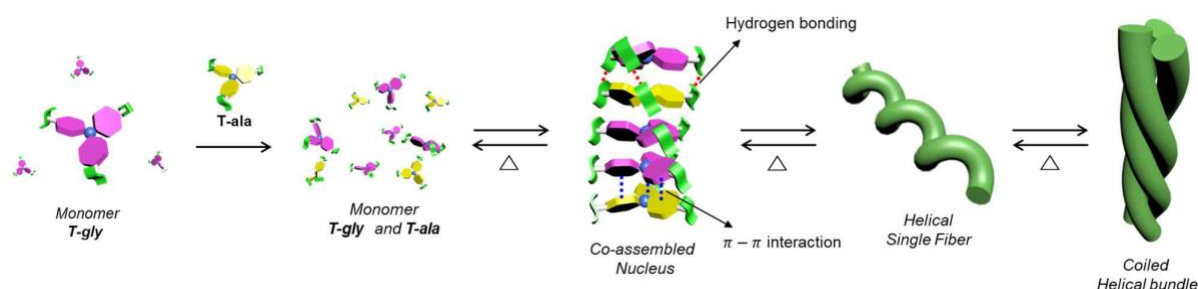
Classical materials readily switch phases (solid to fluid or fluid to gas) upon changes in pressure or heat; however, subsequent reversion of the stimulus returns the material to their original phase. Covalently cross-linked polymer networks, which are solids that do not flow when strained, do not change phase even upon changes in temperature and pressure. However, upon the addition of dynamic cross-links, they become stimuli responsive, capable of switching phase from solid to fluid, but quickly returning to the solid state once the stimulus is removed. **Reported here is the**

**first material capable of a bistable switching of phase.** A permanent solid to fluid transition or vice versa is demonstrated at room temperature, with inherent, spatiotemporal control over this switch in either direction triggered by exposure to light.

**Comment:** The photo-responsive reagents were used to activate the thiol-thioester exchange reactions by light. But the present system can only work once. It's a pity that they did not try other photo-isomerizable reagents to make the transitions recyclable.

### Peculiar Triarylamine-Based Co-assembled Supramolecular Polymers that Exhibit Two Transition Temperatures in the Formation of a Coiled Helical Bundle

Seo, H.; Go, M.; Choi, H.; Kim, K. Y.; Choi, Y.; Lee, S. S.; Jung, S. H.\*; Jung, J. H.\* [\*Chem. Asian J.\* 2018, Accepted Article](#)

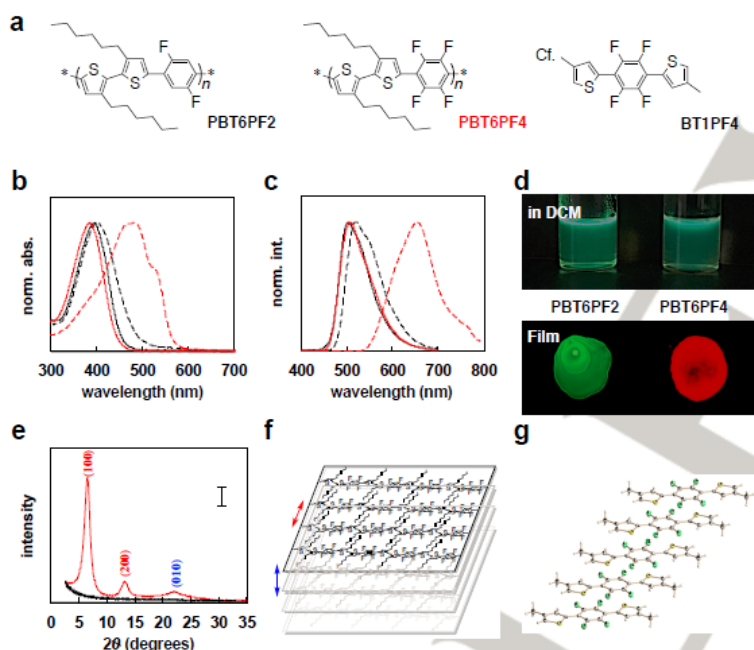


This paper describes the peculiar co-assembly supramolecular polymerization behavior of triphenylamine trisamide derivatives with D-alanine (**T-ala**) or glycine (**T-gly**) moieties. Concentration and temperature-dependent circular dichroism (CD) spectroscopy revealed that the heating curves of co-assemblies obtained at various molar ratios of **T-ala** to **T-gly** exhibited two distinct transition temperatures. The first transition was due to the transformation from coiled helical bundles to single helical fibers without handedness. The second was due to a change from typical elongation to nucleation. These phenomena were confirmed by solvent-dependent decoiling of coiled helical structures and concentration-dependent morphological analysis. The two transitioning temperatures were dependent on the concentration of **T-ala** in the co-assemblies, suggesting that **T-ala** concentration plays an important role in the formation of coiled helical bundles. Our study demonstrated the first observation of two distinct transition temperatures in supramolecular polymers.

**Comment:** I think this work is more a communication than a full paper, because it just covers one point and not a whole story. Anyway, it was interesting to observe the two distinct transition temperatures in supramolecular polymers.

### Solvent Control over Supramolecular Gel Formation and Fluorescence for a Highly Crystalline $\pi$ -Conjugated Polymer

Hayashi, S.\*; Takigami, A.; Koizumi, T.; [\*Chem. Asian J.\* 2018, Accepted Article](#)

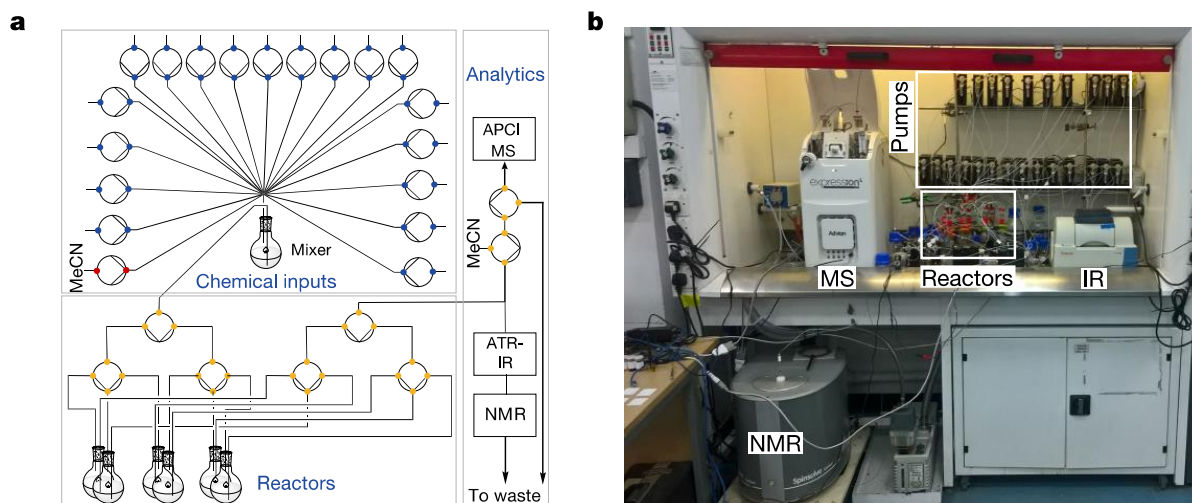


In  $\pi$ -conjugated polymers ( $\pi$ CPs), crystallinity and fluorescence typically exhibit a trade-off relationship. Here, we have synthesised a highly crystalline and fluorescent  $\pi$ -conjugated polymer with a simple alternating structure of 1,2,4,5-tetrafluorophenylene and 3,3'-dihexyl-2,2'-bithiophene units. In film, the polymer exhibited efficient red-coloured fluorescence, an improved quantum yield ( $\Phi_{\text{sol}}=13\% \rightarrow \Phi_{\text{film}}=23\%$ ) and a crystalline structure. Interestingly, supramolecular gel formation occurred in appropriate solvents, and the macrostructure and fluorescence properties of the gel could be directly controlled by the choice of the solvent. The polymer self-assembled into a spherical form that exhibited red fluorescence in non-aromatic solvent (dichloroethane) and into a fibrous form that exhibited yellow fluorescence in aromatic solvent (mesitylene).

**Comment:** Solvent-controlled supramolecular formation of  $\pi$ CPs with fluorescence properties is interesting. Using the transmittance measurements at 1,000 nm to monitor the supramolecular gel formation is interesting, but why at 1000 nm?

## Controlling an Organic Synthesis Robot with Machine Learning to Search for New Reactivity

Granda, J. M.; Donina, L.; Dragone, V.; Long, D.-L.; Cronin, L. [\*Nature\* \*\*2018\*\*, \*559\*, 377.](#)



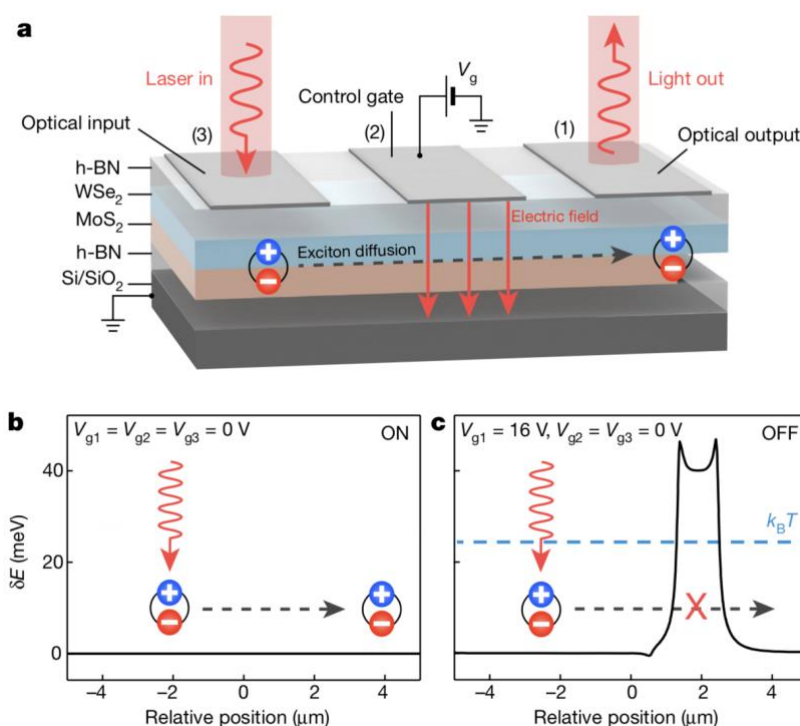
The discovery of chemical reactions is an inherently unpredictable and time-consuming process.

An attractive alternative is to predict reactivity, although relevant approaches, such as computer-aided reaction design, are still in their infancy. Reaction prediction based on high-level quantum chemical methods is complex, even for simple molecules. Although machine learning is powerful for data analysis, its applications in chemistry are still being developed. Inspired by strategies based on chemists' intuition, we propose that a reaction system controlled by a machine learning algorithm may be able to explore the space of chemical reactions quickly, especially if trained by an expert. **Here we present an organic synthesis robot that can perform chemical reactions and analysis faster than they can be performed manually, as well as predict the reactivity of possible reagent combinations after conducting a small number of experiments**, thus effectively navigating chemical reaction space. By using machine learning for decision making, enabled by binary encoding of the chemical inputs, the reactions can be assessed in real time using nuclear magnetic resonance and infrared spectroscopy. **The machine learning system was able to predict the reactivity of about 1,000 reaction combinations with accuracy greater than 80 per cent after considering the outcomes of slightly over 10 per cent of the dataset.** This approach was also used to calculate the reactivity of published datasets. Further, by using real-time data from our robot, these predictions were followed up manually by a chemist, leading to the discovery of four reactions.

**Comment:** 1<sup>st</sup> Look at that fume hood, just look at it! 2<sup>nd</sup> If you had any doubt that machines are taking over: think again. That machine made 969 reactions – and fully analyzed the products – and assigned them – and was actually able to predict outcomes after mere 90 reactions. That's about four PhD students? Of course, this is nowhere near to produce 100 g of motor, but it's pretty dam good I'd say.

### Room-temperature Electrical Control of Exciton Flux in a van der Waals Heterostructure

Unuchek, D.; Ciarrocchi, A.; Avsar, A.; Watanabe, K.; Taniguchi, T.; Kis, A. [Nature 2018, 32, 2466.](#)





Devices that rely on the manipulation of excitons—bound pairs of electrons and holes—hold great promise for realizing efficient interconnects between optical data transmission and electrical processing systems. Although exciton-based transistor actions have been demonstrated successfully in bulk semiconductor-based coupled quantum wells, the low temperature required for their operation limits their practical application. The recent emergence of two-dimensional semiconductors with large exciton binding energies may lead to excitonic devices and circuits that operate at room temperature. Whereas individual two-dimensional materials have short exciton diffusion lengths, the spatial separation of electrons and holes in different layers in heterostructures could help to overcome this limitation and enable room-temperature operation of mesoscale devices. Here we report excitonic devices made of MoS<sub>2</sub>–WSe<sub>2</sub> van der Waals heterostructures encapsulated in hexagonal boron nitride that demonstrate electrically controlled transistor actions at room temperature. **The long-lived nature of the interlayer excitons in our device results in them diffusing over a distance of five micrometres.** Within our device, we further demonstrate the ability to manipulate exciton dynamics by creating electrically reconfigurable confining and repulsive potentials for the exciton flux. **Our results make a strong case for integrating two-dimensional materials in future excitonic devices** to enable operation at room temperature.

**Comment:** I did not pay much attention to excitonics until this article came out. As for Spintronics “one” of the ideas is to construct the equivalent of microelectronics (should we not call it nanoelectronics at this point?). But while spintronics is yet to go anywhere close to a transistor, this paper reports exactly that: An exciton transistor. AND, importantly, they made it really understandable by [this](#) explanation. I’d stay with that explanation rather than trying to understand the paper...