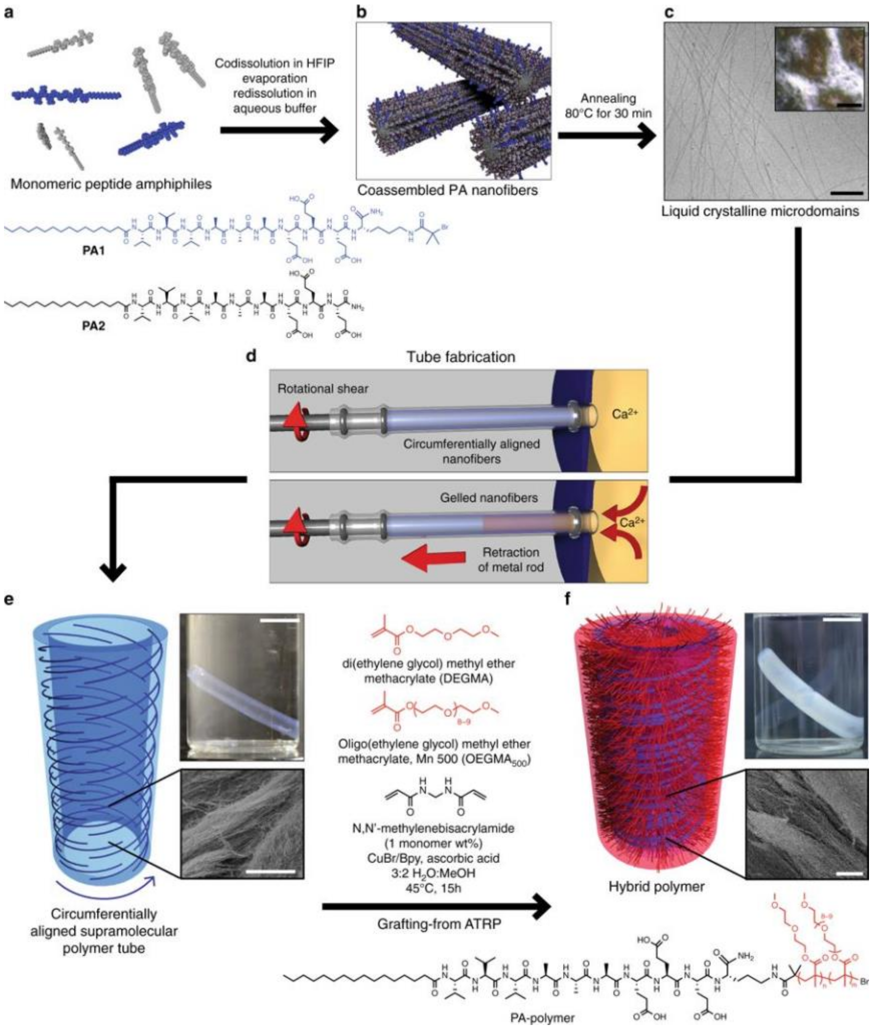
Covalent-supramolecular Hybrid Polymers as Muscle-inspired Anisotropic Actuators

Chin, S.; Synatschke, C.; Liu, S.; Nap, R.; Sather, N.; Wang, Q.; Álvarez, Z.; Edelbrock, A.; Fyrner, T.; Palmer, L.; Szleifer, L.; Cruz, M.; Stupp, S.* *Nat. Commun.* **2018**, *9*, 2395.

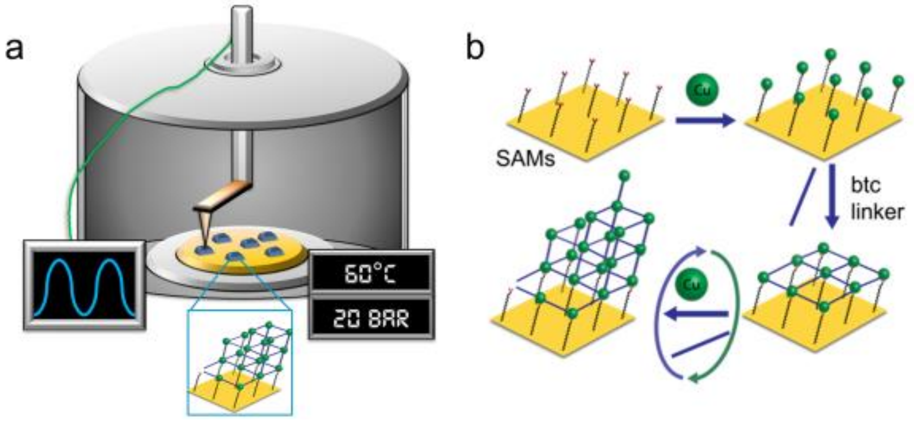


Skeletal muscle provides inspiration on how to achieve reversible, macroscopic, anisotropic motion in soft materials. Here we report on the bottom-up design of macroscopic tubes that exhibit anisotropic actuation driven by a thermal stimulus. The tube is built from a hydrogel in which extremely long supramolecular nanofibers are aligned using weak shear forces, followed by radial growth of thermoresponsive polymers from their surfaces. The hierarchically ordered tube exhibits reversible anisotropic actuation with changes in temperature, with much greater contraction perpendicular to the direction of nanofiber alignment. We identify two critical factors for the anisotropic actuation, macroscopic alignment of the supramolecular scaffold and its covalent bonding to polymer chains. Using finite element analysis and molecular calculations, we conclude polymer chain confinement and mechanical reinforcement by rigid supramolecular nanofibers are responsible for the anisotropic actuation. The work reported suggests strategies to create soft active matter with molecularly encoded capacity to perform complex tasks.

Comment: A new work from Stupp's peptide amphiphile (PA) series. The main concept is still about constructing hierarchically ordered structures but not much about dynamic properties from supramolecular structures (PAs in their systems are very rigid). It is quite common to obtain mechanical contraction based on poly-DEGMA and poly-OEGMA$_{500}$ which show LCST behaviour with varied temperatures. But the present work showed an interesting way to align the PAs by using weak shear forces. Also, the computational model explaining the mechanism is worth a look.

Behavior of a Metal Organic Framework Thin-Film at Elevated Temperature and Pressure as Studied with an Autoclave-Inserted Atomic Force Microscope

Brand, R. P.; Mandemaker, L. D. B.; Delen, G.; Rijnveld, N.; Weckhuysen, M.*
ChemPhysChem **2018**, ASAP.

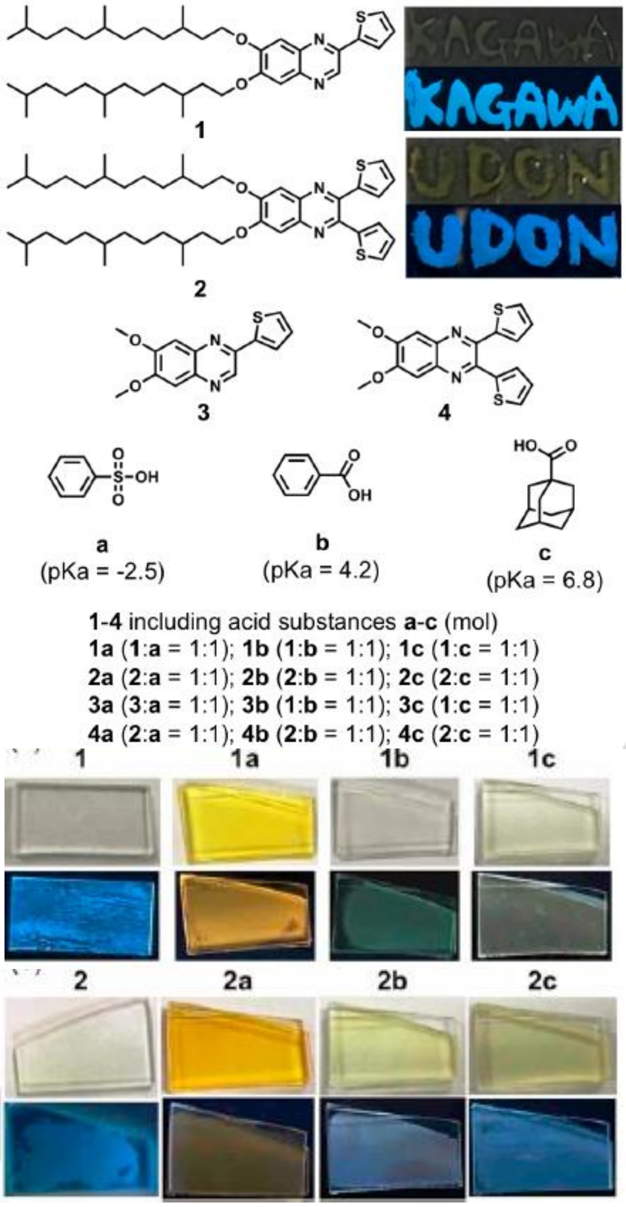


Bridging the gap in studying surface reactions, processes and morphology and measuring at (catalytic) relevant conditions is crucial for our understanding of the working principles of porous crystalline materials. Scanning Tunneling Microscopy is limited because of the required conductivity of the sample, while Atomic Force Microscopy (AFM) is often challenging in use due to the physical underlying mechanism of the technique. Here, we report a **tailor-made autoclave-inserted AFM**, **able to measure at ~ 20 bar and ~ 110°C**. First, we show the ability to obtain **nanometer resolution** on well-defined test samples at before-mentioned conditions. Second, to demonstrate the **possibilities of analyzing morphological evolutions at elevated temperatures and pressures**, we use this setup to measure the stability of a surface-anchored Metal-Organic Framework (SURMOF) *in-situ* at 20 – 60°C and 1 – 20 bar simultaneously. It was found that the showcase HKUST-1 material has a good physical stability, as it is hardly damaged from exposure to 20 bar. However, its thermal stability is weaker, as exposure to elevated T damaged the material by influencing the interaction between organic linker and metal cluster. *In-situ* measurements at elevated T also showed an increased mobility of the material when working at such conditions. Combining the strength of AFM at elevated T and p with *ex-situ* AFM and spectroscopic measurements on this MOF showcases an example of how porous materials can be studied at (industrial) relevant conditions using the autoclave-inserted AFM.

Comment: The purpose of this article is to show the efficiency of a novel AFM capable of measuring samples under high pressure and high temperature. Even if this system is not yet commercially available, it is still interesting, in my opinion, to follow the advance of new methodologies and new equipment in order to integrate them in our future studies.

Tuning Electronic Properties and Acid-Responsive Behavior of N-Heteroacene-based π-Conjugated Liquids by Changing the Number of π-Conjugated Substituents

Sato, Y.; Mutoh, Y.; Matsukuma, D.; Nakagawa, M.; Kawai, T.; Isoda, K.*; *Chem. Asian J.* **2018**, *Accepted Article*



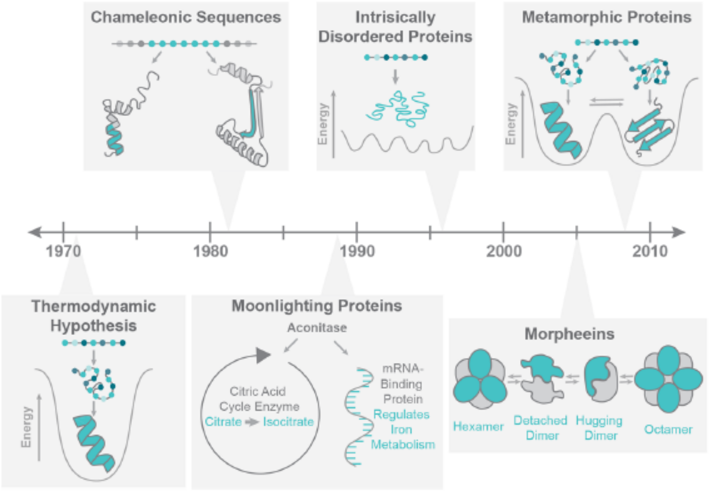
1-4 including acid substances **a-c** (mol)
1a (**1**:**a** = 1:1); **1b** (**1**:**b** = 1:1); **1c** (**1**:**c** = 1:1)
2a (**2**:**a** = 1:1); **2b** (**2**:**b** = 1:1); **2c** (**2**:**c** = 1:1)
3a (**3**:**a** = 1:1); **3b** (**1**:**b** = 1:1); **3c** (**1**:**c** = 1:1)
4a (**2**:**a** = 1:1); **4b** (**2**:**b** = 1:1); **4c** (**2**:**c** = 1:1)

We designed and synthesized two room temperature fluorescent π-conjugated liquids **1** and **2** based on N-heteroacene framework, which have one and two thiophene rings. Two π-conjugated liquids showed different electronic properties and rheology behavior. For dithiophene-appended molecule **4**, single-crystallographic X-ray analysis revealed that two thiophene rings hindered acid-recognizing imino-N atoms as well as S atoms of thiophene rings interacted with imino-N atoms on pyradine. On the other hand, monothiophene-appended molecule **1** and **3** had an unhindered imino-N atom located on opposite site for thiophene ring. Upon dissolving acid substances having various pKa values, these slight differences for **1** and **2** gave rise to marked differences in acid-responsive behavior, resulting in various fluorescent colors in liquid states. Also, when acid with lower pKa value was dissolved in **1** and **2**, phase transition occurred from isotropic liquid states to self-organized liquid-crystalline phases.

Comment: It's an interesting work. Molecules **1** and **2** alone are fluidic liquids, and turn into liquid crystals when forming hydrogen bonds with acids, which also results in different emissions. I think this work can be applied to photochromic materials.

Unfolding the Mysteries of Protein Metamorphosis

Dishman, A. F.; Volkman, B. F.* *ACS Chem. Biol.* **2018**, 13, 1438-1446

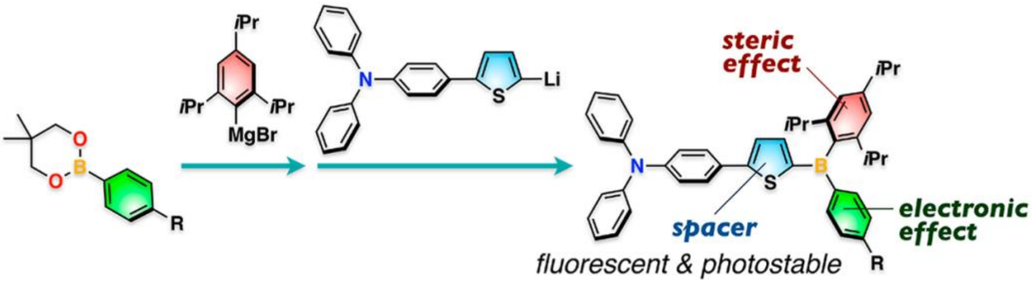


Since the proposal of Anfinsen's thermodynamic hypothesis in 1963, our understanding of protein folding and dynamics has gained significant appreciation of its nuance and complexity. Intrinsically disordered proteins, chameleonic sequences, morpheeins, and metamorphic proteins have broadened the protein folding paradigm. Here, we discuss noncanonical protein folding patterns, with an emphasis on metamorphic proteins, and we review known metamorphic proteins that occur naturally and that have been engineered in the laboratory. Finally, we discuss research areas surrounding metamorphic proteins that are primed for future exploration, including evolution, drug discovery, and the quest for previously unrecognized metamorphs. As we enter an age where we are capable of complex bioinformatic searches and *de novo* protein design, we are primed to search for previously unrecognized metamorphic proteins and to design our own metamorphs to act as targeted, switchable drugs; biosensors; and more.

Comment: The project of protein folding (including natural and non-natural proteins) is still thought to be an important challenge of the 21st century of biological physics. This review describes metamorphic proteins and their implications in evolution, drug discovery, and protein engineering.

Donor－π－Acceptor Type Unsymmetrical Triarylborane-based Fluorophores: Synthesis, Fluorescence Properties, and Photostability

Ito, M.; Ito, E.; Yamaguchi, S.* *J. Org. Chem.* **2018**, ASAP.

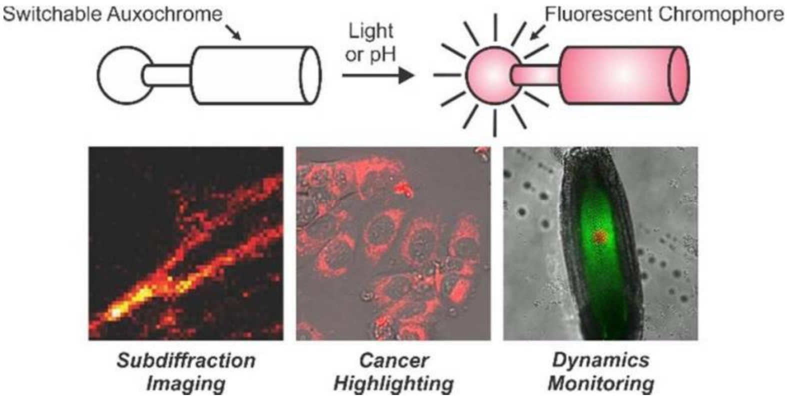


A two-step synthesis to prepare tricoordinate organoboron compounds bearing three different aryl groups has been developed. After the first aryl substitution to an aryl boronic ester took place, the intermediate species, that is, bis(diarylborinate) species, was isolated as an air- and moisture-stable solid, which allowed the second aryl substitution to carry out in a selective manner. Subsequently, a series of unsymmetrical triarylboranes possessing a sterically bulky aryl group, triarylamine moiety, and para-functionalized phenyl ring was synthesized. Not only did these triarylboranes exhibit remarkable solvent-dependent fluorescence as expected for donor-π-acceptor (D-π-A) systems, they were also accompanied by profound persistence against photoirradiation especially for that bearing a 1,3,5-tri-tert-butylphenyl ring. This survey exemplifies that sufficient electronic and steric modification is key to construct photostable D-π-A type triarylborane-based fluorophores.

Comment: The combination of triarylborane and fluorophores may provide more insights on the construction of photostable fluorescence dyes. If endow the compound water solubility, perhaps it could be used in bio-imaging.

Fluorescence Activation with Switchable Oxazines

Zhang, Y.; Tang, S.; Thapaliya, E. R.; Sansalone, L.; Raymo, F. M.* *Chem. Commun.* **2018**, ASAP.

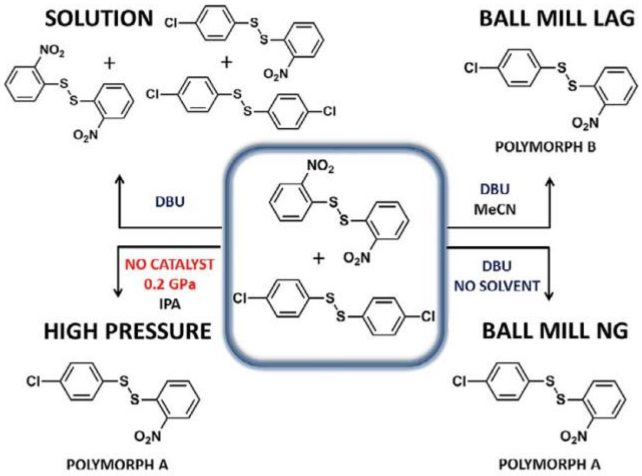


The identification of operating principles to activate fluorescence under the influence of external stimulations is essential to enable the implementation of imaging strategies requiring the spatiotemporal control of emission. In this context, our laboratories designed mechanisms to switch fluorescence with either light or pH based on the unique photochemical and photophysical properties of either **photoresponsive or halochromic oxazines** respectively. These **heterocycles can be connected covalently to fluorescent chromophores** and opened with either light or pH **to impose a significant bathochromic shift on the main absorption of the emissive appendage**. Such a spectral change allows the selective excitation of the resulting species to activate bright fluorescence with infinite contrast and spatiotemporal control. Indeed, these mechanisms for fluorescence activation enable the acquisition of images with subdiffraction resolution, the selective signalling of cancer cells and the monitoring of translocating species in real time. Thus, our structural designs for fluorescence switching under external control can evolve into invaluable probes for the implementation of bioimaging strategies that would be impossible to perform with conventional fluorophores.

Comment: I think that this article is really interesting for those who would like to work with both photo-responsive and chemo- responsive reversible systems. Indeed, the authors based their work on a spiropyran system and then optimized it in order to make it more stable and faster (ring closure step: ~min. for spiropyrans vs. ~μs for oxazines). It may be interesting to use this kind of systems as a regulator integrated with our motor into a contractile gel.

Dynamic Covalent Chemistry under High-Pressure: A New Route to Disulfide Metathesis

Sobczak, S.; Drożdż, W.; Lampronti, G. I.; Belenguer, A. M.; Katrusiak, A.*; Stefankiewicz, A. R.* *Chem. Eur. J.* **2018**, *24*, 8769.

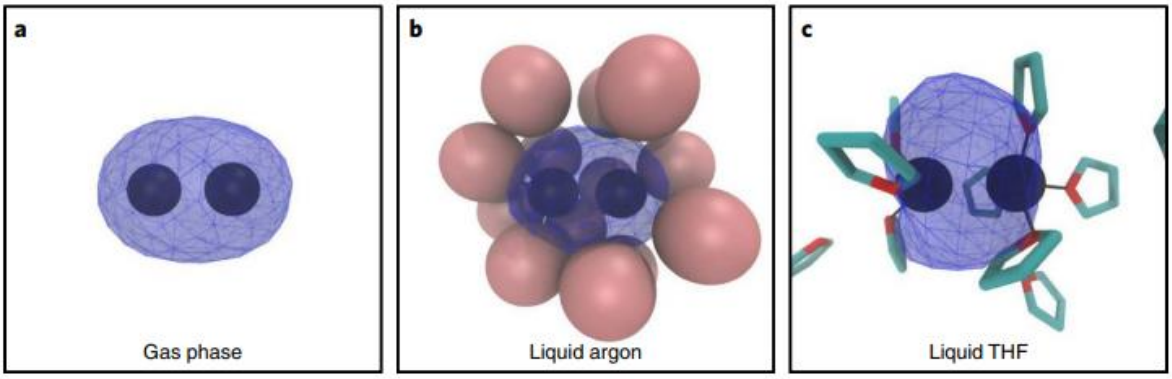


This work describes, for the first time, the application of combined pressure and temperature stimuli in disulfide metathesis reactions. In the system studied, above a pressure of 0.2 GPa, equimolar amounts of symmetric disulfides bis 4-chlorophenyl disulfide [(4-ClPhS)$_2$] and bis 2-nitrophenyl disulfide [(2-NO$_2$PhS)$_2$] react to give the heterodimeric product 4-Cl-PhSSPh-2-NO$_2$. In contrast to experiments conducted in solution at atmospheric pressure or in mechanochemical experiments under ball-mill grinding conditions, there is no necessity to use a base or thiolate anion as a catalyst for the exchange reaction under investigated conditions. Single-crystal and powder X-ray diffraction revealed also that, despite the high-pressure conditions of this reaction, the heterodimeric-disulfide product unexpectedly crystallizes into the low-density polymorph A. This counterintuitive result contrasts with the high-pressure stability of the higher-density polymorph B, confirmed by its compression up to 2.8 GPa with no signs of a phase transition.

Comment: It is quite rare to see exchange reactions being implemented using the effect of pressure instead of catalytic/reducing agents. With careful attention to the absence of any contaminants in their starting materials, the authors prove that disulfide exchange in their chemical system proceeds solely under the influence of **supercritical/close to supercritical** physical stimuli.

Solvents Can Control Solute Molecular Identity

Widmer, D. R.; Schwartz, B. J.* *Nat. Chem.* **2018**, ASAP.

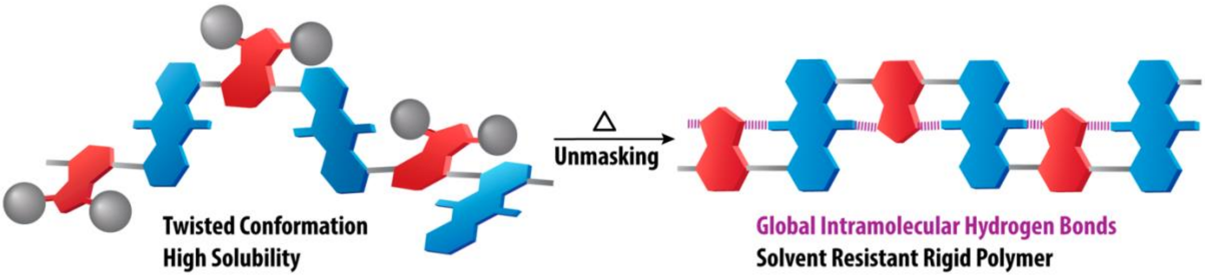


For solution-phase chemical reactions, the solvent is often considered simply as a medium to allow the reactants to encounter each other by diffusion. Although examples of direct solvent effects on molecular solutes exist, such as the compression of solute bonding electrons due to Pauli repulsion interactions, the solvent is not usually considered a part of the chemical species of interest. We show, using quantum simulations of Na_2, that when there are local specific interactions between a solute and solvent that are energetically on the same order as a hydrogen bond, the solvent controls not only the bond dynamics but also the chemical identity of the solute. In tetrahydrofuran, dative bonding interactions between the solvent and Na atoms lead to unique coordination states that must cross a free energy barrier of ~8 kBT—undergoing a chemical reaction—to interconvert. Each coordination state has its own dynamics and spectroscopic signatures, highlighting the importance of considering the solvent in the identity of condensed-phase chemical systems.

Comment: This paper show that solvent plays an intimate role in the bond dynamics, electronic properties and, indeed, chemical identity of simple solutes.

Synthesis and Solution Processing of a Rigid Polymer Enabled by Active Manipulation of Intramolecular Hydrogen Bonds

Zhu, C.; Mu, A. U.; Wang, C; Ji, X.; Fang, J.* *ACS Macro Lett.* 2018, 7, 801−806

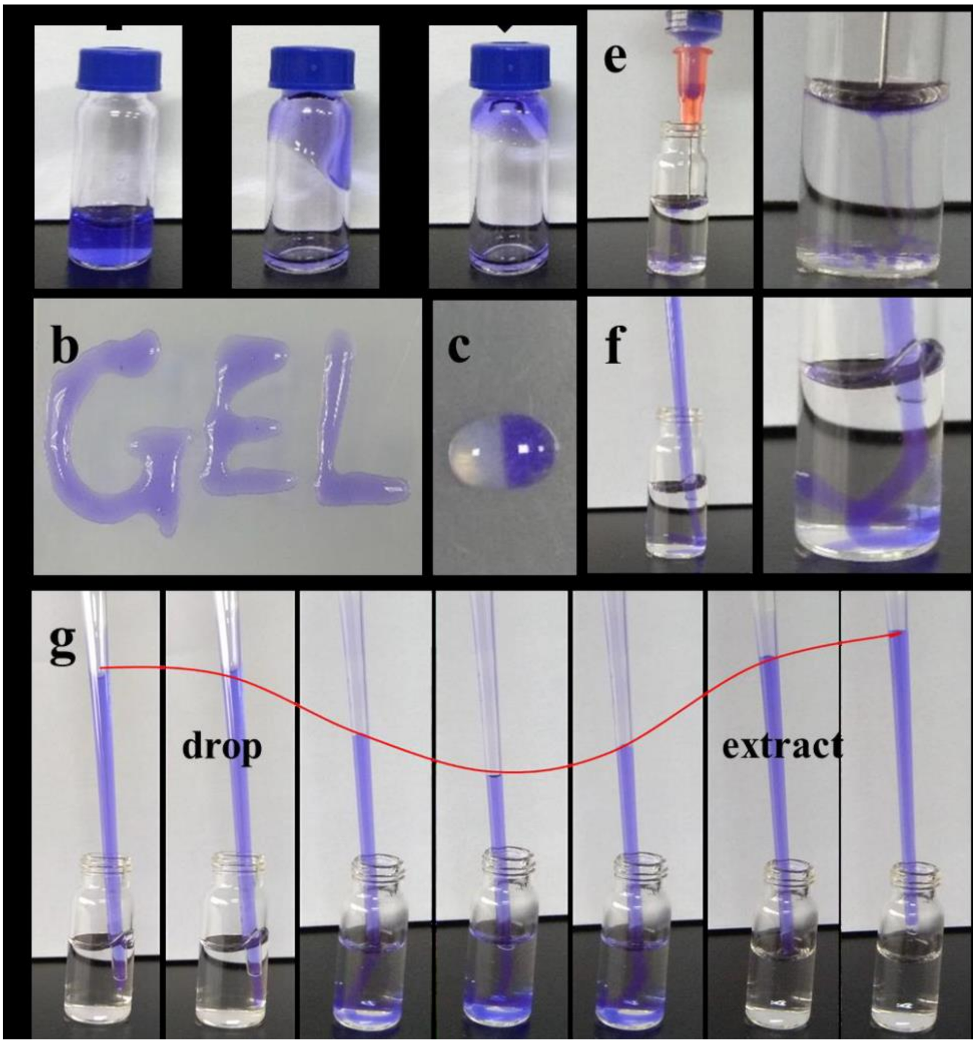


Global intramolecular hydrogen bonds were installed and manipulated in a rigid artificial synthetic polymer in order to actively control its conformation for synthesis and processing. The polymer solubility was switched on and off by chemically inhibiting and regenerating these preorganized intramolecular hydrogen bonds. Such active manipulation made it possible to synthesize this highly rigid polymer with elevated molecular weights. A well-solubilized, noncoplanar polymer precursor with thermally cleavable Boc groups was synthesized (Mn = 32.4 kg/mol). After processing this precursor into thin films, in situ thermal treatment regenerated the latent intramolecular hydrogen bonds and led to a rigid ladder-type conformation. Such manipulation of the intramolecular hydrogen bonds allowed for multilayer deposition of this polymer, laying the foundation for potential additive manufacturing using this strategy

Comment: In this paper, they present a molecular-engineering strategy to manipulate intramolecular hydrogen bonds of rigid macromolecules.

Developing a Self-healing Supramolecular Nucleoside Hydrogel Based on Guanosine and Isoguanosine

Tang, F.; Feng, H.; Zhao, H.; Dan, H.; Du, Y.*; Xiao, Y.*; Chen, Q.; *Chem. Asian J.* **2018**, *Accepted Article*

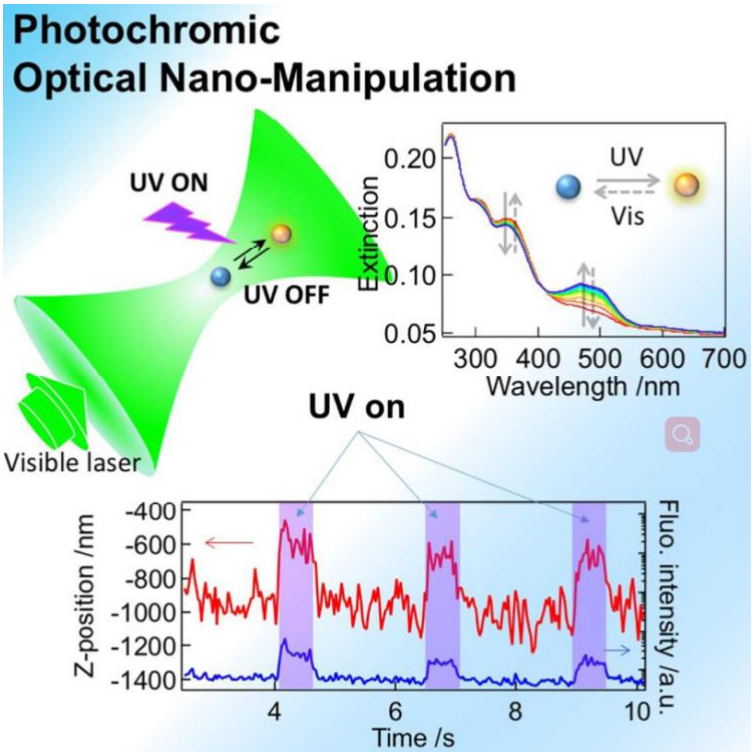


Recently, supramolecular hydrogels have attracted increasing interest owing to their tunable stability and inherent biocompatibility. However, only few studies have been reported in the literature on self-healing supramolecular nucleoside hydrogels, compared to self-healing polymer hydrogels. In this work, we successfully developed a self-healing supramolecular nucleoside hydrogel obtained by simply mixing equimolar amounts of guanosine (G) and isoguanosine (isoG) in the presence of K$^+$. The gelation properties have been studied systematically by comparing different alkali metal ions as well as mixtures with different ratios of G and isoG. To this end, rheological and phase diagram experiments demonstrated that the co-gel not only possessed good self-healing properties and short recovery times (only 20 seconds) but also could be formed at very low concentrations of K$^+$. Furthermore, nuclear magnetic resonance (NMR), powder X-ray diffraction (PXRD), and circular dichroism (CD) spectroscopy suggested that possible G_2isoG$_2$-quartet structures occurred in this self-healing supramolecular nucleoside hydrogel. This co-gel, to some extent, addressed the problem of isoguanosine gels for applications in vivo, which showed the potential to be a new type of drug delivery system for biomedical applications in the future.

Comment: Guanosine (G) and isoguanosine (isoG) form hydrogels with K$^+$ and show self-healing properties, which is quite interesting and has potential applications in biological system.

Mesoscopic Motion of Optically Trapped Particle Synchronized with Photochromic Reactions of Diarylethene Derivatives

Ito, S.; Mitsuishi, M.; Setoura, K.; Tamura, M.; Lida, T.; Morimoto, M.; Irie, M.; Miyasaka, H.* *J. Phys. Chem. Lett.* **2018**, 9, 2659–2664.

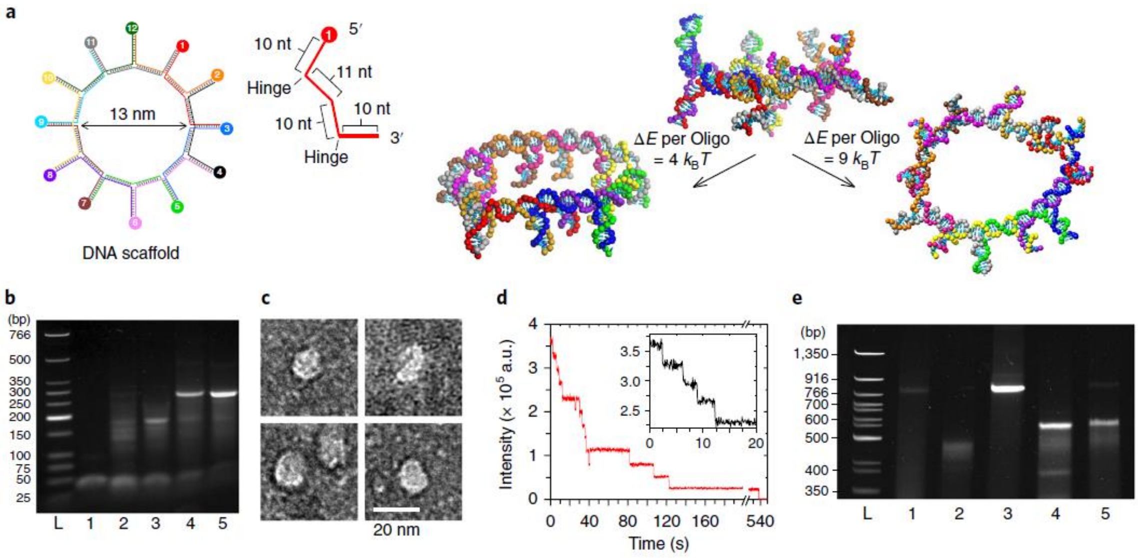


Not only the energy but also the momentum of photons transfers to material via photoabsorption; this momentum transfer, known as radiation pressure, can induce motions of small particles. It can therefore be expected to induce mechanical motions of mesoscopic materials synchronized with the reversible change of their absorption coefficient by external stimuli. We demonstrated quantitative photomechanical motions in mesoscopic regions by combining optical tweezer and photochromic reactions of diarylethene (DAE). A microparticle including DAE was optically trapped with 532 nm laser and the absorption band of the DAE was photoswitched with UV laser, resulting in the modulation of the radiation force through the change in the complex dielectric constant of the particle. In this process, mesoscopic mechanical motions were successfully induced by the photochromic reaction. The present approach is potentially applicable in a wide variety of nano/micromechanical devices and also paves the way for monitoring the absorption of photons by molecules via photomechanical response.

Comment: It would be interesting to try a Janus particle and it's a pity that the movement could not be observed directly by the microscopy. Of course, the experimental equipment seems to be too advanced to make this strategy widely applied, at least for now.

DNA Scaffolds Support Stable and Uniform Peptide Nanopores

Spruijt, E.*; Tusk, S. E.; Hagan, B.* *Nat. Nanotechnol.* **2018**, ASAP.

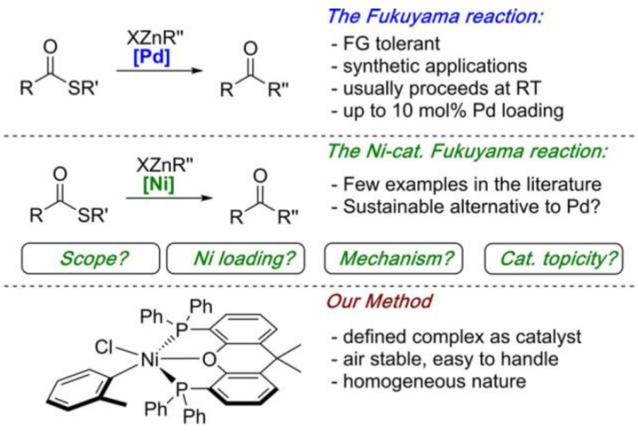


The assembly of peptides into membrane-spanning nanopores might be promoted by scaffolds to pre-organize the structures. Such scaffolds could enable the construction of uniform pores of various sizes and pores with controlled permutations around a central axis. Here, we show that DNA nanostructures can serve as scaffolds to arrange peptides derived from the octameric polysaccharide transporter Wza to form uniform nanopores in planar lipid bilayers. Our ring-shaped DNA scaffold is assembled from short synthetic oligonucleotides that are connected to Wza peptides through flexible linkers. When scaffolded, the Wza peptides form conducting nanopores of which only octamers are stable and of uniform conductance. Removal of the DNA scaffold by cleavage of the linkers leads to a rapid loss of the nanopores from the lipid bilayer, which shows that the scaffold is essential for their stability. The DNA scaffold also adds functionality to the nanopores by enabling reversible and permanent binding of complementary tagged oligonucleotides near the nanopore entrance.

Comment: DNA has proven its potential as scaffold in many research areas such as nanotechnology and bioengineering because of its rigidity. Unlike commonly used β-barrel type nanopores, the pore formed in this article was constructed using α-helical peptides. Completely opposite ideas sometimes may lead to new horizons. How about using a DNA scaffold combined with rotary motors to construct artificial ion channels?

Nickel-Catalyzed Coupling of Arylzinc Halides with Thioesters

Gehrtz, P. H.; Kathe, P.; Fleischer, I.* *Chem. Eur. J.* **2018**, *24*, 8774.

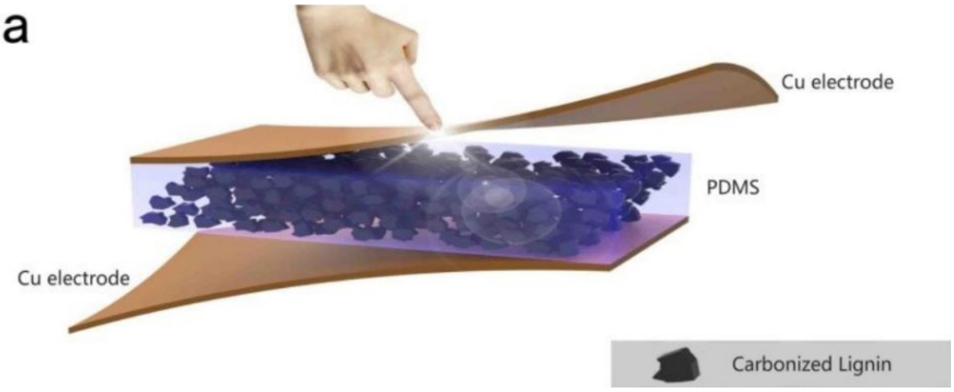


The Pd-catalyzed Fukuyama reaction of thioesters with organozinc reagents is a mild, functional-group-tolerant method for acylation chemistry. Its Ni-catalyzed variant might be a sustainable alternative to expensive catalytic Pd sources. We investigated the reaction of *S*-ethyl thioesters with aryl zinc halides with hetero- and homotopic Ni precatalysts and several ligands. The results show that both homo- and heterotopic species may contribute to catalysis. The substrate scope using an operationally homogeneous defined Ni complex was established. Acyl radicals are postulated as short-lived intermediates.

Comment: The Fukuyama reaction allows access to polyfunctional ketones via the cleavage of bench- and chromatography-stable S-alkyl thioesters. It traditionally employs mild organozinc reagents in conjunction with Pd catalysis and offers advantages over acylations using Grignard reagents in the total synthesis of various natural compounds. In this paper, a new ligand is reported for the homogeneous Ni-catalyzed Fukuyama coupling.

Lignin-Based Highly Sensitive Flexible Pressure Sensor for Wearable Electronics

Wang, B.; Shi, T.; Zhang, Y.; Chen, C.; Li, Q.; Fan, Y.* *J. Mater. Chem. C* **2018**, *6*, 6423–6428.

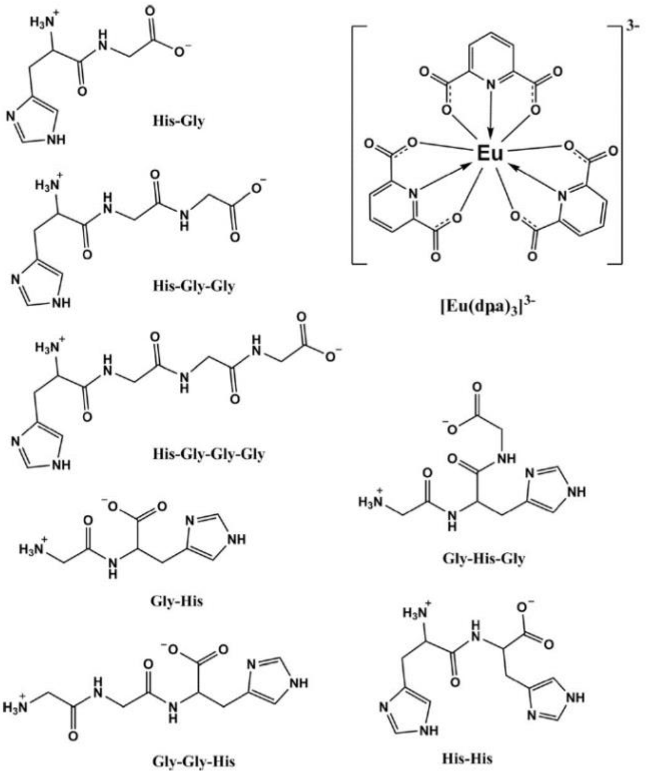


The development of flexible sensors with low cost, facile preparation and good reproducibility is of profound significance for wearable electronics and intelligent systems. Lignin is an aromatic composition of lignocellulosic biomass and known as a **cheap, renewable, and environmentally friendly resource** available everywhere. In this study, we present a simple and low-cost approach for the preparation of a highly electrically sensitive and flexible composite with polydimethylsiloxane and carbonized lignin *via* a facile process (CL/PDMS). This electrically sensitive flexible composite can be used in the preparation of a piezo-resistive sensor, which exhibits stable and fast response to loading and unloading stress in 60 ms and 40 ms, respectively. The sensor prototype displayed high sensitivity (57 kPa^{-1}), wide range of working pressure (from 0 to 130 kPa) and excellent durability. The signals of pulse rates and the force needed for picking up items were successfully collected with this CL/PDMS sensor prototype. With the simple process for fabrication, low-cost of the filling material and excellent performance, we believe that the lignin-based sensitive flexible composite CL/PDMS is promising for applications in **wearable electronics** and intelligent systems such as health monitoring, smart skins, sports and other related areas.

Comment: Frankly, I doubt that this article may be of any interest for any of our projects. However, since biopolymers and smart devices will become more and more important in the (maybe not so) near future, this article presents a way of **"upcycling" carbonized lignin** into a pressure sensor, which is a better fate than just being burnt as fuel.

Binding of Lanthanide Complexes to Histidine-Containing Peptides Probed by Raman Optical Activity Spectroscopy

Brichtová, E.; Brichtová, J.; Vršková, N.; Šebestík, J; Bouř, P; Wu, T.* *Chem. Eur. J.* **2018,** *24,* 8664.

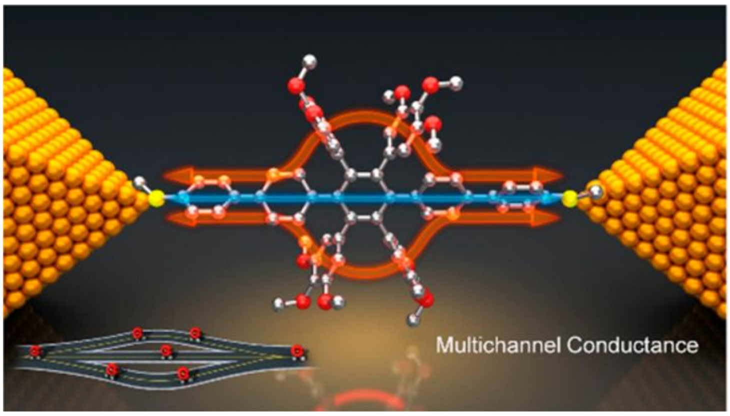


Lanthanide complexes are used as convenient spectroscopic probes for many biomolecules. Their binding to proteins is believed to be enhanced by the presence of histidine, but the strength of the interaction significantly varies across different systems. To understand the role of peptide length and sequence, short histidine-containing peptides have been synthesized (His-Gly, His-Gly-Gly, His-Gly-Gly-Gly, Gly-His, Gly-His-Gly, His-His, and Gly-Gly-His) and circularly polarized luminescence (CPL) induced at the [Eu(dpa)$_3$]$^{3-}$ complex has been measured by means of a Raman optical activity (ROA) spectrometer. The obtained data indicate relatively weak binding of the histidine residue to the complex, with a strong participation of other parts of the peptide. Longer peptides, low pH, and a histidine residue close to the *N*-peptide terminus favor the binding. The binding strengths are approximately proportional to the CPL intensity and roughly correlate with predictions based on molecular dynamics (MD) simulations. The specificity of lanthanide binding to the peptide structure and its intense luminescence and high optical activity make the ROA/CPL technique suitable for probing secondary and tertiary structures of peptides and proteins.

Comment: Most of the luminescent labels of living cell components used in analytical biochemistry and imaging are based on lanthanides (metals which exhibit extremely rich environment-dependent luminescence spectra). Using a series of histidine-containing peptides, the results in this paper show that both the length of these peptides and the position of histidine profoundly affect the Eu^{III} binding mode.

Remarkable Multichannel Conductance of Novel Single-Molecule Wires Built on Through-Space Conjugated Hexaphenylbenzene

Zhen, S.; Mao, J. C.; Chen, L.; Ding, S.; Luo, W.; Zhou, X. S.; Qin, A.; Zhao, Z.;* Tang, B. Z.* *Nano Lett.* **2018**, ASAP.

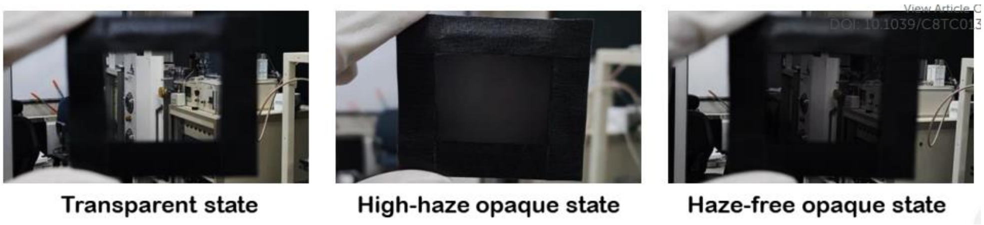


Through-bond conjugated molecules are the major frameworks for traditional molecular wires, while through-space conjugated units are rarely utilized and studied although they have shown unique conducting potential. Herein, we present novel single-molecule wires built on through-space conjugated hexaphenylbenzene. Their conductance, measured by the scanning tunneling microscopy based break-junction technique, increases with the improvement of through-space conjugation and finally reaches a remarkable value (12.28 nS) which greatly exceeds that of conventional through-bond conjugated counterpart (2.45 nS). The multichannel conducting model by integrating through-space and through-bond conjugations could be a promising strategy for the further design of robust single-molecule wires with advanced conductance and stability

Comment: Even if this article is not completely related to the topics studied in our group, I think that the idea of building single-molecule wires via through-space conjugation is really fascinating.

Thermal Control of Transmission Property by Phase Transition in Cholesteric Liquid Crystals

Oh, S.-W.; Kim, S.-H.; Yoon, T.-H.* *J. Mater. Chem. C* **2018**, *6* (24), 6520–6525.

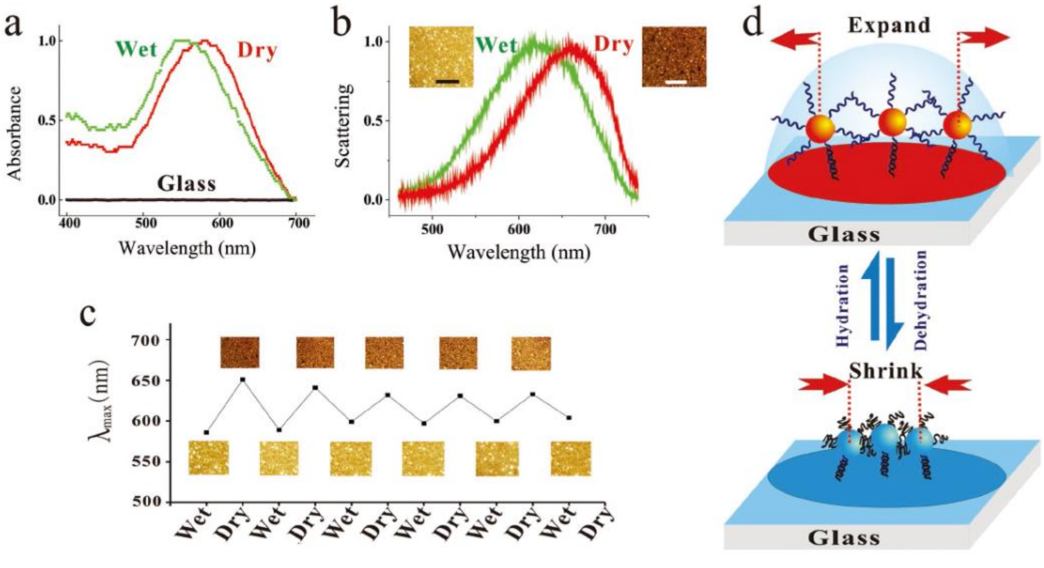

Transparent state **High-haze opaque state** **Haze-free opaque state**

Cholesteric liquid crystals (LCs) responsive to external stimuli, such as temperature or light, can be used for **color switching** or tuning through the change in the cholesteric pitch. This paper presents the thermal control of the transmission property via the phase transition of cholesteric LCs without any change in the cholesteric pitch. We used the chiral smectic A, chiral nematic, and isotropic phases as the transparent, high-haze opaque, and haze-free opaque states of a dye-doped cholesteric LC cell. We showed that the proposed device could be used as a temperature sensor or self-shading smart window for energy saving.

Comment: This article highlights another use of phase transitions in liquid crystalline materials. Usually, the colour is changed by tuning the pitch of the cholesteric (helical) phase, but, in this example, the scattered light is modified only because of a change in temperature, hence the application in smart windows.

Humidity-Responsive Single-Nanoparticle-Layer Plasmonic Films

Shen, J.; Luan, B.; Pei, H.; Yang, Z.; Zuo, X.; Liu, G.; Shi, L.; Wang, L.*; Cheng, W. *; Fan, C. * *Adv. Mater.* **2017**, 29, 1606796.

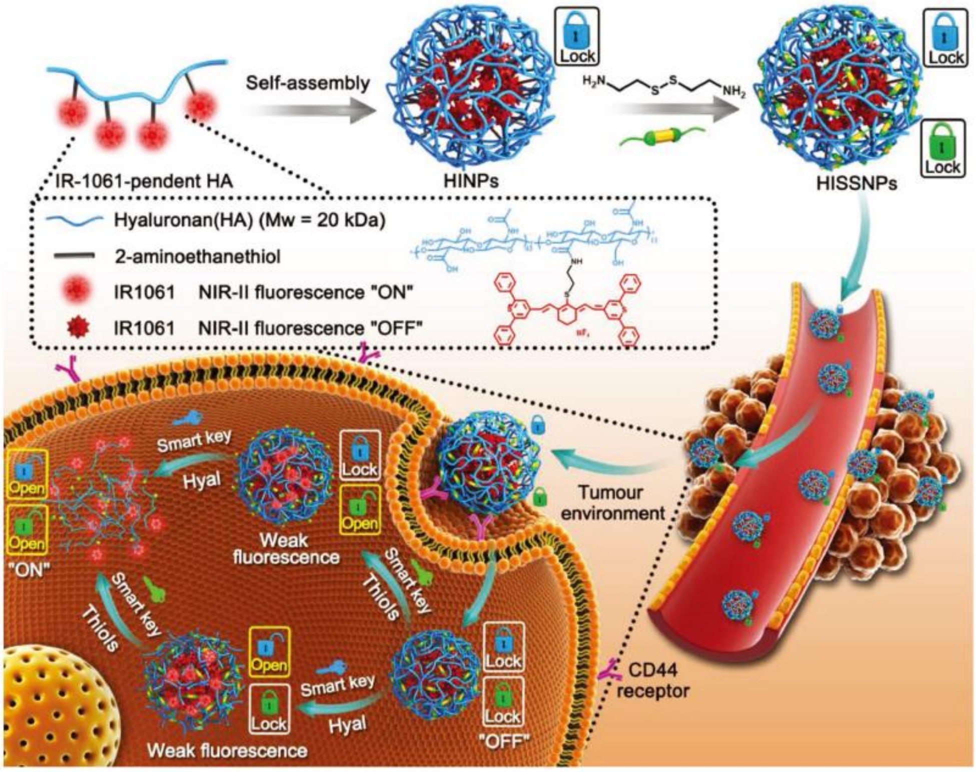


2D materials possess many interesting properties, and have shown great application potentials. In this work, the development of humidity-responsive, 2D plasmonic nanostructures with switchable chromogenic properties upon wetting–dewetting transitions is reported. By exploiting DNA hybridization directed anchoring of gold nanoparticles (AuNPs) on substrates, a series of single-nanoparticle-layer (SNL) plasmonic films is fabricated. Due to the collective plasmonic responses in SNL, these ultrathin 2D films display rapid and reversible red-blue color change upon the wetting–dewetting transition, suggesting that hydration-induced microscopic plasmonic coupling between AuNPs is replicated in the macroscopic, centimeter-scale films. It is also found that hydration finely tunes the electric field distribution between AuNPs in the SNL film, based on which responsive surface-enhanced Raman scattering substrates with spatially homogeneous hot spots are developed. Thus it is expected that DNA-mediated 2D SNL structures open new avenues for designing miniaturized plasmonic nanodevices with various applications.

Comment: Recently, I have read lots of literature on gold nanoparticles plasmonic resonance. This paper hits me because the design is quite clever. Compared with other papers, this hydration-induced process not only affects the optical absorption of the film but also the electric field distribution between AuNPs in the film.

"Dual Lock-and-Key"-Controlled Nanoprobes for Ultrahigh Specific Fluorescence Imaging in the Second Near-Infrared Window

Tang, Y.; Li, Y.; Hu, X.; Zhao, H.; Ji, Y.; Chen, L.; Hu, W.; Zhang, W.; Li, X.; Lu, X.; Huang, W.; Fan, Q.* *Adv. Mater.* **2018**, ASAP.

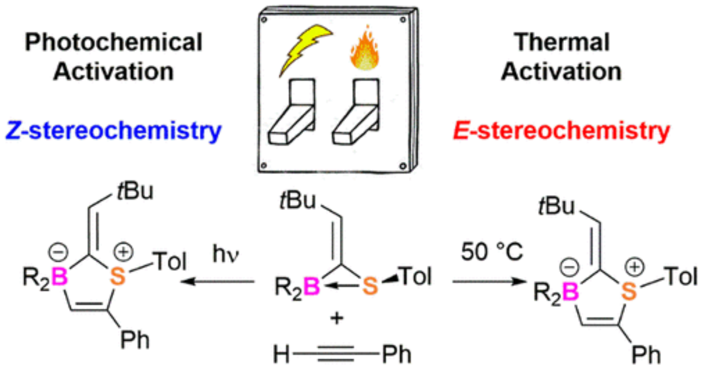


Fluorescence imaging in the second near-infrared window (NIR-II) is a new technique that permits visualization of deep anatomical features with unprecedented spatial resolution. Although attractive, effectively suppressing the interference signal of the background is still an enormous challenge for obtaining target-specific NIR-II imaging in the complex and dynamic physiological environment. Herein, dual-pathological-parameter cooperatively activatable NIR-II fluorescence nanoprobes (HISSNPs) are developed whereby hyaluronic acid chains and disulfide bonds act as the "double locks" to lock the fluorescence-quenched aggregation state of the NIR-II fluorescence dyes for performing ultrahigh specific imaging of tumors in vivo. The fluorescence can be lit up only when the "double locks" are opened by reacting with the "dual smart keys" (overexpressed hyaluronidase and thiols in tumor) simultaneously. In vivo NIR-II imaging shows that they reduce nonspecific activitation and achieve ultralow background fluorescence, which is 10.6-fold lower than single-parameter activatable probes (HINPs) in the liver at 15 h postinjection. Consequently, these “dual lock-and-key”-controlled HISSNPs exhibit fivefold higher tumor-to-normal tissue ratio than “single lock-and-key”-controlled HINPs at 24 h postinjection, attractively realizing ultrahigh specificity of tumor imaging. This is thought to be the first attempt at implementing ultralow background interference with the participation of multiple pathological parameters in NIR-II fluorescence imaging.

Comment: This kind of “dual locks and keys” strategy provides a promising approach to design collaboratively activatable probes. The method that stepwise actives or opens self-assemblies could be induced to supramolecular self-assemblies to simulate intracellular motions.

Remote Stereochemistry of a Frustrated Lewis Pair Provides Thermal and Photochemical Control of Reactivity

Fan, L.; Jupp, A. R.; Stephan, D. W.* *J. Am. Chem. Soc.* **2018**, *ASAP.*

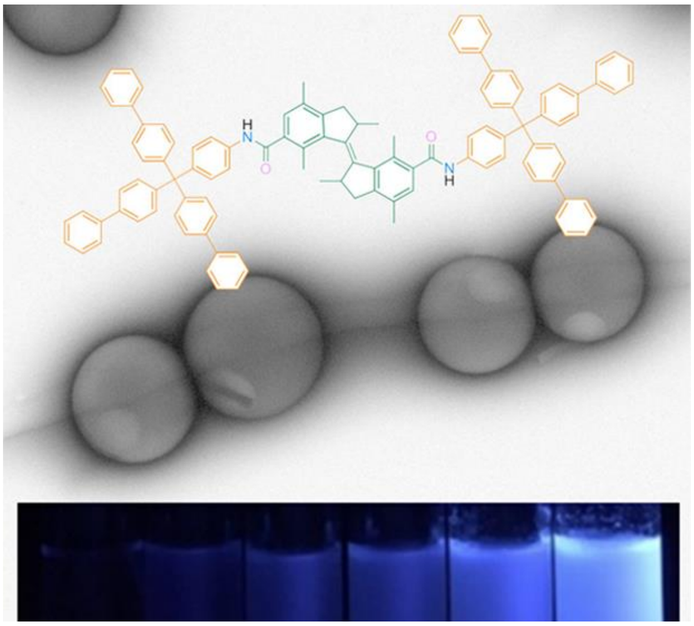


Hydroboration of $tBuC\equiv CSR$ with $(C_6F_5)_2BH$ generate the B/S FLPs, $(C_6F_5)_2B(RS)C\equiv CH(tBu)$ (R = ptol, Me). For R = ptol the product Z-1 exhibits Z stereochemistry, is monomeric in solution and is capable of both classical Lewis acid−base and FLP reactivity. Photoisomerization of Z-1 affords E-1, which features an intramolecular S−B interaction promoted by the remote steric influence of the tert-butyl group. E-1 is not active as an FLP under ambient conditions but reacts with phenylacetylene when activated with either heat or light. The stereochemical outcome of the product is dependent on the stimulus employed.

Comment: A quite easy method to control the reactivity of Frustrated Lewis Pairs through thermal or light activation. Of course, the authors just show one example (reaction with phenylacetylene) where everyone expects to see the reaction with hydrogen been deactivated through isomerization of the double bond.

Solvent Mixing to Induce Molecular Motor Aggregation into Bowl-Shaped Particles: Underlying Mechanism, Particle Nature, and Application to Control Motor Behavior

Franken, L. E.; Wei, Y.; Chen, J.; Boekema, E. J.; Zhao, D.; Stuart, M. C. A.*; Feringa, B. L.* *J. Am. Chem. Soc.* **2018**, *ASAP.*

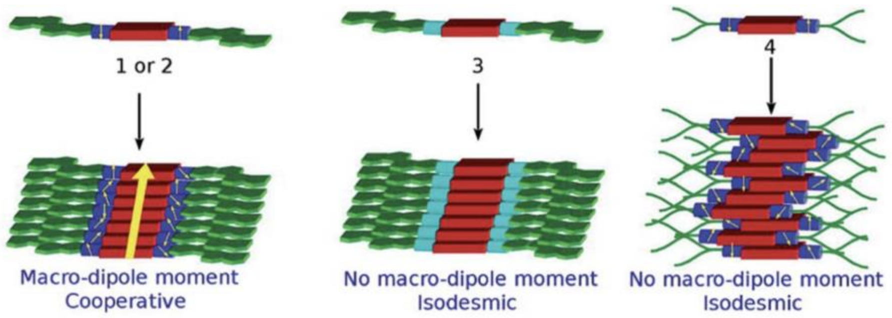


Control over dynamic functions in larger assemblies is key to many molecular systems, ranging from responsive materials to molecular machines. Here we report a molecular motor that forms bowl-shaped particles in water and how confinement of the molecular motor affects rotary motion. Studying the aggregation process in a broader context, we provide evidence that, in the case of bowl-shaped particles, the structures are not the product of self-assembly, but a direct result of the mixing a good solvent and a (partial) non-solvent and highly independent of the molecular design. Under the influence of the non-solvent, droplets are formed, of which the exterior is hardened due to the increase in the glass transition temperature by the external medium, while the interior of the droplets remains plasticized by the solvent, resulting in the formation of stable bowl-shaped particles with a fluid interior, a glass-like exterior, and a very specific shape: dense spheres with a hole in their side. Applying this to a bulky first-generation molecular motor allowed us to change its isomerization behavior. Furthermore, the motor shows in situ photo-switchable aggregation-induced emission. Strong confinement prohibits the thermal helix inversion step while altering the energy barriers that determine the rotary motion, such that it introduces a reverse trans−cis isomerization upon heating. These studies show a remarkable control of forward and backward rotary motion by simply changing solvent ratios and extent of confinement.

Comment: In this paper, the authors try to show that one can observe bowl-shaped particles that do not result from molecular design directed self-assembly but rather from solvent mixing. Indeed, analyzing a slow molecular motor, they show that different morphologies can be observed by varying the ratios between a good and a bad solvent. Furthermore, they can use this phenomenon to control the rotary motion. TEM has been extensively used in this paper to probe the effect of solvent ratios.

Molecular Modelling of Supramolecular One Dimensional Polymers

Korlepara, D. B.; Balasubramanian, S.* *RSC Advances* **2018**, *8*, 22659–22669.

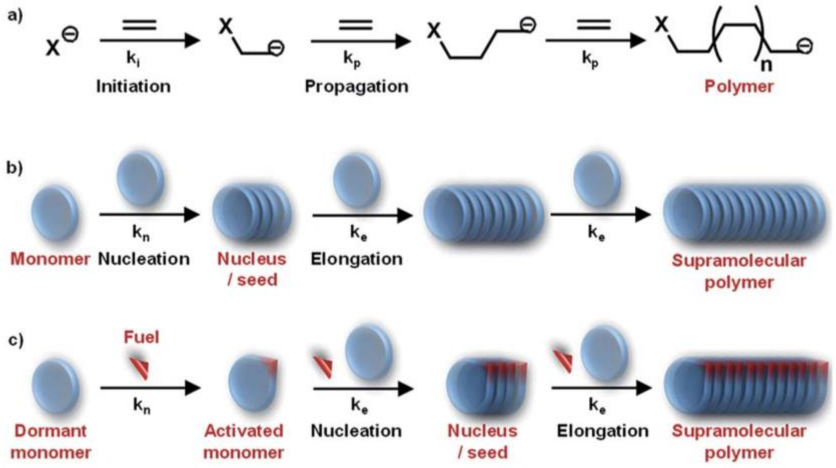


Supramolecular polymers exemplify the need to employ several computational techniques to study processes and phenomena occuring at varied length and time scales. Electronic processes, conformational and configurational excitations of small aggregates of chromophoric molecules, solvent effects under realistic thermodynamic conditions and mesoscale morphologies are some of the challenges which demand hierarchical modelling approaches. **This review focusses on one-dimensional supramolecular polymers, the mechanism of self-assembly of monomers in polar and non-polar solvents and properties they exhibit.** Directions for future work are as well outlined.

Comment: You might have noticed that *RSC Advances* is now in the list of journals. It is, partially, because I recurrently had ChemBrows suggesting articles, and most of them were actually rather interesting, based on the titles at least. For instance, the two reviews I am submitting this week. This one focuses on computational approaches to model supramolecular polymers. Going from fairly quantum-based methods to more crude approaches like coarse grain. It is, I believe, a light review to read to get a general idea. But do not expect the level of a Chem. Soc. Rev. tutorial review.

Making Molecular and Macromolecular Helical Tubes: Covalent and Noncovalent Approaches

Dhiman, S.; Sarkar, A.; George, S. J.* *RSC Advances* **2018**, *8*, 18913–18925.



Thriving natural systems precisely regulate their complex chemical organizations in space and time by recruitment of a complex network of **fuel-driven, kinetically controlled, out-of-equilibrium transformations**. Indeed this provides an active, adaptive and autonomous smart actions & functions. In contrast, synthetic systems exhibit simpler behavior owing to thermodynamically driven supramolecular polymerization with no temporal modulation of spatial organization. Stimulated by an outstanding control that nature demonstrates, a drive towards artificial **out-of-equilibrium systems** with the ambition to program activation and duration of structural transformations has emerged. To realize this vision, overwhelming efforts across the globe have been initiated to design temporally programmed synthetic supramolecular polymers. In an attempt to contribute to **this trending field**, our supramolecular chemistry group has thoroughly investigated a structure–property relationship that determines the mechanism of supramolecular polymerization. Exploiting these mechanistic insights, along with a bio-inspired fuel-driven enzyme mediated approach, we further attempted to program supramolecular polymers in both structural and temporal regimes. We believe, nature is the inspiration to the current era challenges and it also provides with the solution, a fuel-driven approach to address these. In this account, we shall discuss the efforts made by our group to build generic concept to create temporally programmable supramolecular polymers.

Comment: While the other article is written in the style of a *Chem. Soc. Rev.* tutorial review, this one would be the equivalent of an *Acc. Chem. Res.* And both are in *RSC Advances*. Here, they discuss mainly their contributions to the field of "out-of-equilibrium" systems –in the supramolecular chemical sense. It mainly involves a good part of bio (ATP, enzymes, DNA) mixed with supramolecular polymers. It is a field that **really** benefits from a huge hype, and a very supportive community (they all know each other and most have been one time or another in the Netherlands). Do have a quick look and make yourselves a quick idea! This review is perfect for it.