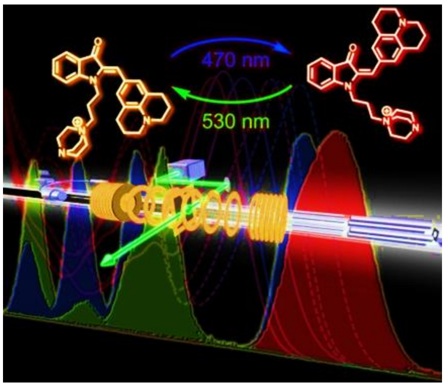
Reversible Photoswitching of Isolated Ionic Hemiindigos with Visible Light

Carrascosa, E; Petermayer, C; Scholz, M. S; Bull, J. N; Dube, H;* Bieske, E. J.* *ChemPhysChem*, **2020**, 21, 1-7.

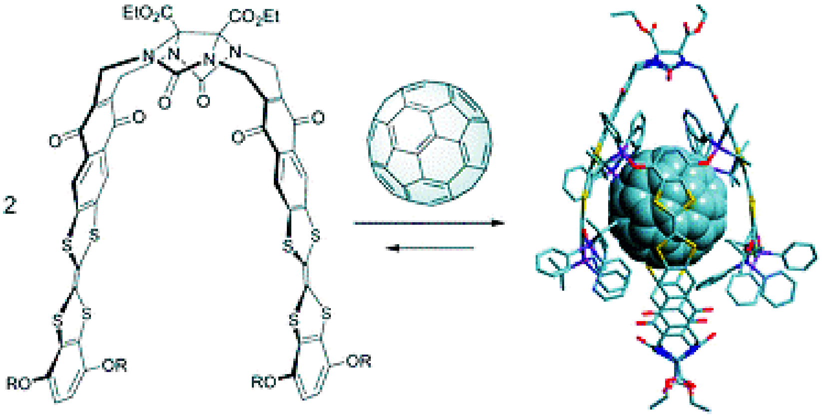


Indigoid chromophores have emerged as versatile molecular photoswitches, offering efficient reversible photoisomerization upon exposure to visible light. Here we report synthesis of a new class of permanently charged hemiindigos (HIs) and characterization of photochemical properties in gas phase and solution. Gas-phase studies, which involve exposing mobility-selected ions in a tandem ion mobility mass spectrometer to tunable wavelength laser radiation, demonstrate that the isolated HI ions are photochromic and can be reversibly photoswitched between *Z* and *E* isomers. The *Z* and *E* isomers have distinct photoisomerization response spectra with maxima separated by 40–80 nm, consistent with theoretical predictions for their absorption spectra. Solvation of the HI molecules in acetonitrile displaces the absorption bands to lower energy. Together, gas-phase action spectroscopy and solution NMR and UV/Vis absorption spectroscopy represent a powerful approach for studying the intrinsic photochemical properties of HI molecular switches.

Comment: Usually, theoretical calculations of the photochemical behaviour of these photoswitches are performed in the gas phase. These results are compared with experimental ones obtained usually in solution or solid state. Then, in order to compare the theoretical predictions with the experimental results under the same conditions, the authors carried out a study of the photochemical behaviour of these photoswitches free from the environment influences in the gas phase using ion mobility mass spectrometry, which is an analytical technique that separates gas phase ions based on two things, their interaction with a collision gas (in this case, N_2) and their masses.

An original self-assembly using a tetrathiafulvalene-based molecular clip for the recognition of fullerene C_{60}

Cotelle, Y; Hardouin-Lerouge, M; Lemasson, E; Morille, Y; Canevet, D; Legoupy, S; Hudhomme, P.* *Chem. Commun*, **2020**, ASAP.



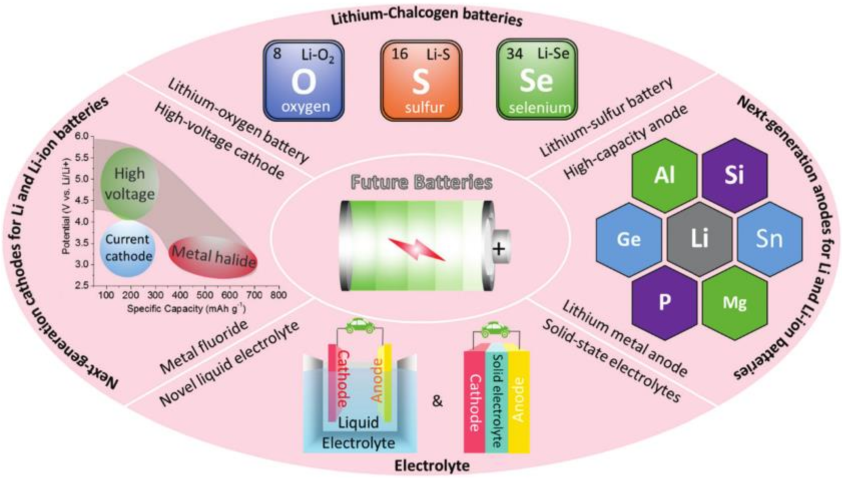
A glycoluril-based molecular clip incorporating two tetrathiafulvalene (TTF) sidewalls has been synthesized using a straightforward Diels–Alder synthetic route and its ability to self-assemble with fullerene C_{60} in a 2 : 1 stoichiometry has been demonstrated in solution.

Comment: Several molecular receptors adopting clip or tweezer shapes have been synthesized in order to host fullerene derivatives and form stable complexes with them. In that sense, corannulenes, calixarenes, exTTF among other moieties have been used as scaffolds to construct these fullerene receptors. However, this is the first time that the glycouril moiety has been used to build a molecular clip containing TTF units for binding spherical C60. The glycouril scaffold enables the face-to-face position of the TTF redox units at the suitable distance (9.6 Å) to form a complex with C_{60}. The authors were able to form a host-guest complex in a 2:1 stoichiometry of clips:C_{60}

From the synthetic point of view, the authors carried out a synthetic step involving a Diels-Alder reaction, which provides atomic economy but unfortunately they obtained the product in poor yield.

Guidelines and Trends for Next-Generation Rechargeable Lithium and Lithium-Ion Batteries

Wu, F.; Maier, J.; Yu, Y. *Chem. Soc. Rev.* **2020**

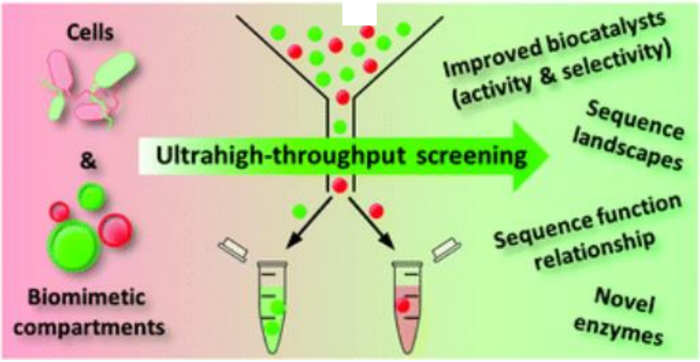


Commercial lithium-ion (Li-ion) batteries suffer from low energy density and do not meet the growing demands of the energy storage market. Therefore, building next-generation rechargeable Li and Li-ion batteries with higher energy densities, better safety characteristics, lower cost and longer cycle life is of outmost importance. To achieve smaller and lighter next-generation rechargeable Li and Li-ion batteries that can outperform commercial Li-ion batteries, several new energy storage chemistries are being extensively studied. In this review, **we summarize** the **current trends** and **provide guidelines** towards achieving this goal, by addressing batteries using **high-voltage cathodes**, **metal fluoride electrodes**, **chalcogen electrodes**, **Li metal anodes**, **high-capacity anodes** as well as useful **electrolyte solutions**. We discuss the choice of active materials, practically achievable energy densities and challenges faced by the respective battery systems. Furthermore, strategies to overcome remaining challenges for achieving energy characteristics are addressed in the hope of providing a useful and balanced assessment of current status and perspectives of rechargeable Li and Li-ion batteries.

Comment: This review is obviously quite long but is definitely well constructed. A lot of efforts have been put in the accessibility of this subject to the neophytes. The schemes are helpful to grasp the organisation and the structure of the different types of batteries. Overall, I would suggest to at least read the introduction.

Advances in Ultrahigh-Throughput Screening for Directed Enzyme Evolution

Markel, U.; Essani, K. D.; Besirlioglu, V.; Schiffels, J.; Streit, W. R.; Schwaneberg, U. *Chem. Soc. Rev.* **2020**, *49*, 233–262.

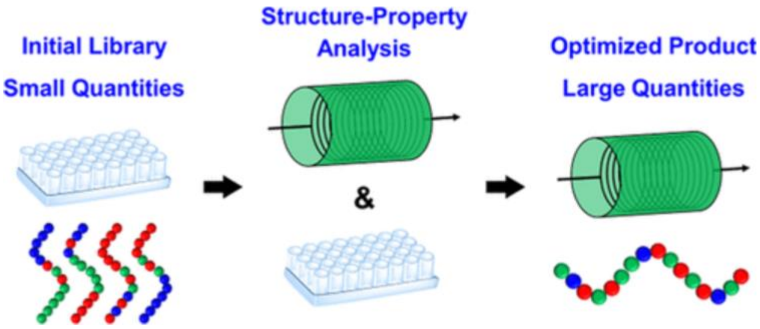


Enzymes are versatile catalysts and their synthetic potential has been recognized for a long time. In order to exploit their full potential, enzymes often need to be re-engineered or optimized for a given application. (Semi-) rational design has emerged as a powerful means to engineer proteins, but requires detailed knowledge about structure function relationships. In turn, **directed evolution methodologies**, which consist of **iterative rounds of diversity generation** and **screening**, can **improve an enzyme's properties** with virtually no structural knowledge. Current diversity generation methods grant us access to a vast sequence space (libraries of $>10_{12}$ enzyme variants) that may hide yet unexplored catalytic activities and selectivity. However, the time investment for conventional agar plate or microtiter plate-based screening assays represents a major bottleneck in directed evolution and limits the improvements that are obtainable in reasonable time. **Ultrahigh-throughput screening** (uHTS) methods **dramatically increase the number of screening events per time**, which is crucial to speed up biocatalyst design, and to widen our knowledge about sequence function relationships. In this review, we summarize recent advances in uHTS for directed enzyme evolution. We shed light on the importance of compartmentalization to preserve the essential link between genotype and phenotype and discuss how cells and biomimetic compartments can be applied to serve this function. Finally, we discuss how uHTS can inspire novel functional metagenomics approaches to identify natural biocatalysts for novel chemical transformations.

Comment: This paper is also an excellent work that summarizes efficiently what has been done in the field of directed evolution so far (awarded with a Nobel Prize in 2018). Even if some parts of this review are quite difficult to follow, the article remains interesting overall.

High-Throughput Process for the Discovery of Antimicrobial Polymers and Their Upscaled Production via Flow Polymerization.

Judzewitsch, P. R.; Corrigan, N.; Trujillo, F.; Xu, J.; Moad, G.; Hawker, C. J.; Wong, E. H. H.; Boyer, C.* *Macromolecules* **2020**, *53*, 631–639.

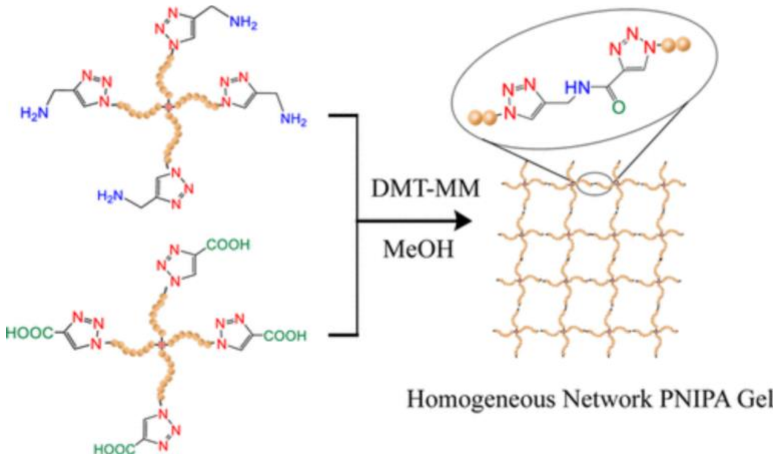


The combination of high-throughput (HTP) processes and flow-mediated synthesis allows large data sets to be generated quickly while also permitting large quantities of materials to be prepared in a continuous fashion. In this work, the benefits of well-plate-based HTP polymerization and flow-mediated chemistry are used to **streamline the screening and upscaling of value-added biomedical materials** through a robust photopolymerization strategy, namely, photoinduced electron/energy transfer-reversible addition–fragmentation chain transfer (PET-RAFT) polymerization. A library of potential antimicrobial polymers was generated from an initial pool of monomers and tested for their activity against *Pseudomonas aeruginosa* (PA). The antimicrobial activity of the most promising candidates was then elucidated through structure–property analyses performed via both plate and flow polymerization processes; interestingly, terpolymerization of mixtures of acrylate and acrylamide monomers produced terpolymers with gradient architectures due to their reactivity ratios, which ultimately dictated the resulting antimicrobial activity. Finally, the polymers found to have the highest antimicrobial activity were upscaled in a flow reactor. This workflow provides a general and highly accessible methodology for **the discovery and synthetic scaling of optimized polymer structures for biomedical applications** such as new antimicrobial agents.

Comment: Combining HTP processes, for screening, and flow chemistry, for upscale synthesis, proves to be efficient in the case presented here, that is, optimizing a polymeric structure to obtain antimicrobial properties. I am not sure it can be easily generalized to other systems, however, but PET-RAFT polymerization already opens a wide library of polymer backbones.

Precise Synthesis of a Homogeneous Thermoresponsive Polymer Network Composed of Four-Branched Star Polymers with a Narrow Molecular Weight Distribution

Okaya, Y.; Jochi, Y.; Seki, T.; Satoh, K.; Kamigaito, M.; Hoshino, T.*; Nakatani, T.; Fujinami, S.; Takata, M.; Takeoka, Y.* *Macromolecules* **2020**, *53*, 374–386.

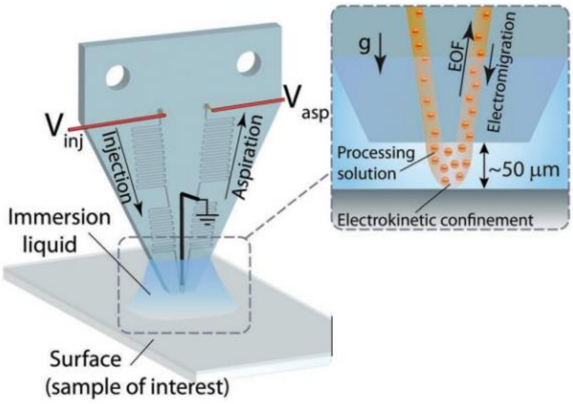


In this study, the synthesis of a **star-shaped polymer with a narrow molecular weight distribution** and subsequent formation of a **homogeneous polymer network** composed of the star-shaped polymer were realized by combining single-electron transfer living radical polymerization, click reaction, and amide bond formation with a condensing agent, which are toolized reactions. First, a 4-armed star polymer consisting of *N*-isopropylacrylamide was synthesized by living radical polymerization using *N*,*N*'-ethylenebis (2,2-dichloroacetamide) as a 4-branched initiator. By this polymerization method, a terminal Cl 4-branched star poly(*N*-isopropylacrylamide) (PNIPA) with a narrow molecular weight distribution could be obtained, but it was found that the reaction activity of the polymer terminal was lost in the process of purification and isolation. Therefore, after obtaining the terminal Cl 4-branched star PNIPA by living radical polymerization, an azide reaction was carried out in one pot without purification and isolation of the star-shaped polymer. As a result, the azide group was successfully introduced to all ends of the star-shaped polymer. By introducing a carboxyl group or an amino group into the 4-branched star polymer with azide groups using a click reaction, two types of 4-branched star polymers with different end groups were obtained. Equal amounts of both 4-branched star polymers were mixed at a polymer concentration equal to or higher than the overlapping concentration, and as a result of forming an amide bond with a condensing agent, a polymer gel was obtained. **The swelling behaviors of the polymer gel indicate that almost no unreacted carboxyl group or amino group was present in the obtained polymer gel.** That is, it was found that both 4-branched star polymers reacted efficiently to form a polymer network. In addition, structural observation of the polymer network by the small-angle X-ray scattering method showed that **a polymer gel consisting of a network of uniform size was obtained.** As mentioned above, we succeeded in constructing a polymer gel consisting of a homogeneous network structure using a temperature-responsive 4-branched star polymer as the building block. The living radical polymerization method, the click reaction, and the amide formation by condensation reaction used in this study can be applied not only to the NIPA used here but also to various other monomers. If the construction of a precise network structure is realized by many polymers and the relation with the functional expression derived from the structure is clarified, it will be possible to design the network structure in accordance with the usage of the polymer gel.

Comment: The reticulation of star-shaped polymers leads to a network where the number of inelastic strands is greatly reduced. The synthesis presented here is a good strategy to obtain such functional macromolecular structures with complementary chemical functions which can be coupled (i.e. amidation reaction) to form gels. Moreover, Takeoka's group works on polyrotaxanes as well, if you are interested in the topic.

Electrokinetic Scanning Probe

Ostromohov, N.; Rofman, B.; Bercovici, M.*; Kaigala, G.* *Small* **2020**, *16*, 1904268.

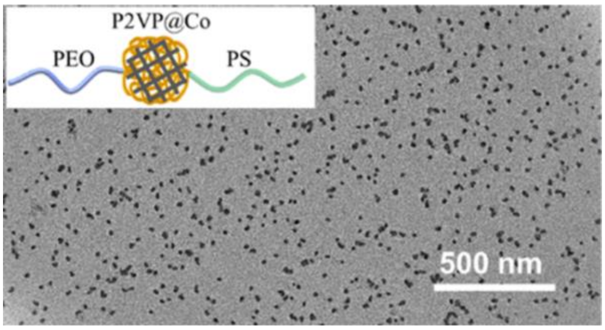


The theoretical analysis and experimental demonstration of a new concept are presented for a **non-contact scanning probe**, in which transport of fluid and molecules is controlled by electric fields. **The electrokinetic scanning probe (ESP)** enables local chemical and biochemical interactions with surfaces in liquid environments. The physical mechanism and design criteria for such a probe are presented, and its compatibility with a wide range of processing solutions and pH values are demonstrated. The applicability of the probe is shown for surface patterning in conjunction with localized heating and 250-fold analyte stacking.

Comment: The technique presented here allows to deposit analytes in solution on a surface, with a decent spatial resolution (you can check the picture of the cat they drew with DNA). The main advantages claimed by the authors is the possibility to use this method for biomedical applications, which often use rough surfaces.

Single-Chain Janus Nanoparticle by Metallic Complexation

Xiang, D.; Jiang, B.*; Liang, F.; Yan, L.; Yang, Z.* *Macromolecules* **2020**, *53*, 1063–1069.

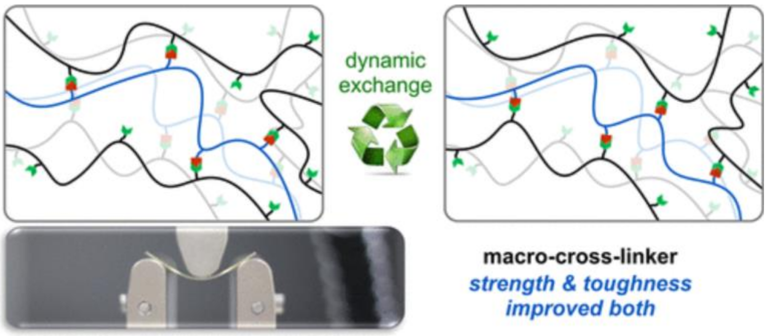


Single-chain Janus nanoparticle of the example polymer polystyrene-*block*-poly(2-vinylpyridine)-*block*-polyethylene oxide (PS-*b*-P2VP-*b*-PEO) was achieved by intramolecular crosslinking via complexation of P2VP with cobalt octacarbonyl, while the metallic complex was incorporated within the crosslinked core. It is crucial to introduce electrostatic interaction along the chain by pretreatment and thus ensure the intramolecular crosslinking in concentrated solutions, for example, 30 mg/mL. After thermolysis in the dispersion, the complex is decomposed achieving cobalt within the P2VP core. **A magnetic responsive single-chain Janus composite nanoparticle** was derived with the P2VP/Co core conjugated with PS and PEO single chains onto the opposite sides. The Janus composite nanoparticle displays highly catalytic activity and magnetic responsive performance from the metallic cobalt and interfacial activity from the PS and PEO single chains. **A highly efficient catalytic reduction of nitroaromatic compounds** at emulsion interfaces was demonstrated thereby, which was easily recycled with a magnet.

Comment: Single-chain nanoparticles are a rising topic as they hold the promise to function as artificial enzymes with catalytic properties. Here, the design proposed by the authors can work even at high concentrations, and they successfully incorporated cobalt ions into the structure.

Strong, Reconfigurable, and Recyclable Thermosets Cross-Linked by Polymer–Polymer Dynamic Interaction Based on Commodity Thermoplastics

Wang, Z.; Gu, Y.; Ma, M.; Chen, M.* *Macromolecules* **2020**, *53*, 956–964.

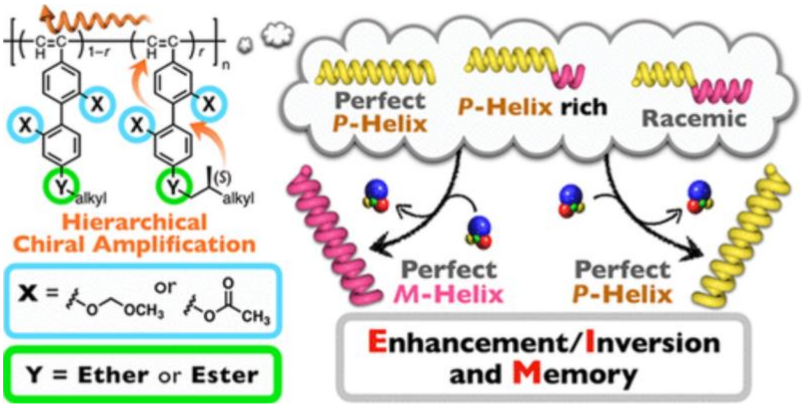


Polymer networks cross-linked by dynamic covalent bonds possess outstanding mechanical and rheological properties and are expected to be potential alternatives to conventional thermosets. However, while many recent studies of dynamically cross-linked thermosets focused on the employment of small molecular cross-linkers, the **macro-cross-linking approach** and the corresponding thermosets have been less demonstrated. In this work, reconfigurable and catalyst-free thermosets were synthesized by dynamic polymer–polymer interaction based on **reversible boronic ester bond**, providing simple and efficient access toward materials with improved mechanical strength and toughness in comparison to related commodity thermoplastics. The dynamic exchange of covalent bonds dispersed between polymer chains enables the materials to be malleable, recyclable, and healable under thermal conditions and readily processable with mechanical mixing without solvent. Moreover, the materials' mechanical and rheological properties could be tuned by changing the cross-linking density. Although the dynamic networks exhibited good resistance against organic solvents, they could be cleaved as triggered by acids or diols and recycled through the de-cross-linking/re-cross-linking pathway. Given the dramatically increasing interest in environmentally sustainable materials, this polymer–polymer interaction mode provides a robust approach to engineering polymers with improved performance compared with the thermoplastic counterparts.

Comment: More and more articles about recyclable thermosets based on reversible crosslinking units can be found. Even though it is quite far from the design being developed in our team, it may still be something to have in your bibliography, because boronic esters are widely used in this field.

Chiral/Achiral Copolymers of Biphenylylacetylenes Bearing Various Substituents: Chiral Amplification through Copolymerization, Followed by Enhancement/Inversion and Memory of the Macromolecular Helicity

Ikai, T.; Ishidate, R.; Inoue, K.; Kaygisiz, K.; Maeda, K.; Yashima, E.* *Macromolecules* **2020**, *53*, 973–981.

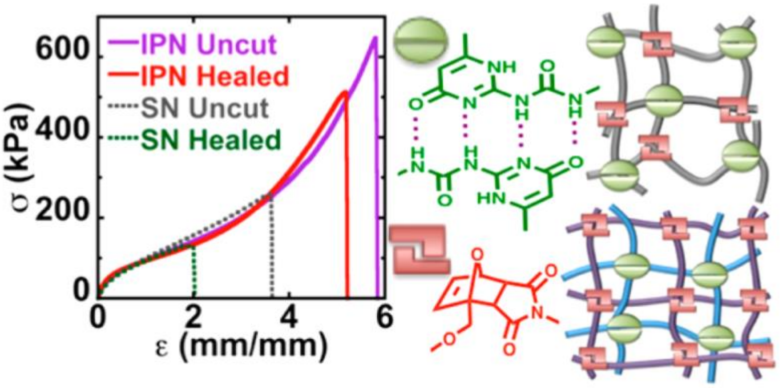


A series of dynamic helical homo- and copolymers of chiral and/or achiral biphenylylacetylenes (PBPAs) bearing achiral methoxymethoxy or acetyloxy groups at the 2,2'-positions along with a chiral or achiral alkyl ether or alkoxy carbonyl group at the 4'-position of the biphenyl pendants were synthesized. The effects of the chiral/achiral substituents at different positions on their helical structures and **amplification of the helicity** through covalent and further noncovalent chiral interactions followed by the memory of the helicity were investigated. The chiral homopolymers formed a preferred-handed helical structure as revealed by their circular dichroism (CD) spectra, whose Cotton effect signs and intensities were significantly dependent on the chiral/achiral pendant groups introduced at the 2,2',4'-positions of the biphenyl units as well as the solvents and temperatures, while the corresponding poly(phenylacetylene)s carrying the identical chiral substituents exhibited negligible CDs. Among the chiral homopolymers, a PBPA bearing the 2,2'-methoxymethoxy and 4'-chiral alkyl ether groups showed a unique helix-inversion/switching in aliphatic hydrocarbons according to whether they are cyclic or acyclic. The chiral/achiral copolymers displayed a moderate amplification of the helicity due to the chiral units covalently bonded to the pendants (the sergeants-and-soldiers effect). The macromolecular helicity of the copolymers with imperfect or no helical sense excesses was, however, significantly enhanced to the almost completely one-handed helices or inverted to the opposite ones through noncovalent chiral interactions with enantiomeric alcohols, which could be further memorized after the complete removal of the chiral alcohols.

Comment: The authors previously developed this new class of macromolecules where the chirality of the monomers (even a small percentage of them) can be amplified to the polymeric backbone. The most interesting aspect of their polymers, in my opinion, is the “memory” effect where the interaction with chiral alcohols induces a chiral conformation of the polymer that is retained even after the removal of the alcohols; therefore, it paves the way towards new switchable chiral materials.

Effect of Polymer Network Architecture, Enhancing Soft Materials Using Orthogonal Dynamic Bonds in an Interpenetrating Network

Foster, E. M.; Lensmeyer, E. E.; Zhang, B.; Chakma, P.; Flum, J. A.; Via, J. J.; Sparks, J. L.; Konkolewicz, D. ACS Macro Lett., **2017**, *6*, 495–499

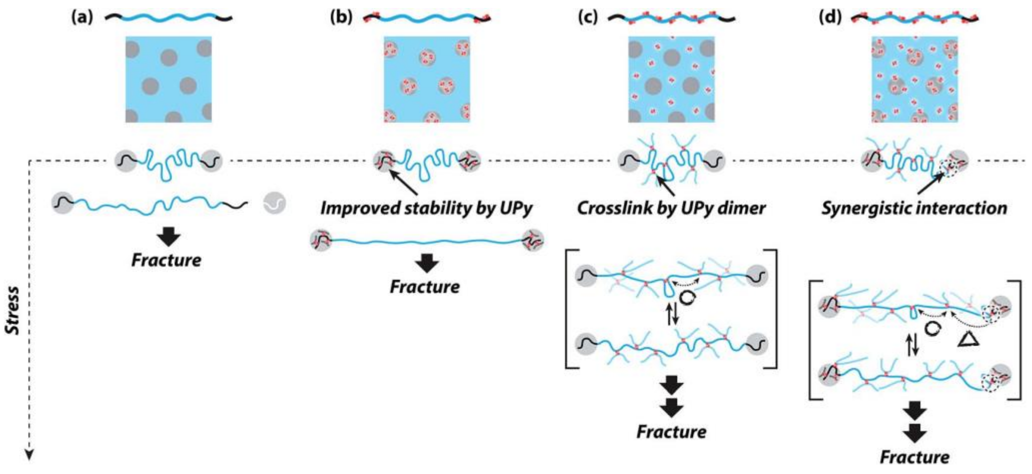


Doubly dynamic polymer networks were synthesized with two distinct exchangeable cross-linkers. The first linker is highly dynamic and rapidly exchanging hydrogen bonded 2-ureido-4[1H]-pyrimidinone (UPy) and the second is a thermoresponsive furan- maleimide Diels−Alder adduct (FMI). Two network architectures were considered: an interpenetrating network (IPN) where one network is cross-linked with the UPy linker and the other is cross-linked with the FMI linker, and a single network (SN) where both the UPy and FMI linkers are in the same single network. Remarkably, the IPNs were superior to the SNs with the same composition of the UPy and FMI cross-linkers when comparing peak stress, strain at break, fracture toughness, malleability, and self-healing. Both materials studied were stable and creep resistant under ambient conditions.

Comment: One has to keep in mind that topology also plays a crucial role in material properties. Here, the authors compare interpenetrated networks and single networks. It appears that interpenetrated networks display enhanced mechanical properties. They propose the explanation that this could come from an apparent lower crosslinking density of each chain, which is then freer to rearrange.

Interphase synergistic effects of dynamic bonds in multiphase thermoplastic elastomers

Kawana, S.; Nakagawa, S.; Nakai, S.; Sakamoto, M.; Ishii, Y.; Yoshie, N. *J. Mater. Chem. A*, **2019**, *7*, 21195–21206.

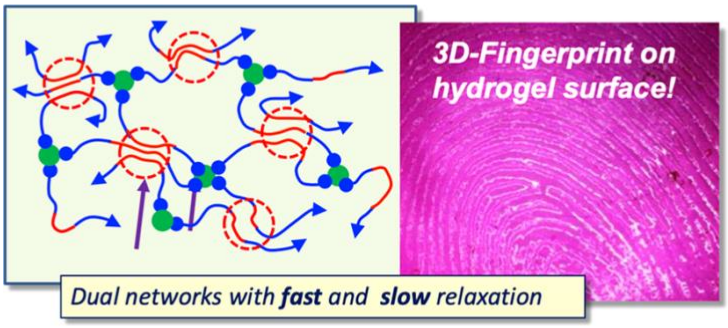


Enhancing the mechanical reliability of thermoplastic elastomers (TPEs) is a key issue for their application as a structural material. Here we systematically investigated the effects of dynamic bonds on the mechanical properties of ABA triblock copolymer-type TPEs. We prepared a series of TPEs having strong hydrogen- bonding side groups, ureidopyrimidinone (UPy), in either or both of the hard A blocks and soft B blocks. The TPEs formed microphase-separated structures consisting of spherical hard A domains surrounded by soft B matrices. When the dynamic bonds were introduced in dynamic bonds in both phases: a robust synergistic interaction existed between the dynamic the hard A blocks, the mechanical stability of the hard domains was improved. The stress in the tensile tests also increased but only at relatively large strains. Dynamic bonds in the soft B block served as transient crosslinks in the soft matrix that enhanced stress across the entire range of strain. The effect of introducing dynamic bonds in both the hard domains and soft matrix was more than just the sum of the effects of the bonding moieties in the two phases. This synergistic interaction enhanced the rigidity of the material (tensile stress >13 MPa) while maintaining high tensile toughness (>58 MJ m$_{-3}$). The dynamicity of the interactions in the different phases and its effect on fatigue recoverability in the large strain regime were also discussed using the classical theory of nonlinear viscoelasticity.

Comment: Another topological effect on dynamicity in phase segregation. The mechanical properties as well as healing efficiencies are enhanced when the dynamic moieties are at the interface and can interact together.

Fingerprintable Hydrogel from Dual Reversible Cross-Linking Networks with Different Relaxation Times

Li, H.; Liu, F.; Li, Z.; Wang, S.; Jin, R.; Liu, C.; Chen, Y. *ACS Appl. Mater. Interfaces*, **2019**, *11*, 17925–17930.

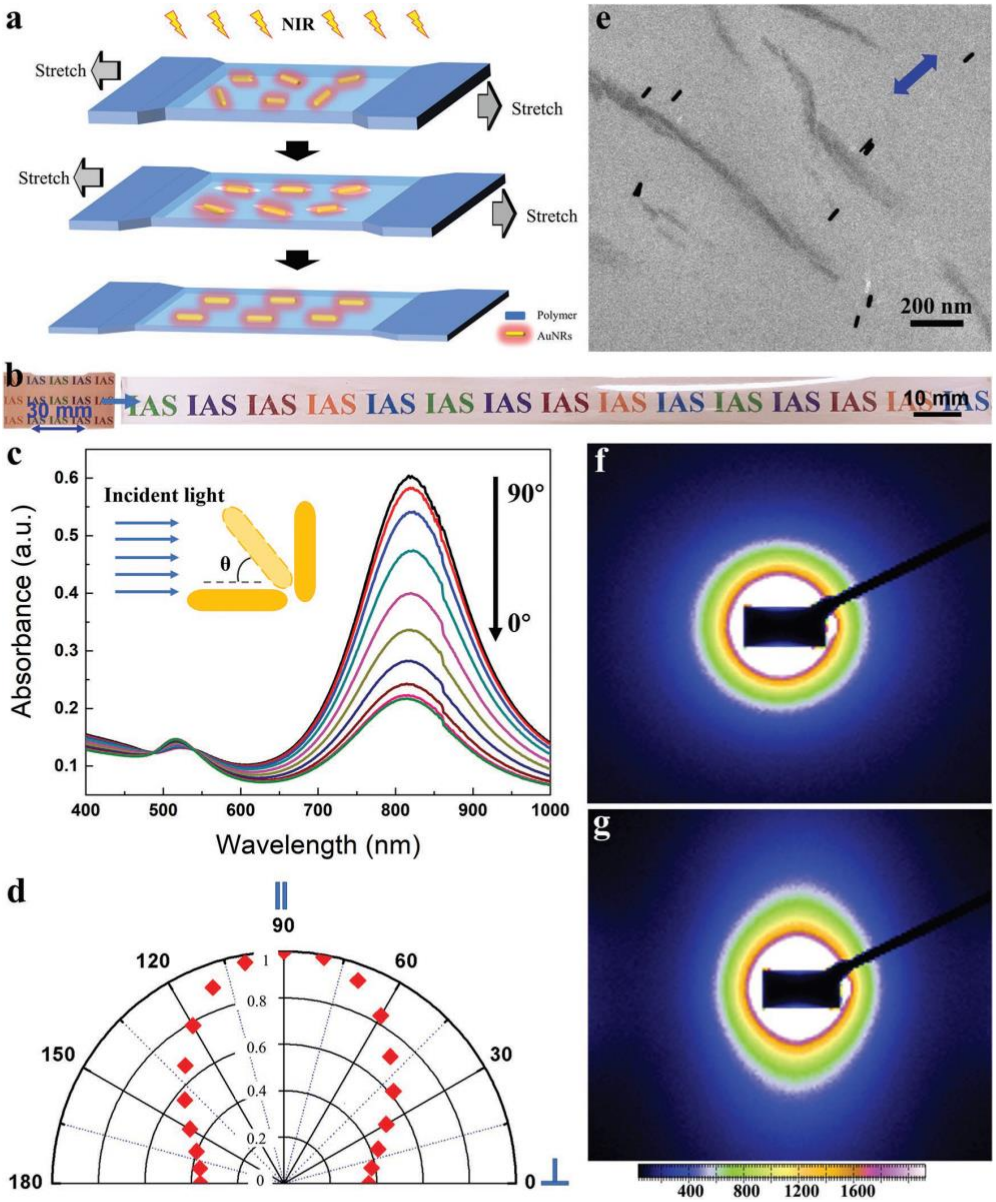


Most of the chemical hydrogels are stretchable, and deformed hydrogels may be recovered when the strain is removed. Such a hydrogel with viscoelastic property cannot be remolded under mild conditions. Here, we demonstrated that a combination of dual reversible cross-linking with different relaxation time scales could be used to develop a remoldable hydrogel responding to mild external stress. We fabricated the hydrogel with the surface-primary amine-rich silica nanodots (ca. 2.0 nm) and benzaldehyde-terminated poly(ethylene oxide)−poly(propylene oxide) (PPO)−poly(ethylene oxide) triblock copolymers (BAF127) at low temperature (<10 °C) to form the chemical cross-linking by Schiff-base bonding. Increasing temperature (>15 °C) induced the formation of physical cross-linking between the hydrophobic PPO segments. The latter network is weak and shows fast relaxation, whereas the former shows slow relaxation. The unique structural characteristics provides this hydrogel high stretchability and self-healability, as well as moldability. In particular, we demonstrated that this transparent hydrogel can keep the fine three-dimensional patterns of a fingerprint, which may be applied for collecting digital information of fingerprints for identification.

Comment: Interesting example of what can be done with double dynamic. Here owing to slow and fast kinetics, the authors describe a pressure sensitive material. The fast dynamic allow deformation while the slow one holds the network, both providing malleability.

Self-Healing of Polarizing Films via the Synergy between Gold Nanorods and Vitrimer

Zhao, G.; Zhou, Y.; Wang, J.; Wu, Z.; Wang, H.; Chen, H. *Adv. Mater.*, **2019**, *31*, ASAP.

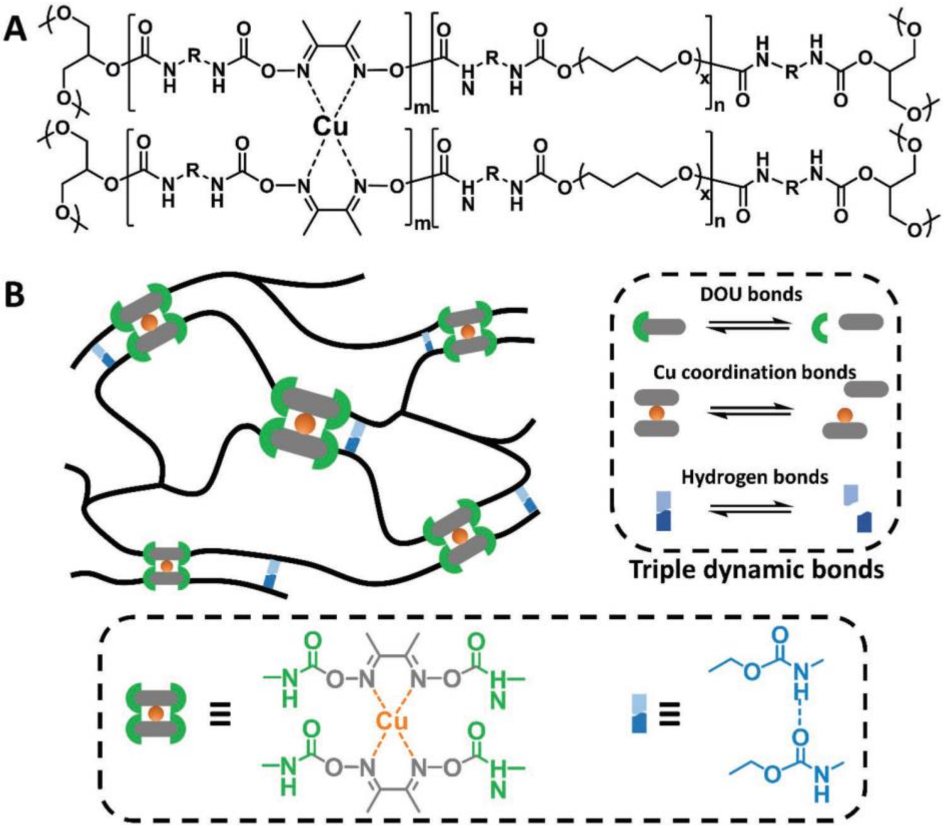


Conventional self-healing is about the recovery of shape and mechanical properties. In contrast, recovery of functional properties is still a great challenge, especially for optical functional materials, as the known self-healing methods are incompatible with optical properties. By utilizing the synergistic effect between Au nanorods and vitrimer, the alignment of Au nanorods can be achieved in the crosslinked polymer. The optical properties of the resulting polarizing film, such as light transmittance and polarization degree, can be fully recovered without an external repair agent. With simple laser irradiation to induce the photothermal effect of Au nanorods, the shape-memory effect of vitrimer returns the Au nanorods to their initial orientation, and the plasticity achieves in situ self-healing of the cutting area. The self-healing of polarizing film provides a new research direction and reference for the application of self-healing systems in functional materials.

Comment: An article combining the properties of double dynamic materials and gold nanorods. The authors describe here a novel and smart way to orient Au-nanorods: they classically stretch the polymeric film to orient the rods, then they irradiate the film. Taking advantage of the photothermal effect of the rods, the material heats promoting its self-healing in the aligned conformation.

A Highly Efficient Self-Healing Elastomer with Unprecedented Mechanical Properties

Zhang, L.; Liu, Z.; Wu, X.; Guan, Q.; Chen, S.; Sun, L.; Guo, Y.; Wang, S.; Song, J.; Jeffries, E. M.; et al. *Adv. Mater.*, **2019**, *31*, 32–34.

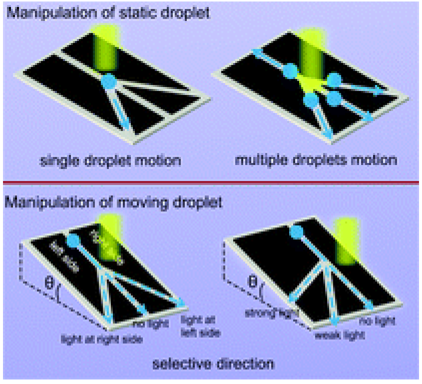


It is highly desirable, although very challenging, to develop self-healable materials exhibiting both high efficiency in self-healing and excellent mechanical properties at ambient conditions. Herein, a novel Cu(II)–dimethylglyoxime–urethane-complex-based polyurethane elastomer (Cu–DOU–CPU) with synergetic triple dynamic bonds is developed. Cu–DOU–CPU demonstrates the highest reported mechanical performance for self-healing elastomers at room temperature, with a tensile strength and toughness up to 14.8 MPa and 87.0 MJ m−3, respectively. Meanwhile, the Cu–DOU–CPU spontaneously self-heals at room temperature with an instant recovered tensile strength of 1.84 MPa and a continuously increased strength up to 13.8 MPa, surpassing the original strength of all other counterparts. Density functional theory calculations reveal that the coordination of Cu(II) plays a critical role in accelerating the reversible dissociation of dimethylglyoxime–urethane, which is important to the excellent performance of the self-healing elastomer. Application of this technology is demonstrated by a self-healable and stretchable circuit constructed from Cu–DOU–CPU.

Comment: Probably the best example so far describing a synergetic effect in double dynamic materials. The introduction of reversible covalent bonds, here Cu coordination, increases the kinetic rate of dimethylglyoxime urethane exchange.

Light-Driven Motion of Water Droplets with Directional Control on Nanostructured Surfaces

An, S.; Zhu, M.; Gu, K.; Jiang, M.; Shen, Q.; Fu, B.; Song, C.; Tao, P.; Deng, T.*; Shang, W.* *Nanoscale* **2020**, Advanced Article.

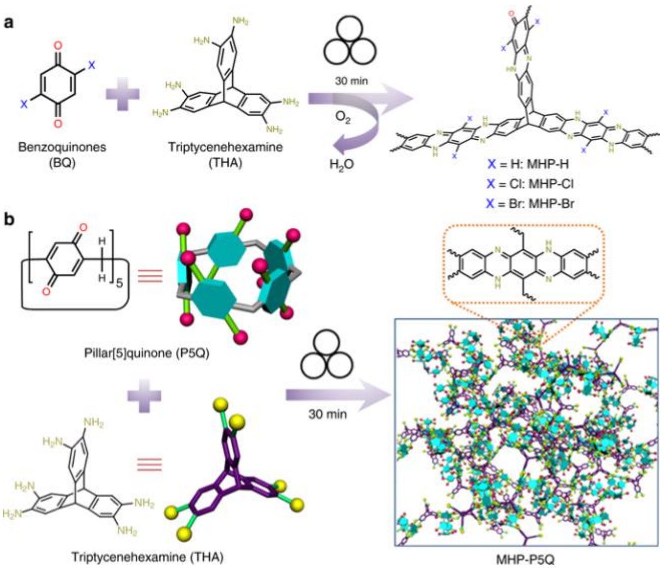


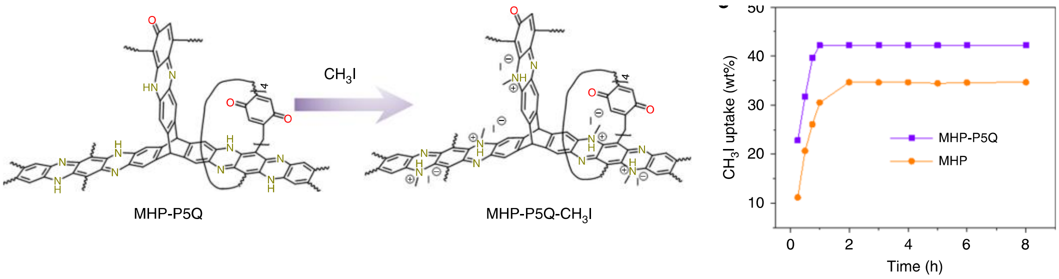
Discrete droplet transport has drawn much interest in a broad range of applications. Controlling the motion direction in droplet transport, however, is a long-lasting challenge. In this work, a simple yet efficient approach is demonstrated to realize the motion of droplets with directional control on nanostructured surfaces with predefined channels. Light is used as the external stimulus to induce the uneven thermal expansion of the substrate, which leads to the tilting of nanostructured channels so that the droplet is driven to move along the channel. Due to the easy manipulation of light, including both the light position and power density, this study demonstrates the controllable entrance of static water droplets into targeted channels and the simultaneous control of the motion of multiple droplets in multi-channel systems, using just one light source. Besides static droplets, this approach can also be applied for the directional control of moving droplets in multi-channel systems. As a proof-of-concept, such an approach has been utilized for efficient multiplexed reactions for chemical sensing or microreactor applications. This work offers an alternative approach for the manipulation of droplet movement in applications that involve the control of droplet motion

Comment: This work describes a simple way to directionally control the motion of a water droplet. When illuminating a specific position of a nano-structured surface with different channels, the thermal expansion-induced bending guides the droplet to move into a specific channel. This is a simple yet efficient approach to control motion of a droplet on a surface.

Mechanochemical synthesis of pillar[5]quinone derived multi-microporous organic polymers for radioactive organic iodide capture and storage

K. Jie, Y. Zhou, Qi S., B Li, R. Zhao, D. Jiang, W. Guo, H. Chen, Z. Yang, F. Huang, S. Dai* *Nat. Commun.* **2020**, *11*, 1086.



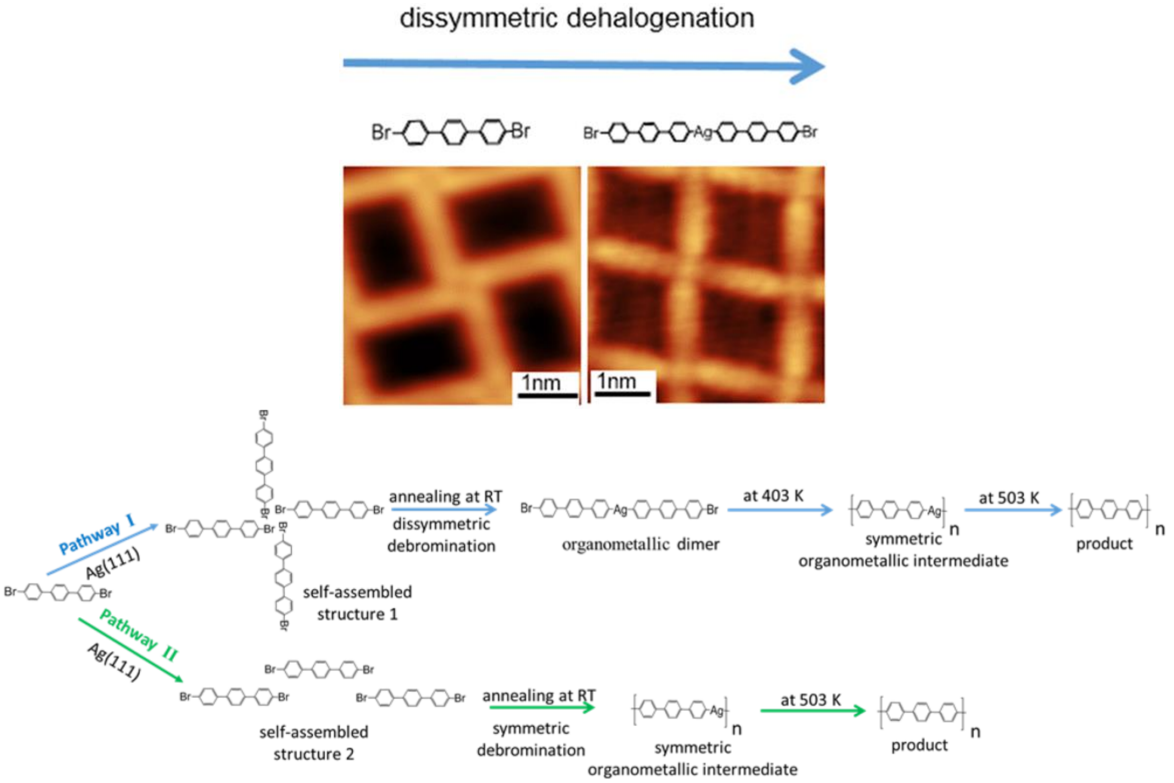


The incorporation **of supramolecular macrocycles into porous organic polymers** may endow the material with enhanced uptake of specific guests through host−guest interactions. Here we report a **solvent and catalyst-free mechanochemical synthesis** of pillar[5]quinone (P5Q) derived multi-microporous organic polymers with hydrophenazine linkages (MHP-P5Q), which show a unique 3-step N_2 adsorption isotherm. In comparison with analogous microporous hydrophenazine-linked organic polymers (MHPs) obtained using simple twofold benzoquinones, MHP-P5Q is demonstrated to have a superior performance in radioactive iodomethane (CH3I) capture and storage. Mechanistic studies show that the rigid pillar[5]arene cavity has additional binding sites though **host−guest interactions as well as the halogen bond (−I···N = C−) and chemical adsorption in the multi-microporous** MHP-P5Q mainly account for the rapid and high- capacity adsorption and long-term storage of CH_3I.

Comment: The author successfully synthesized solvent- and catalyst-free organic polymers with two-types of porosity. One is the chemical absorption between guest molecule (CH_3I) and triptychenehexamine(THA)-based polymer backbone, the other is the host-guest interaction that the same guest incorporates into the pillar[5]quinone (P5Q) which is connected with the THA-based polymer. This material is thermally/chemically stable due to the chemical structure composed of covalent bonds. If these types of porous materials have selectivity for guest molecules and the guest ones are important to be absorbed, they will be excellent porous materials for absorption or filtration. To understand the absorption mechanism deeply, it is much better to do single crystal analysis of model compound (e.g. one THA molecule with pillar[5]quinone).

Dissymmetric On-Surface Dehalogenation Reaction Steered by Preformed Self-Assembled Structure

H. Lu, W. E, L. Cai, Z. Ma,* W. Xu,* and X. Yang* *J. Phys. Chem. Lett.* **2020**, *11*, 1867.

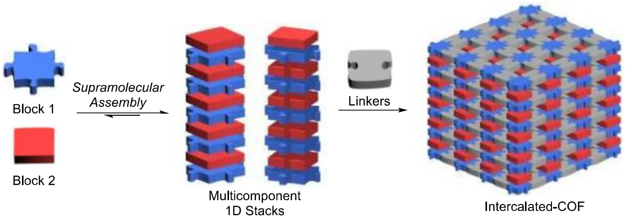


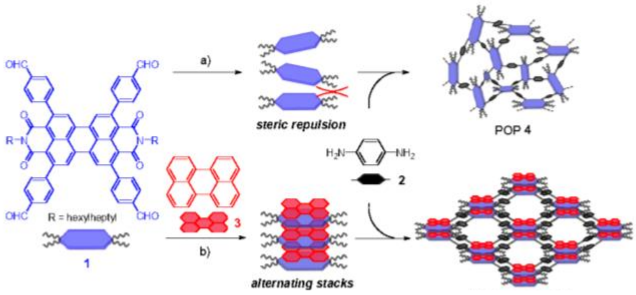
Ullmann coupling of 4,4''-dibromo-*p*-terphenyl (DBTP) thermally catalyzed on a Ag(111) surface was studied by scanning tunneling microscopy. Detailed experimental measurement shows that the **Ullmann coupling reaction pathways of DBTP molecules can be controlled by pre-self-assembly**, and the dissymmetric dehalogenation reaction is realized. Moreover, self-assembly of the reactants in a rectangular network undergoes a dissymmetric debromination transfer to a newly observed rhombic network formed by organometallic dimers prior to the formation of longer symmetric organometallic intermediates on a Ag(111) surface, while the ladder assembled phase is more likely to induce the symmetric debromination reaction and converts into the symmetric organometallic intermediate. These findings help us to understand the essentials of the dissymmetric dehalogenation reaction that originated from a symmetric compound and pave new avenues for advancing the emerging field of on-surface synthesis.

Comment: The authors observed the kinetically-stable organometallic dimers upon annealing DBTP molecules on Ag surface judging from beautiful and high-resolution STM images. Following the careful annealing of DBTP on Ag surface, it was found that the formation of symmetric organometallic intermediates and hydrocarbon polymers. These careful observations can give us details about the mechanism in the field of "on-surface synthesis". If the author would show not only a narrow (microscopic or molecular-level) area but also a wide (macroscopic) area, this work would become more rigorous and interesting. Moreover, it looks appealing to clarify the reason why rhombic network finally changed to ladder assemblies upon debromination by heating and the relationship between the direction of ladder and the structure of the Ag surface.

Supramolecular Alternating Donor–Acceptor Assembly toward Intercalated Covalent Organic Frameworks

Li, H.; Shao, P.; Chen, S.; Li, G.; Feng, X.; Chen, X.; Zhang, H.-J.; Lin, J.; Jiang, Y.-B. *J. Am. Chem. Soc.* **2020**, ASAP



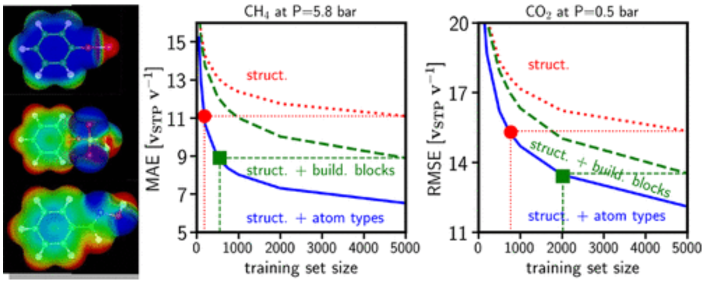


Conventionally, z-direction modulation of two-dimensional covalent organic frameworks (2D-COFs) is difficult to achieve because they rely on spontaneous π-π interactions to form 3D architectures. Herein, we report **a facile construction of a novel intercalated covalent organic framework** (Intercalated-COF) by **synchronizing operations of supramolecular donor-acceptor** (D-A) **interactions** (A unit: 2,5,8,11-tetra(*p*-formylphenyl)-perylene diimide (PDI) 1; D unit: perylene 3, as intercalator) in the vertical directions**, with polymerizations** (by only reacting 1 with *p*- phenylenediamine 2) in the lateral directions. In this Intercalated-COF, the PDI-based covalent 2D layers are uniformly separated by perylene guest layers. This supramolecular strategy opens the possibility for z-direction modulation of 2D-COFs through "intercalating" various guest molecules and thus may contribute to the exploration of advanced applications of these porous and crystalline frameworks.

Comment: I think that this article describes an interesting supramolecular framework. However, I have to admit that I am definitely not convinced by the novelty of this work. It looks like this kind of self-assembled structures was described for years now. Thus, I don't understand how it could have been published in *JACS*. Overall, we can still enjoy the design used, particularly the reversible imine bonds.

A Universal Machine Learning Algorithm for Large Scale Screening of Materials

Fanourgakis, G. S.; Gkagkas, K.; Tylianakis, E.; Froudakis, G. E. *J. Am. Chem. Soc.* **2020**

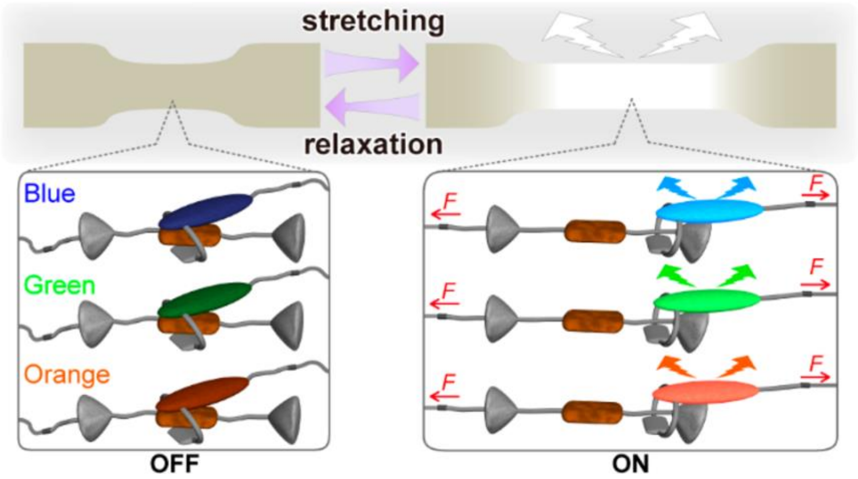


Application of **machine learning** (ML) **methods** for the **determination of the gas adsorption capacities of nanomaterials**, such as metal–organic frameworks (MOF), has been extensively investigated over the past few years as a computationally efficient alternative to time-consuming and computationally demanding molecular simulations. Depending on the thermodynamic conditions and the adsorbed gas, ML has been found to provide very accurate results. In this work, we go one step further and **we introduce chemical intuition in our descriptors** by using the "type" of the atoms in the structure, instead of the previously used building blocks, to account for the chemical character of the MOF. ML predictions for the methane and carbon dioxide adsorption capacities of several tens of thousands of hypothetical MOFs are evaluated at various thermodynamic conditions using the random forest algorithm. For all cases examined, the use of atom types instead of building blocks leads to significantly more accurate predictions, while the number of MOFs needed for the training of the ML algorithm in order to achieve a specified accuracy can be reduced by an order of magnitude. More importantly, since practically there are an unlimited number of building blocks that materials can be made of but a limited number of atom types, the proposed approach is more general and can be considered as universal. The universality and transferability was proved by predicting the adsorption properties of a completely different family of materials after the training of the ML algorithm in MOFs.

Comment: I think that this article allows us to get an insight of what chemistry could become in the future. With the evolution of machine-learning and data analysis, it is obvious that, one day, it should be possible to predict the reactivity and/or the properties of species without synthesizing them. Of course, the road to reach this goal is long and difficult. This paper is interesting, since the complexity of the predictions has been increased one step further, and the authors managed to remain quite understandable even for neophytes in chemo-informatics.

Rotaxane-Based Mechanophores Enable Polymers with Mechanically Switchable White Photoluminescence

Yoshimitsu S.;* Marc K.; Atsushi S.; Mehboobali P.; Nobuyuki T.; Christoph W.;**ACS Cent. Sci.* ***2019***, *5*, 874−881*

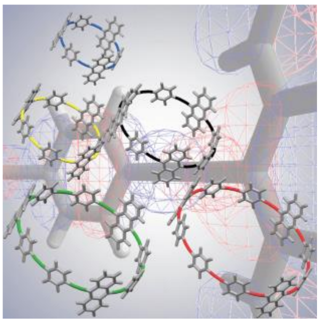


Three mechanoresponsive polyurethane elastomers whose blue, green, and orange photoluminescence can be reversibly turned on by mechanical force were prepared and combined to create a blend that exhibits deformation-induced white photoluminescence. The three polyurethanes contain rotaxane-based supramolecular mechanoluminophores based on π-extended pyrene, anthracene, or 4-(dicyanomethylene)-2- methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) luminophores, respectively, and 1,4,5,8-naphthalenetetracarboxylic diimide as an electronically matched quencher. Each polymer shows instantly reversible, strain-dependent switching of its photoluminescence intensity when stretched and relaxed, as deformation leads to a spatial separation of the luminophore and quencher. The present study shows that the photoluminescence color can easily be tailored by variation of the luminophore and also by combining several mechanophores in one material and demonstrates that adaptability is a key advantage of supramolecular approaches to create mechanoresponsive polymers.

Comment: This is the first white-light-emitting polymer that can exhibit reversible ON/OFF photoluminescence switching based on rotaxane-based supramolecular mechanophores. The limitation of this material is that it can only emit white light under very specific conditions.

π-Conjugated Macrocycles Bearing Angle-Strained Alkynes

Koji, M.;* Kouichi, O.* *Chem. Eur. J.* **2020**, *26,* 2529-2575 .

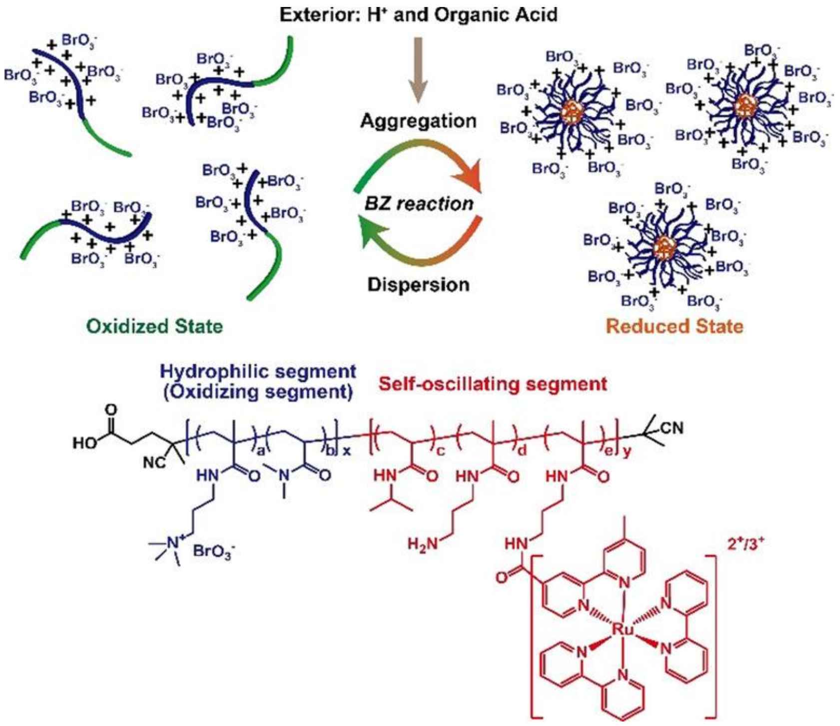


Angle-strained alkyne-containing π-conjugated macrocycles are attractive compounds both in functional materials chemistry and biochemistry. Their interesting reactivity as well as photophysical and supramolecular properties have been revealed in the past three decades. This review highlights the recent advances in angle-strained alkyne-containing π-conjugated macrocycles, especially their synthetic methods, the bond angles of alkynes, and their functions. The theoretical and experimental research on cyclo[n]carbons and para-cyclophynes consisting of ethynylenes and para-phenylenes are mainly summarized. Related macrocycles bearing other linkers, such as ortho-phenylenes, meta-phenylenes, heteroaromatics, biphenyls, extended aromatics, are also overviewed. Bond angles of strained alkynes in π-conjugated macrocycles, which are generable, detectable, and isolable, are summarized at the end of this review.

Comment: A detailed and interesting review about the π-conjugated macrocycles.

Fabrication of Self-Oscillating Micelles with a Built-In Oxidizing Agent

Yoshizawa, T.; Onoda, M.; Ueki, T.*; Tamate, R.; Akimoto, A. M.; Yoshida, R.* *Angew. Chem. Int. Ed.* **2020**.

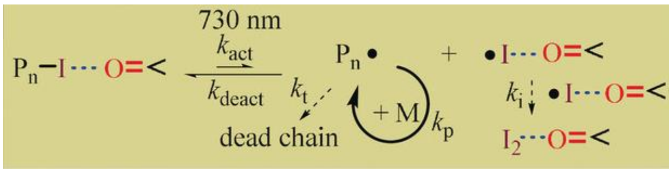


Various biological behaviors are fueled by “respiration”, which is an example of catabolism. So far, we have reported various self-oscillating soft materials exhibiting bioinspired dynamic movements. These autonomous polymer systems are driven by the **Belousov–Zhabotinsky (BZ) reaction**, which is analogous to the tricarboxylic acid (TCA) cycle that is an integral part of respiration. However, in the BZ reaction, the external addition of an oxidizing agent is necessary to initiate the oxidation process, which is realized by intracellular moieties such as ubiquinone in living systems. Herein, we realized self-oscillating micelles that are driven without the external addition of an oxidizing agent. This was achieved by **embedding the oxidizing source into the structure** of the self-oscillating AB diblock copolymers. This strategy introduces a new function equivalent to intracellular oxidizing moieties, and is useful for the design of completely autonomous bioinspired materials.

Comment: The authors already published a few systems where the chemical oscillations of the BZ reaction are translated into oscillations of mechanical or structural properties of polymeric materials. In this paper, they included the oxidizing agent into the polymer backbone; they still need, however, to add the organic acid to initiate the oscillations. All in all, even if these systems are interesting, **this work does not present remarkable advances**, in my opinion.

Photocontrolled Iodine-Mediated Reversible-Deactivation Radical Polymerization System: Solution Polymerization of Methacrylates by Irradiation with NIR LED Light

Tian, C.; Wang, P.; Ni, Y.; Zhang, L.*; Cheng, Z.*; Zhu, X. *Angew. Chem. Int. Ed.* **2020**.

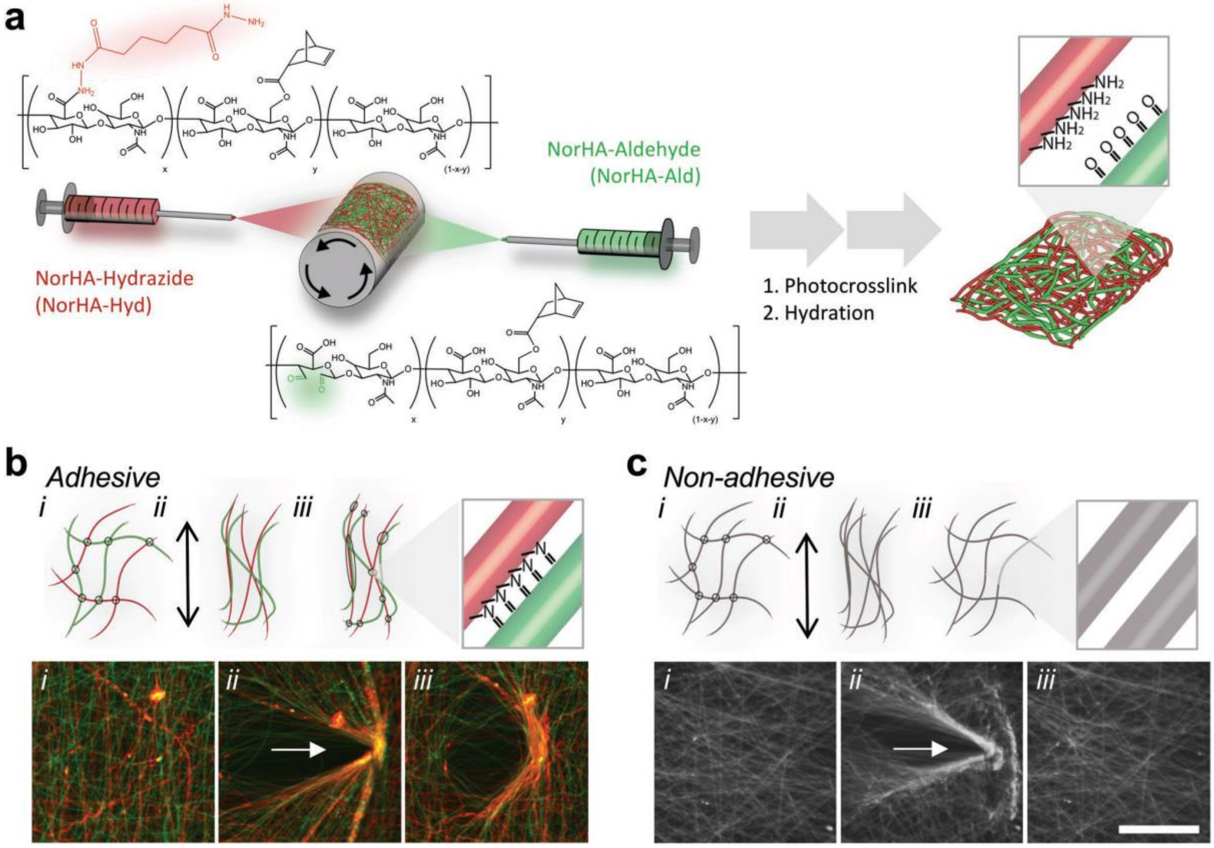


Herein, **near-infrared (NIR) photocontrolled iodide-mediated reversible-deactivation radical polymerization (RDRP)** of methacrylates, without an external photocatalyst, was developed using an alkyl iodide (e.g., 2-iodo-2-methyl-propionitrile) as the initiator at room temperature. This example is the first use of a series of special solvents containing carbonyl groups (e.g., 1,3-dimethyl-2-imidazolidinone) as both solvent and catalyst for photocontrolled RDRP using long-wavelength (λ_{max}=730 nm) irradiation. The polymerization system comprises monomer, alkyl iodide initiator, and solvent. Well-defined polymers were synthesized with excellent control over the molecular weights and molecular weight distributions ($M_w/M_n < 1.21$). The living features of this system were confirmed by polymerization kinetics, multiple controlled "on-off" light switching cycles, and chain extension experiments. Importantly, the polymerizations proceeded successfully with various barriers (pork skin and A4 paper), demonstrating the advantage of high-penetration NIR light.

Comment: The discovery of new polymerization conditions is always something to look at, especially when it leads to living-like kinetics. While this paper focuses on methacrylates as a proof-of-concept, it may open possibilities for other, less conventional, monomers that were not easily polymerized before in such "mild" conditions.

Mechanochemical Adhesion and Plasticity in Multifiber Hydrogel Networks

Davidson, M. D.; Ban, E.; Schoonen, A. C. M.; Lee, M. H.; D'Este, M.; Shenoy, V. B.; Burdick, J. A. *Adv. Mater.*, **2019**, *1905719*, 1–8.

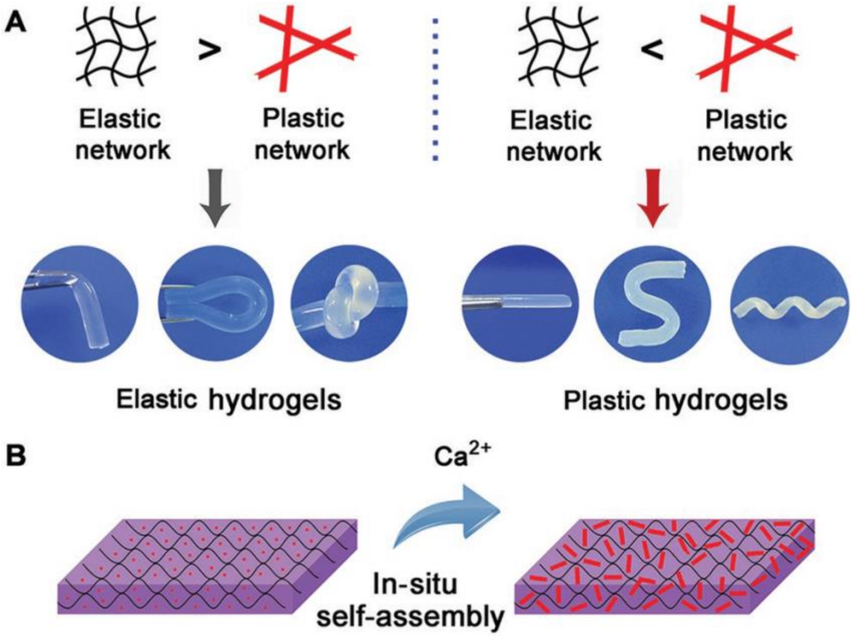


The extracellular matrix (ECM) has force-responsive (i.e., mechanochemical) properties that enable adaptation to mechanical loading through changes in fibrous network structure and interfiber bonding. Imparting such properties into synthetic fibrous materials will allow reinforcement under mechanical load, the potential for material self-adhesion, and the general mimicking of ECM. Multifiber hydrogel networks are developed through the electrospinning of multiple fibrous hydrogel populations, where fibers contain complementary chemical moieties (e.g., aldehyde and hydrazide groups) that form covalent bonds within minutes when brought into contact under mechanical load. These fiber interactions lead to microscale anisotropy, as well as increased material stiffness and plastic deformation. Macroscale structures (e.g., tubes and layered scaffolds) are fabricated from these materials through interfiber bonding and adhesion when placed into contact while maintaining a microscale fibrous architecture. The design principles for engineering plasticity described can be applied to numerous material systems to introduce unique properties, from textiles to biomedical applications.

Comment: The principle is cool: once blended, the two polymers containing hydrazide and aldehyde respectively can form a dynamic covalent network. It is a room temperature vitrimeric hydrogel. The novelty lies on the fabrication method layer-by-layer that can then self-adhere to each other and eventually merge.

Mechanochemical Adhesion and Plasticity in Multifiber Hydrogel Networks

Ming, Z.; Pang, Y.; Liu, J. *Adv. Mater.*, **2019**, *1906870*, 1–8.

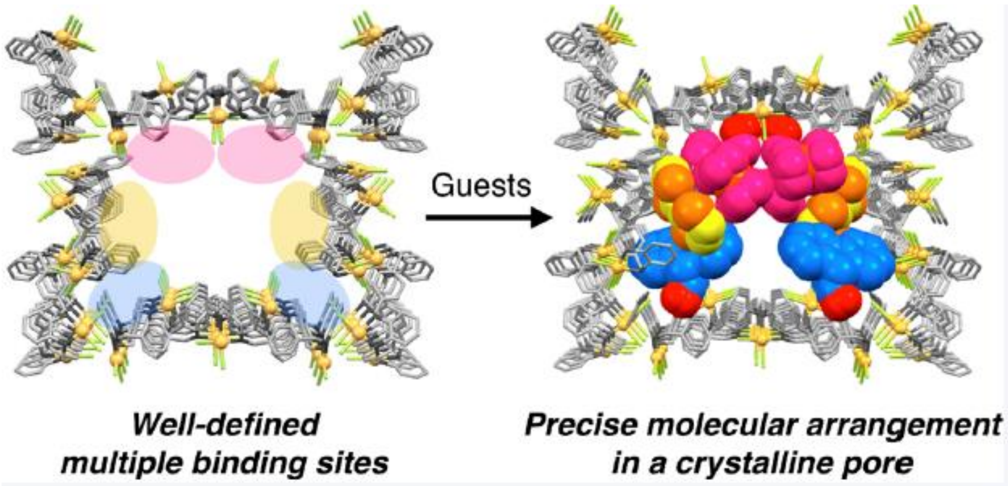


Switching a material between highly elastic and plastic would be of great use in many fields but has proven to be extremely challenging. Here, the use of mechanical strength competition between two networks in a hybrid material is reported to switch between elasticity and plasticity. In a gel material composed of an elastic polymer network and a shear-thinning nanofiber network, the excellent elasticity of the gel is demonstrated when the former is stronger than the latter. In contrast, the gel exhibits an extraordinary plasticity, which can be stretched to form a permanent anisotropic and tough gel due to the orientation of the nanofibers. The mechanical strength of each network can be simply tuned by adjusting either the crosslinking density or the loading of the nanofibers. This work may open a window to transform a material between superior elastic and plastic, which is useful for the development of adaptable materials.

Comment: The transition between plasticity and elasticity comes from the different ratios of shear thickening dexamethasone phosphate. So, you actually have to change your material to exhibit different behaviors.

Novel Porous Crystals with Macrocycle-Based Well-Defined Molecular Recognition Sites

Tashiro. S.; Shionoya, M.* *Acc. Chem. Res.* **2020**, ASAP



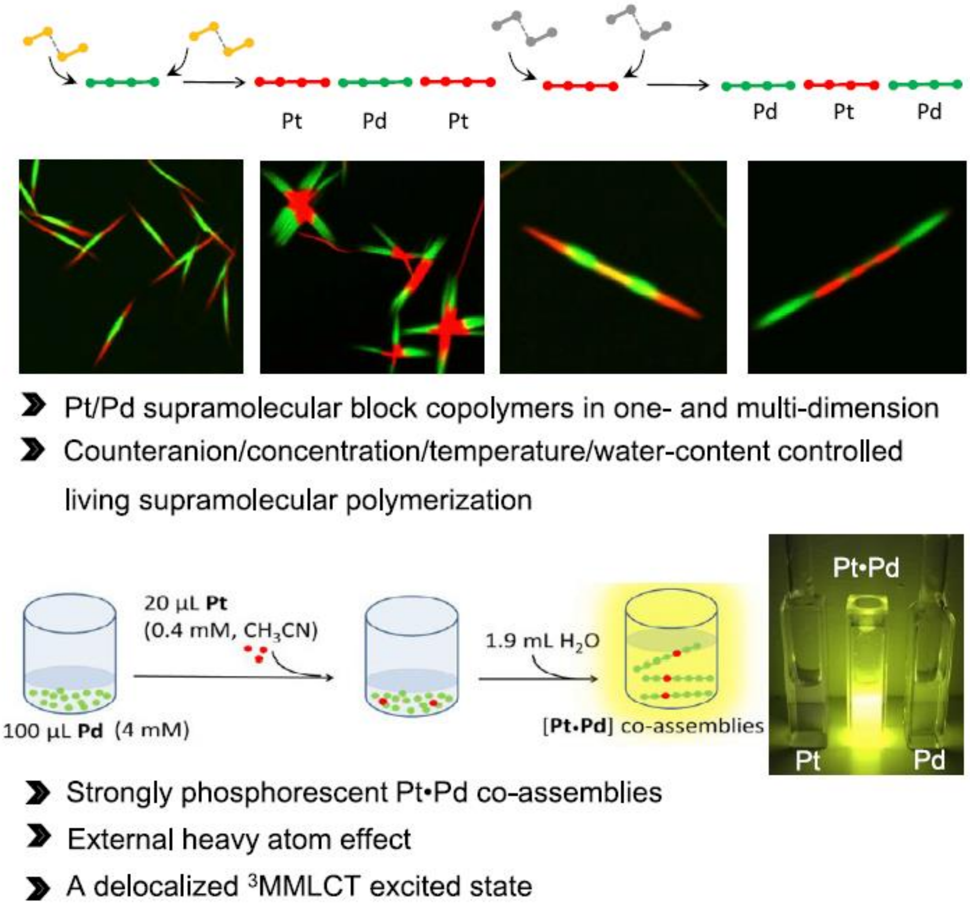
Molecular recognition is one of the fundamental events in biological systems, as typified by enzymes that enable highly efficient and selective catalytic reactions through precise recognition of substrate(s) and cofactor(s) in the binding pockets. Chemists therefore have long been inspired by such excellent molecular systems to develop various synthetic receptors with well-defined binding sites. Their effort is currently being devoted to the construction of not only molecular receptors but also self-assembled host compounds possessing connected cavities (pores) in the crystalline frameworks to rationally design functional porous materials capable of efficiently adsorbing molecules or ions at binding sites on the pore walls. However, it is still challenging to design multiple distinct binding sites that are precisely arranged in an identical framework, which is currently one of the most important targets in this field to realize elaborate molecular systems beyond natural enzymes.

In this Account, we provide an overview of porous crystals with well-defined molecular recognition sites. We first show several strategies for arranging macrocyclic binding sites in crystalline frameworks such as metal−organic frameworks, porous molecular crystals, and covalent organic frameworks. Porous metal−macrocycle frameworks (MMFs) that we have recently developed are then described as a new type of porous crystals with well-defined multiple distinct binding sites. The MMF-1 crystal, which was developed first and is composed of four stereoisomers of helical $\mathrm{Pd^{II}_3}$−macrocycle complexes, has one-dimensional channels with dimensions of 1.4 nm × 1.9 nm equipped with enantiomeric pairs of five distinct binding sites. This structural feature of MMF-1 therefore allows for site-selective and asymmetric arrangement of not only single but also multiple guest molecules in the crystalline channels based on molecular recognition between the guests and the multiple binding sites. This characteristic was also exploited to develop a heterogeneous catalyst by non-covalently immobilizing an organic acid on the pore surface of MMF-1 to conduct size-specific catalytic reactions. In addition, adsorption of a photoreactive substrate in MMF was found to switch the photoreaction pathway to cause another reaction with the aid of photoactivated $\mathrm{Pd^{II}}$ centers arranged on the pore walls. Furthermore, the dynamic, transient process of molecular arrangement incorporated in MMF-1 has been successfully visualized by single-crystal X-ray diffraction analysis. The formation of homochiral MMF-2 composed of only (P)- or (M)-helical PdII 3−macrocycle complexes is also described. Thus, macrocycle-based porous crystals with a complex structure such as MMFs are expected to serve as novel porous materials that have great potential to mimic or surpass enzymes by utilizing well-defined multiple binding sites capable of spatially arranging a catalyst, substrate, and effector for highly selective and allosterically tunable catalytic reactions, which can be also visualized by crystallographic analysis because of their crystalline nature.

Comment: This account describes different types of porous crystals with molecular recognition site, which are capable of binding various guest molecules. If you are interested in these materials, I also suggest you to read some papers about non-porous adaptive crystals based on macrocycles. It is a novel concept which is rising in recent years.

Controlled Synthesis of PdII and PtII Supramolecular Copolymer with Sequential Multiblock and Amplified Phosphorescence

Wan, Q.; To, W.-P.; Chang, X.; Che, C.-M.* *Chem* **2020**, *6*, 1-23.



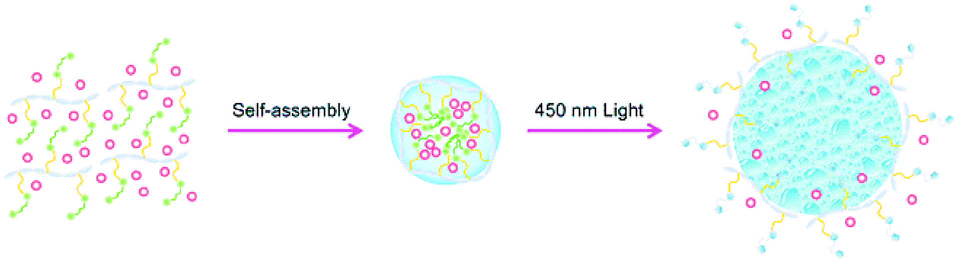
- Pt/Pd supramolecular block copolymers in one- and multi-dimension
- Counteranion/concentration/temperature/water-content controlled living supramolecular polymerization
- Strongly phosphorescent Pt•Pd co-assemblies
- External heavy atom effect
- A delocalized ^{3}MMLCT excited state

Supramolecular copolymers constitute a fundamental new class of functional materials attracting burgeoning interest, but examples that display phosphorescence and long-lived excited states are rare. Herein, we describe the synthesis of sequential phosphorescent multi-block supramolecular copolymers in one and multiple dimensions using pincer PtII and PdII complexes as building blocks by manipulating out-of-equilibrium self-assemblies via the living supramolecular polymerization approach. Doping a small amount of Pt^{II} complexes (2 mol %) into the Pd^{II} assemblies significantly boosted the emission efficiency and radiative decay rate constant (Φ_{em} = 3.7%, K_r = 1.8 ×10^4 s^{-1} in Pd^{II} assemblies; Φ_{em} = 76.2%, K_r = 58.6 × 10^4 s^{-1} in Pt^{II}-Pd^{II} co-assemblies), which is ascribed to an external heavy-atom spin-orbital coupling effect arising from the doped Pt^{II} complex with a delocalized $^3[d\sigma^*/p^*]$ excited state. The findings on Pt^{II} and Pd^{II} supramolecular copolymers with controlled sequences and greatly enhanced phosphorescence efficiencies open the door to new photofunctional and responsive luminescent metal-organic supramolecular materials.

Comment: It is an interesting paper, in which the copolymer is constructed by living supramolecular polymerization approach. They studied this growth process and light-induced properties in detail. By the way, I really like the confocal images in this paper.

Visualizing intracellular particles and precise control of drug release using an emissive hydrazone photochrome

Guo, X; Shao, B; Zhou, S; Aprahamian, I;* Chen, Z* *Chem. Sci.*, **2020**, ASAP.



The spatiotemporal control over the structure of nanoparticles while monitoring their localization in tumor cells can improve the precision of controlled drug release, thus enhancing the efficiency of drug delivery. Here, we report on a photochromic nanoparticle system (**LSNP**), assembled from fluorescent bistable hydrazone photoswitch-modified amphiphilic copolymers. The intrinsic emission of the hydrazone switch allows for the visualization of particle uptake, as well as their intracellular distribution. The $Z \rightarrow E$ photoswitching of the hydrazone switch within the nanoparticle leads to the expansion of the nanoparticles (*i.e.*, drug release) accompanied by emission quenching, the degree of which can function as an internal indicator for the amount of drug released. The bistability of the switch enables the kinetic trapping of particles of different sizes as a function of irradiation time, and allows for the exhibition of light-dependent cell cytotoxicity in MDA-MB-231 cells using **LSNP** loaded with doxorubicin.

Comment: An interesting application in the biomedical field. The authors took advantage of the photochromic properties of the hydrazone switches that they had synthesized previously in their research team. They functionalized an amphiphilic copolymer with these switches in order to track the nanoparticles inside the cellular media and disrupt the core-shell structure formed by self-assembly when they are irradiated with visible light, allowing the releasing of the encapsulated drug doxorubicin.