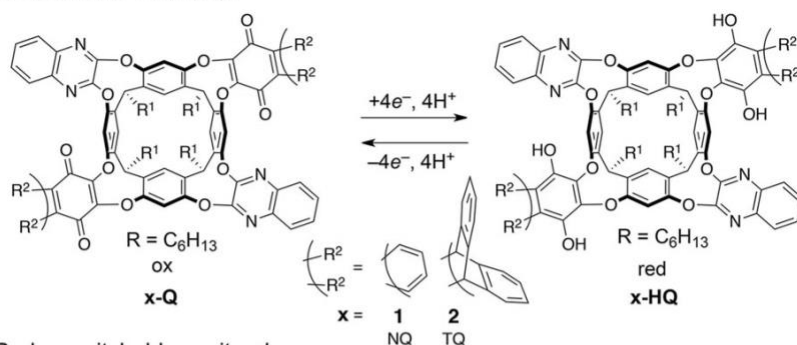


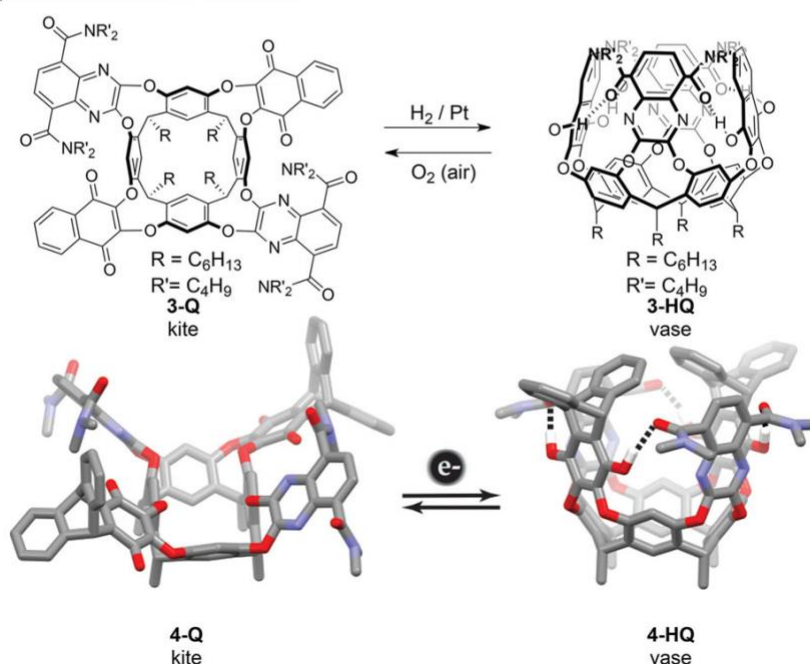
The Quest for Molecular Grippers: Photo-Electric Control of Molecular Gripping Machinery

Milič, J. V.;* Diederich, F.* *Chem. Eur. J.* **2019**, *25*, 8440-8452

a) Redox-active cavitands



b) Redox-switchable cavitands

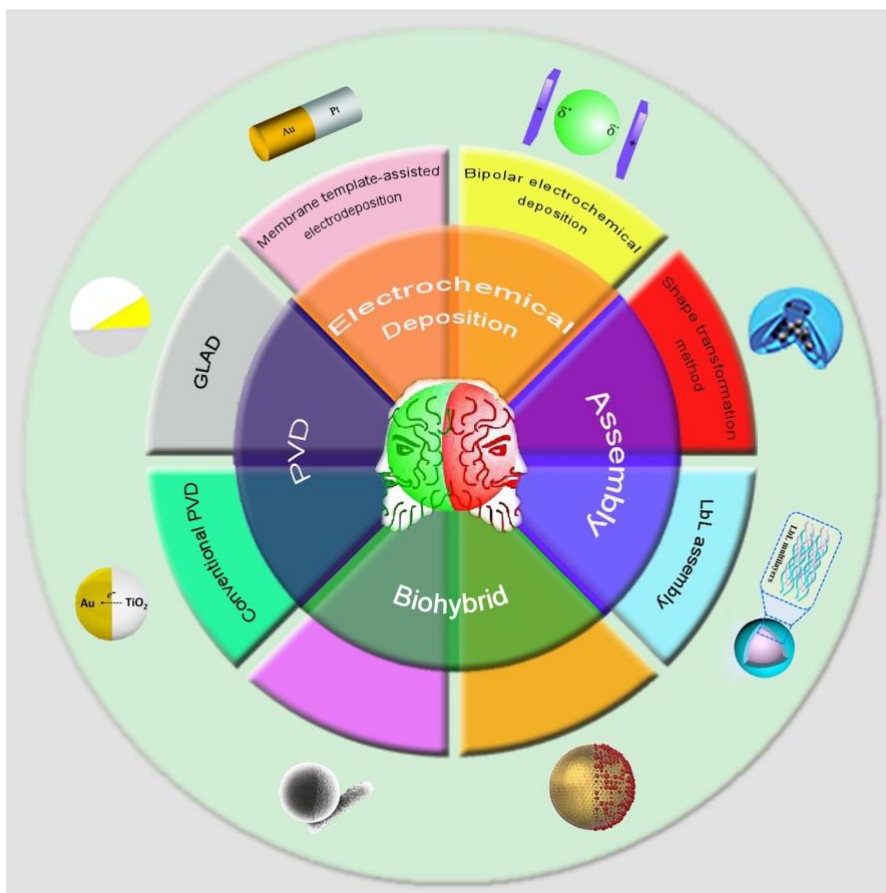


The quest for nanoscale molecular machines has inspired the search for their close relatives, molecular grippers. This path was paved by the development of resorcin[4]arene cavitands and their quinone-based redoxactive congeners. In this Concept article, the efforts to design and establish the control of quinone-functionalized resorcin[4]arenes by electronic and electromagnetic stimuli is described. This was achieved by relying on paramagnetic semiquinone radical anions formed electrochemically or by photoredox catalysis. **The gripper-like motion of such species could not be studied by conventional NMR spectroscopy. Instead, an entirely different approach had to be developed** that included various electroanalytical and spectroelectrochemical methods, including UV/Vis/NIR spectroelectrochemistry, pulsed EPR and Davies 1H ENDOR spectroscopy, transient absorption spectroscopy, and time-resolved luminescence measurements, besides density functional theory calculations and X-ray crystallography. The conceptual breakthroughs are reviewed as well as the current state and future perspectives of photoredox switchable molecular grippers.

Comment: If you want further information about the presentation Jovana Milic gave, this article is for you. The most interesting part relies on the smart use of complementary techniques to prove and monitor molecular motion. A must read.

Fabrication of Self-Propelled Micro- and Nanomotors Based on Janus Structures

Ye, Y.; Luan, J.; Wang, M.; Chen, W.; Wilson, D. A.; Peng, F.*; Tu, Y.* *Chem. Eur. J.* **2019**, *25*, 8663-8680



Delicate molecular and biological motors are tiny machines capable of achieving numerous vital tasks in biological processes. To gain a deeper understanding of their mechanism of motion, researchers from multiple backgrounds have designed and fabricated artificial micro- and nanomotors. These nano-/microscale motors can self-propel in solution by exploiting different sources of energy; thus showing tremendous potential in widespread applications. As one of the most common motor systems, Janus motors possess unique asymmetric structures and integrate different functional materials onto two sides. This review mainly focuses on the fabrication of different types of micro- and nanomotors based on Janus structures. Furthermore, some challenges still exist in the implementation of Janus motors in the biomedical field. With such common goals in mind, it is expected that the elaborate and multifunctional design of Janus motors will overcome their challenges in the near future.

Comment: The authors review here the different kinds of Janus particles, their synthesis, and some of the potential applications of self-propelled micro/nano motors. It's not going deep in details but it describes well the fundamental aspects of the field. An article for self-propelled Janus particles newbies like myself.

Micro-/Nanomachines Driven by Ultrasonic Power Sources

Lu, X.;* Shen, H.; Zhao, K.; Wang, Z.; Peng, H.; Liu, W. [Chem. Asian J. 2019, ASAP](#).

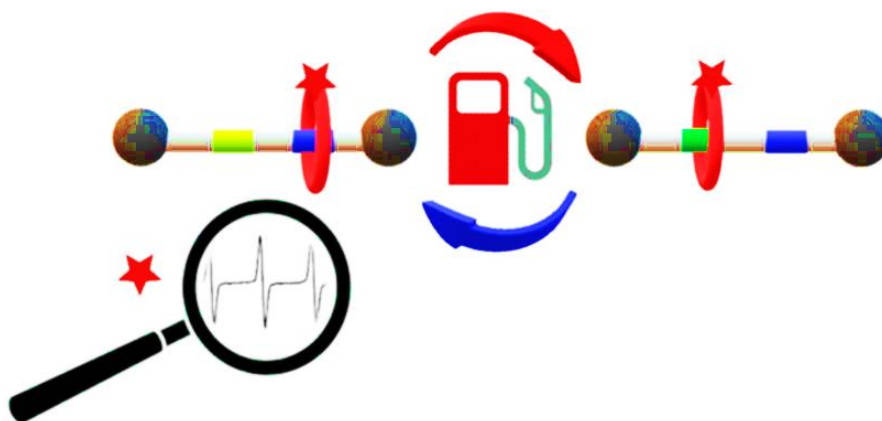


Autonomous micro-/nanomachines that can convert diverse energy sources into effective locomotion under the constraint of low Reynolds numbers hold considerable promise for a variety of applications, such as cargo delivery, localized biosensing, nanosurgery, and detoxification. In this Minireview, we briefly overview recent advances in the development of micro-/nanomachines that are specifically powered by ultrasound, in particular new concept design, their working principles, and their fabrication and manipulation strategies. Finally, the exclusive biocompatibility and sustainability of ultrasound-powered micro-/nanomachines, as well as the critical challenges that face there in vivo application, are discussed to provide insight for the next phase of micro-/nanomachines with versatile functionalities and enhanced capabilities.

Comment: A progress report in the development of micro and nanomachines triggered by ultrasonic sources. From working principles, going through the fabrication and manipulation of these systems, until the potential applications of these tiny machines. In addition, the authors claim two main challenges to be solved, which are the in vivo operation and the intelligence for sensing variations in the experimental conditions and also the ability to communicate with other nanomachines.

2-Cyano-2-phenylpropanoic Acid Triggers the Back and Forth Motions of an Acid–Base-Operated Paramagnetic Molecular Switch

Franchi, P.; Poderi, C.; Mezzina, E.; Biagini, C.; Di Stefano, S.;* Lucarini, M.* [J. Org. Chem. 2019, ASAP](#)

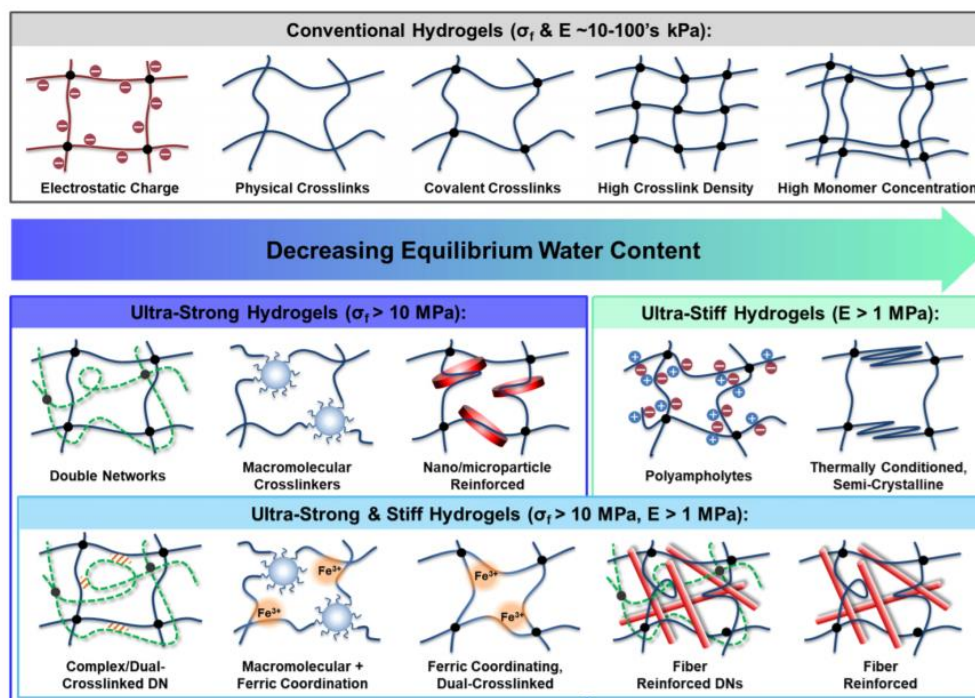


The back and forth motions of a crown-ether based wheel along the axis of a bistable rotaxane are triggered by the decarboxylation of 2-cyano-2-phenylpropanoic acid and detected by the oscillation of the EPR nitrogen splitting of a dialkyl nitroxide function mounted within the macrocyclic ring. When the *p*-Cl derivative of the acid is used, back and forth motions are accelerated. Conversely, with *p*-CH₃ and *p*-OCH₃ derivatives, the back motion is strongly inhibited by the insurgence of collateral radical reactions.

Comment: In this article, the authors demonstrate the back and forth movement of a macrocycle in a [2]rotaxane using EPR and in the presence of activated carboxylic acids. The macrocycle contains a radical fragment that can be modified in order to modulate the magnetic properties of the system.

Modern Strategies To Achieve Tissue-Mimetic, Mechanically Robust Hydrogels

Means, A. K.; Grunlan, M. A.* [ACS Macro Lett. 2019, 8, 705-713.](#)

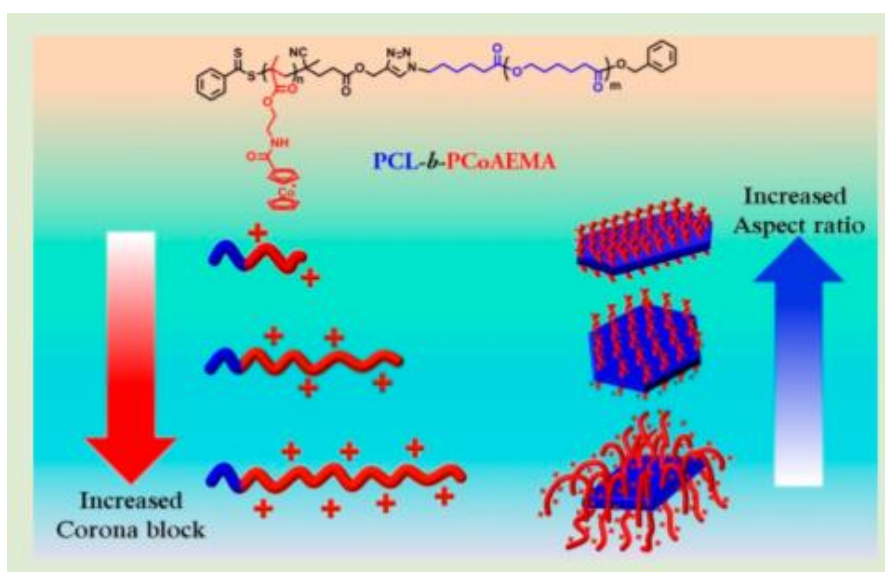


Hydrogels are frequently used biomaterials due to their similarity in hydration and structure to biological tissues. However, their utility is limited by poor mechanical properties, namely, a lack of strength and stiffness that mimic that of tissues, particularly load-bearing tissues. Thus, numerous recent strategies have sought to enhance and tune these properties in hydrogels, including interpenetrating networks (IPNs), macromolecular cross-linking, composites, thermal conditioning, polyampholytes, and dual cross-linking. Individually, these approaches have achieved hydrogels with either high strength ($\sigma_f > 10$ MPa), high stiffness ($E > 1$ MPa), or, less commonly, both high strength and stiffness ($\sigma_f > 10$ MPa and $E > 1$ MPa). However, only certain unique combinations of these approaches have been able to synergistically achieve retention of a high, tissue like water content as well as high strength and stiffness. Applying such methods to stimuli responsive hydrogels has also produced robust, smart biomaterials. Overall, methods to achieve hydrogels that simultaneously mimic the hydration, strength, and stiffness of soft and load-bearing tissues have the potential to be used in a much broader range of biomedical applications.

Comment: I recommend this viewpoint because it could provide some useful information about the construction of tissue-mimetic and mechanically robust hydrogels.

Crystallization-Driven Self-Assembly of Metallo-Polyelectrolyte Block Copolymers with a Polycaprolactone Core-Forming Segment

Cha, Y.; Jarrett-Wilkins, C.; Rahman, M. A.; Zhu, T.; Sha, Y.; Manners, I.*; Tang, C.* [ACS Macro Lett.](#) **2019**, *8*, 835-840.

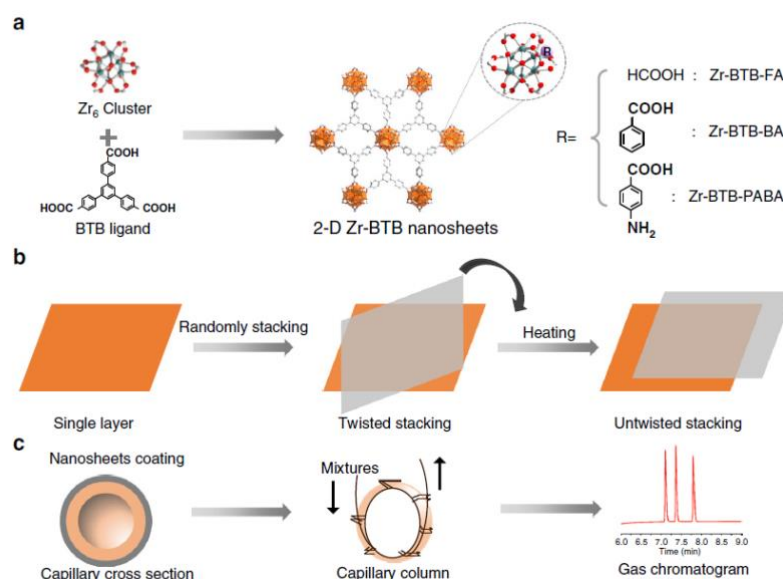


We report crystallization-driven self-assembly (CDSA) of metallo-polyelectrolyte block copolymers that contain cationic polycobaltocenium in the corona-forming block and crystallizable polycaprolactone (PCL) as the core-forming block. Dictated by electrostatic interactions originating from the cationic metalloblock and crystallization of the PCL, these amphiphilic block copolymers self-assembled into two-dimensional platelet nanostructures in polar protic solvents. The 2D morphologies can be varied from elongated hexagons to diamonds, and their stability to fragmentation was found to be dependent on the ionic strength of the solution.

Comment: It is interesting that the interplay between electrostatic repulsion of the corona and crystallization of the core dictates the transformation of morphologies.

Untwisted Restacking of Two-Dimensional Metal-Organic Framework Nanosheets for Highly Selective Isomer Separations

Tao, Z.-R.; Wu, J.-X.; Zhao, Y.-J.; Xu, M.; Tang, W.-Q.; Zhang, Q.-H.; Gu, L.; Liu, D.-H.; Gu, Z.-Y. *Nat. Commun.* **2019**, *10*, 2911.

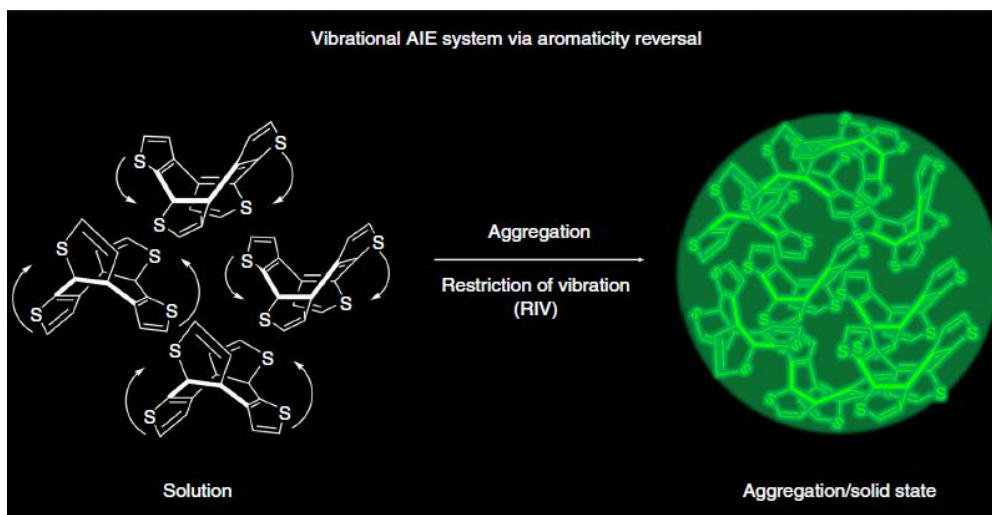


The stacking between nanosheets is an intriguing and inevitable phenomenon in the chemistry of nano-interfaces. Two-dimensional metal-organic framework nanosheets are an emerging type of nanosheets with ultrathin and porous features, which have high potential in separation applications. Here, the stacking between single-layer metal-organic framework nanosheets is revealed to show three representative conformations with tilted angles of 8°, 14°, and 30° for Zr-1, 3, 5-(4-carboxylphenyl)-benzene framework as an example. Efficient untwisted stacking strategy by simple heating is proposed. A detailed structural analysis of stacking modes reveals the creation of highly ordered sub-nanometer micropores in the interspacing of untwisted nano-layers, yielding a high-resolution separator for the pair of para-/meta-isomers over the twisted counterparts and commercial HP-5MS and VF-WAXMS columns. This general method is proven by additional nanosheet examples and supported by Grand Canonical Monte Carlo simulation. This finding will provide a synthetic route in the rational design of functionalities in two-dimensional metal-organic framework nanosheet.

Comment: In this article the authors present an application for a porous material obtained from a MOF, the porous material shows high ability in separating a group of six isomers.

Non-Aromatic Annulene-Based Aggregation-Induced Emission System via Aromaticity Reversal Process

Zhao, Z.; Zheng, X.; Du, L.; Xiong, Y.; He, W.; Gao, X.; Li, C.; Liu, Y.; Xu, B.; Zhang, J.; et al. *Nat. Commun.* **2019**, *10*, 2952.

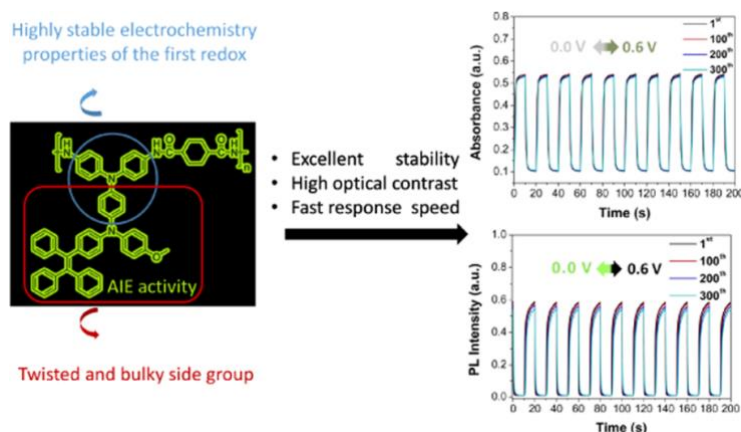


Aggregation-induced emission (AIE) is a photophysical phenomenon correlated closely with the excited-state intramolecular motions. Although AIE has attracted increasing attention due to the significant applications in biomedical and optoelectronics, an in-depth understanding of the excited-state intramolecular motion has yet to be fully developed. Here we found the nonaromatic annulene derivative of cyclooctatetrathiophene shows typical AIE phenomenon in spite of its rotor-free structure. The underlying mechanism is investigated through photoluminescence spectra, time-resolved absorption spectra, theoretical calculations, circular dichroism as well as by pressure-dependent fluorescent spectra etc., which indicate that the aromaticity reversal from ground state to the excited state serves as a driving force for inducing the excited-state intramolecular vibration, leading to the AIE phenomenon. Therefore, aromaticity reversal is demonstrated as a reliable strategy to develop vibrational AIE systems. This work also provides a new viewpoint to understand the excited-state intramolecular motion behavior of lumiongens.

Comment: in this article the authors present a new family of non-aromatic annulene-based luminescent molecules, and for the first time the AIE phenomenon has been considered from the viewpoint of aromaticity inversion.

High-Performance Emission/Color Dual-Switchable Polymer-Bearing Pendant Tetraphenylethylene (TPE) and Triphenylamine (TPA) Moieties

Sun, N.; Su, K.; Zhou, Z.; Tian, X.; Zhao, J.; Chao, D.; Wang, D.; Lissel, F.; Zhao, X.; Chen, C. *Macromolecules* **2019**, *ASAP*.

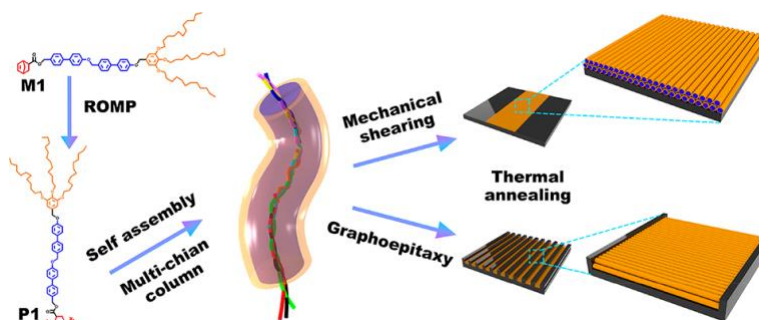


Electrofluorochromic (EFC) materials have aroused great interest owing to their interesting ability of tuning fluorescence in response to the applied potential. However, some crucial characteristics, such as response speed, fluorescence contrast, and switching stability, are still not well realized to meet the requirements of practical applications. Herein, we designed and synthesized a novel polyamide-bearing aggregation-induced emission (AIE)-active tetraphenylethylene (TPE) and a highly conjugated triphenylamine (TPA) pendant group. The rational combination of the highly conjugated TPA and TPE caused the resultant polymer to exhibit highly integrated electrochromic (EC) and EFC performances including multiple color-changing (colorless to green to blue), fast response speed (1.8/1.1 s for EC and 0.4/2.9 s for EFC process), high fluorescence contrast (82 at the duration time of 20s), and excellent long-term stability over 300 cycles. The strategy of AIE functionality by combing a highly conjugated redox unit demonstrates a synergistic effect to prepare high-performance emission/color dual-switchable materials, greatly promoting their applications in sensors, smart windows, and displays.

Comment: This paper introduces the AIE active TPE and highly conjugated TPA units to make a novel electro-AIE active polymer with high electrochromic and electrofluorochromic performance. I think it provides us a new way for developing high-performance emission/color dual switchable materials.

Highly Ordered Sub-10 nm Patterns Based on Multichain Columns of Side-Chain Liquid Crystalline Polymers

Jiang, X.; Zhao, R.; Chang, W.; Yin, D.; Guo, Y.; Wang, W.; Liang, D.; Yang, S.; Shi, A.; Chen, E. *Macromolecules*. 2019. ASAP.

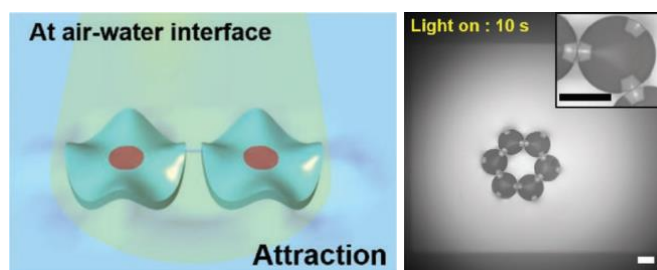


The development of nanotechnology relies crucially on the ability to fabricate materials with desired nanostructures. Because of their precise side-chain structure and versatile ordered morphologies, side-chain liquid crystalline polymers can provide a novel material platform to obtain sub-10 nm structures via their self-assembly. Here we show that for a newly designed side-chain liquid crystalline (LC) polynorbornene (**P1**) with a slim hemiphasmid mesogen microphase separation between the main and side chains drives the spontaneous formation of hexagonal columnar phase (Φ_h) composed of cylinders with a uniform diameter of 8.3 nm. At every cross section of the cylinder there are more than a dozen **P1** chains laterally bundled together. The cylinders can grow axially when more chains join in becoming extraordinarily long to over several micrometers. Simple shearing can produce **P1** thin films with very good orientation of the Φ_h phase at the macroscopic scale. More interestingly, we show that directed self-assembly of graphoepitaxy of **P1** also provides an efficient route to obtain the patterned cylinders, making its applications in nanotechnology highly possible.

Comment: In this paper, the authors use the norbornene unit to construct a side-chain liquid crystalline polymer through olefin metathesis. How about coupling the **Norbornene** with Triphenylamine or some other groups to make interesting materials?

Light-Driven Shape Morphing, Assembly, and Motion of Nanocomposite Gel Surfers

Kim, H.; Kang, J.; Zhou, Y.; Kuenstler, A. S.; Kim, Y.; Chen, C.; Emrick, T.*; Hayward, R. C.* *Adv. Mater.* **2019**, *1900932*.

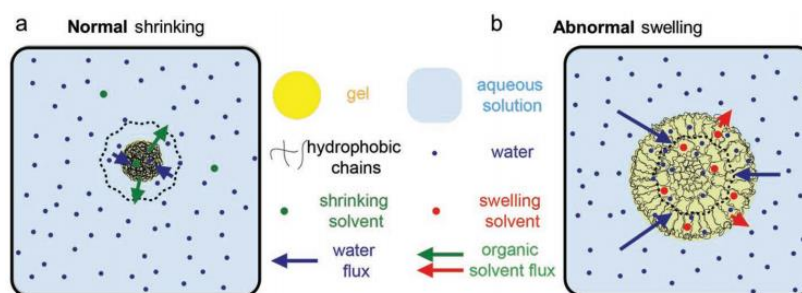


Patterning of nanoparticles (NPs) via photochemical reduction within thermally responsive hydrogel films is demonstrated as a versatile platform for programming light-driven shape morphing and materials assembly. **Responsive hydrogel disks**, containing patterned metal NPs, form characteristic wrinkled structures when illuminated at an air/water interface. The resulting distortion of the three-phase (air/water/hydrogel) contact lines induces capillary interactions between two or more disks, which are either attractive or repulsive depending on the selected pattern of light. By programming the shapes of the NP-rich regions, as well as of the hydrogel objects themselves, the number and location of attractive interactions are specified, and the assembly geometry is controlled. Remarkably, appropriately patterned illumination enables sustained rotation and motion of the hydrogel disks. Overall, these results offer insight into a wide variety of **shape-programmable materials and capillary assemblies**, simply by controlling the NP patterns and illumination of these soft materials

Comment: Two points are interesting to me in this paper. First, the formation of the thermoresponsive hydrogels is clever. They are formed by two-step photopatterning in a mixture of polymer (containing a radical initiator) and gold salt, hence it seems easily accessible to form these objects. Second, with an asymmetric irradiation with light, the authors managed to initiate motion in the gels and their assemblies. Therefore, as they say in their abstract, I agree that it might open the way towards a wide variety of light-sensitive assemblies.

Hydrophobic Hydrogels with Fruit-Like Structure and Functions

Guo, H.; Nakajima, T.; Hourdet, D.; Marcellan, A.; Creton, C.; Hong, W.; Kurokawa, T.; Gong, J. P.* *Adv. Mater.* **2019**, *1900702*.



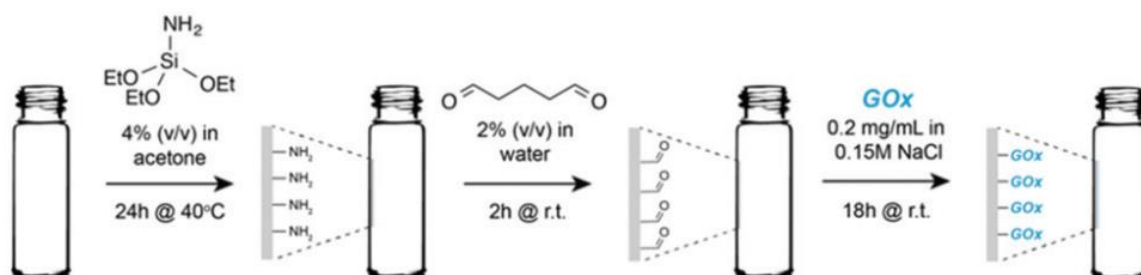
Normally, a polymer network swells in a good solvent to form a gel but the gel shrinks in a poor solvent. Here, an abnormal phenomenon is reported: some **hydrophobic gels significantly swell in water**, reaching water content as high as 99.6 wt%. Such abnormal swelling behaviors in the nonsolvent water are observed universally for various hydrophobic organogels containing

omniphilic organic solvents that have a higher affinity to water than to the hydrophobic polymers. **The formation of a semipermeable skin layer due to rapid phase separation, and the asymmetric diffusion of water molecules into the gel driven by the high osmotic pressure of the organic solvent–water mixing, are found to be the reasons.** As a result, the hydrophobic hydrogels have a fruit-like structure, consisting of hydrophobic skin and water-trapped micropores, to display various unique properties, such as significantly enhanced strength, surface hydrophobicity, and antidrying, despite their extremely high water content. Furthermore, the hydrophobic hydrogels exhibit selective water absorption from concentrated saline solutions and rapid water release at a small pressure like squeezing juices from fruits. These novel functions of hydrophobic hydrogels will find promising applications, e.g., as **materials that can automatically take the fresh water from seawater.**

Comment: It is interesting to see that phenomenon that we think we understand can still surprise us. In this paper, the authors show that hydrophobic gels can still swell in water, with a proper balance of the interactions with the polymer chains and the initial organic solvent. They demonstrated this “abnormal swelling” with several polymers, in some selected solvent however. Still, if one day you see that your hydrophobic gel swells in water, do not be so surprised anymore!

Self-Deoxygenating Glassware

Nothling, M. D.; McKenzie, T. G.; Eastland, I. A.; Chien, H.-C.; Collins, J.; Meyer, A. S.; Qiao, G. G.* [Chem. Commun. 2019, 55, 8544–8547.](#)

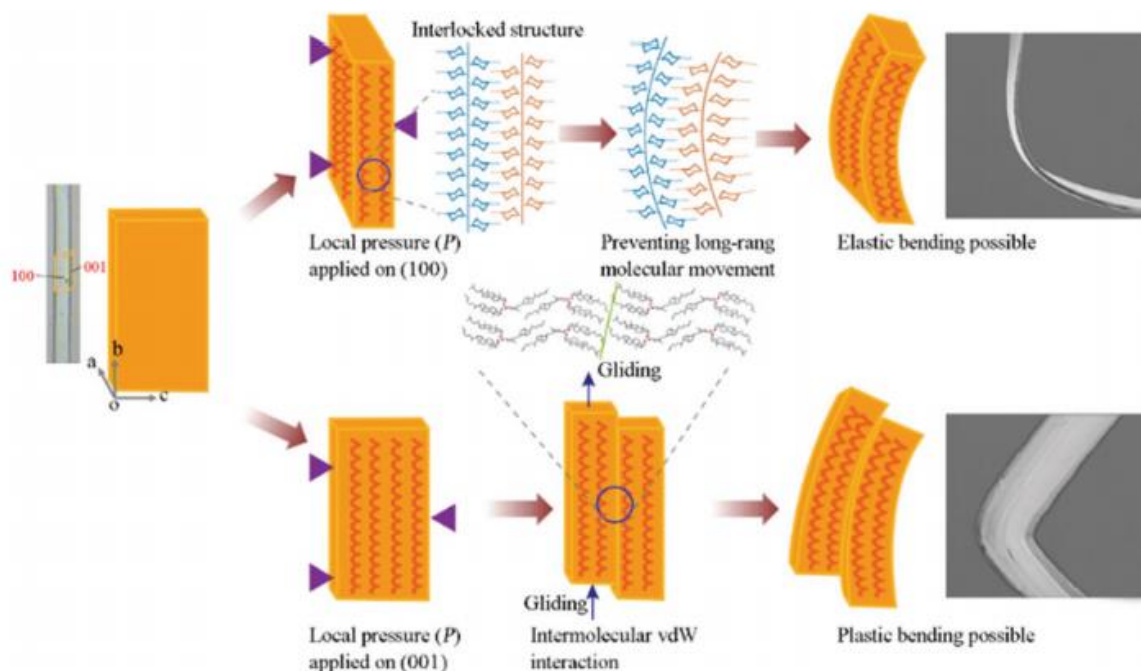


The removal of dissolved oxygen (O_2) from solution is a prerequisite for many reactions, frequently requiring specialized equipment/reagents or expertise. Herein, we introduce a range of **reusable, shelf-stable enzyme-functionalized glassware**, which biocatalytically removes O_2 from contained aqueous solutions. The effectiveness of the activated glassware is demonstrated by facilitating several O_2 -intolerant RAFT polymerizations.

Comment: Glucose oxidase (GOx) is already a widely used enzyme to remove oxygen in reaction mixtures sensitive to air. When it is free in solution, however, it is hard to recycle it, hence rising the price of the final product. The authors **covalently functionalized glassware with GOx** to limit this issue. This design seems efficient for a few cycles in aqueous solutions, which is still better than no functionalization at all. Unfortunately, they do not clearly prove it is ‘shelf-stable’, as stated in their abstract.

Anisotropic Elasticity and Plasticity of an Organic Crystal

Wang, J.-R.; Li, M.; Yu, Q.; Zhang, Z.; Zhu, B.; Qin, W.*; Mei, X.* [Chem. Commun. 2019, 55, 8532–8535.](#)

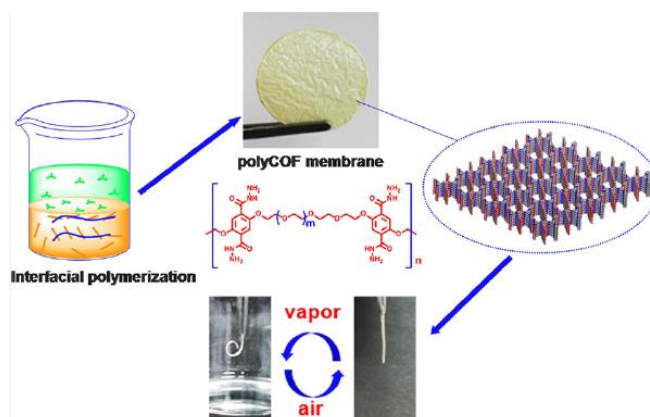


Organic crystals are generally considered to be brittle, inelastic materials, which pose challenges for application in flexible devices. Inspired by α helical proteins for their key structural role in flexible hair, here, we describe the construction of a **spring-like hydrogen bonded network** through the self-assembly of a-OH/e-OH cyclohexanol derivatives.

Comment: More and more articles are published about flexible organic crystals. Here, the authors describe a ‘bioinspired’ crystal that is prepared from cyclohexanol.

PolyCOFs: A New Class of Freestanding Responsive Covalent Organic Framework Membranes with High Mechanical Performance

Wang, Z.; Yu, Q.; Huang, Y.; An, D.; Zhao, Y.; Feng, Y.; Li, X.; Shi, X.; Liang, J.; Pan, F.; Cheng, P.; Chen, Y.; Ma, S.;* Zhang, Z.* [ACS Cent. Sci., DOI: 10.1021/acscentsci.9b00212](https://doi.org/10.1021/acscentsci.9b00212).



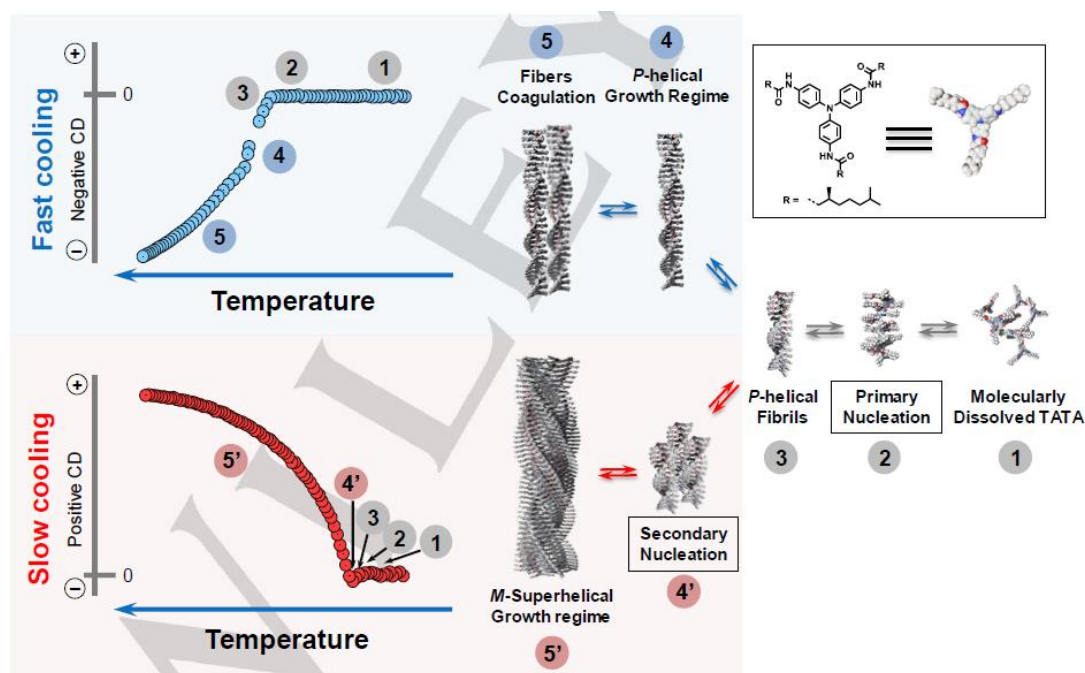
Traditional covalent organic frameworks (COFs) are prepared via polymerization based on small molecular monomers. However, the employment of polymers as building blocks to construct COFs has not been reported yet. Herein, we create a new concept of polymer covalent organic

frameworks (polyCOFs) formed by linear polymers as structural building blocks, which inherit the merits from both COFs and linear polymers. PolyCOFs represent a new category of porous COF materials that demonstrate good crystallinity and high stability. More importantly, benefiting from the flexibility and processability of a linear polymer, polyCOFs can spontaneously form defect-free, flexible, and freestanding membranes that exhibit excellent mechanical properties and undergo reversible mechanical transformation upon exposure to various organic vapors. For the first time, we demonstrated that polyCOF membranes can be used as artificial muscles to perform various complicated motions (e.g., lifting objects, doing “sit-ups”) triggered by vapors. This study bridges the gap between one-dimensional amorphous linear polymers and crystalline polymer frameworks and paves a new avenue to prepare stimuli-responsive actuators using porous COF materials.

Comment: A new strategy to construct COFs materials. By this method, they could get a stable film. Interestingly, this polyCOFs is solvent-vapor responsive and could be implemented as serious motion like muscles.

Temperature Control of Sequential Nucleation-Growth Mechanisms in Hierarchical Supramolecular Polymers

Osypenko, A.; Moulin, E.; Gavot, O.; Fuks, G.; Maaloum, M.; Koenis, M.; Buma, W. J.; Giuseppone, N.* *Chem. Eur. J.* DOI: [10.1002/chem.201902898](https://doi.org/10.1002/chem.201902898).

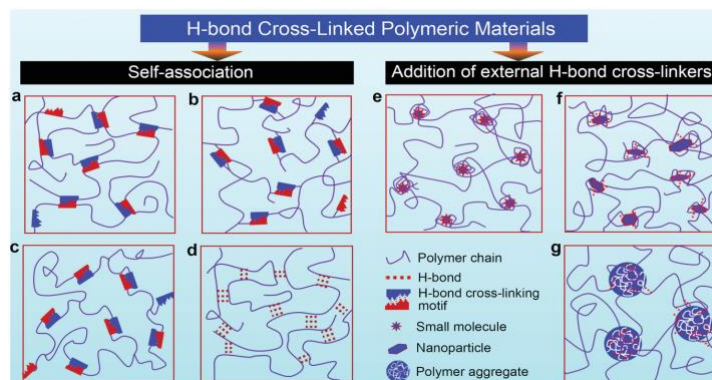


Upon cooling in various solvents, chiral triarylamine trisamide unimers produce organogels by stacking into helical supramolecular polymers which subsequently bundle into larger fibers. Interestingly, AFM imaging, circular dichroism, and vibrational circular dichroism of the chiral self-assemblies reveal that, while monocolumnar P-helical fibrils are formed upon fast cooling, bundled M-superhelical fibers are formed upon slow cooling. The mechanistic study of this structural bifurcation demonstrate the presence of a strong memory effect, reminiscent of a complex stepwise combination of primary and secondary nucleation-growth processes. These results highlight the instrumental role of pathway complexity to influence sequential self-assembly processes and to control supramolecular architectures of multiple hierarchical order.

Comment: Here is one from our group's work, I am interested in the secondary nucleation process at slow cooling rate.

High-Performance Polymeric Materials through Hydrogen-Bond Cross-Linking

Song, P.; Wang, H.* *Adv. Mater.* **2019**, *1901244*.

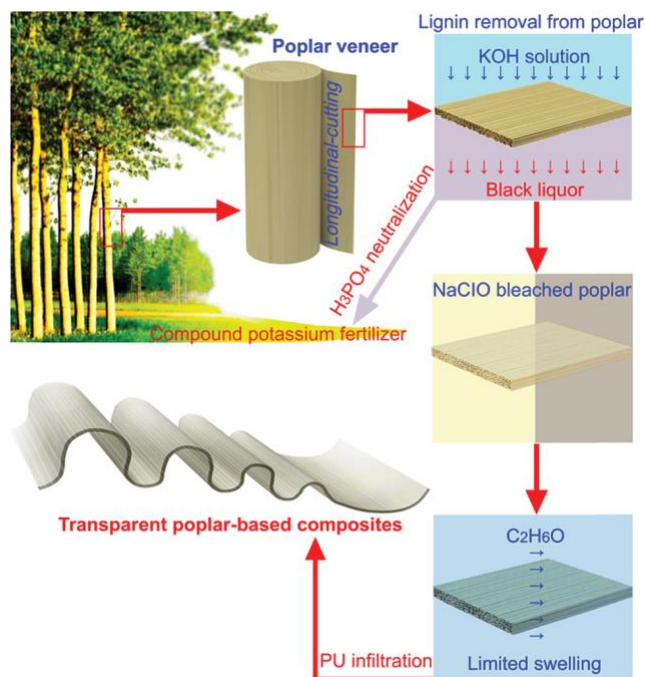


It has always been critical to develop high-performance polymeric materials with exceptional mechanical strength and toughness, thermal stability, and even healable properties for meeting performance requirements in industry. Conventional chemical cross-linking leads to enhanced mechanical strength and thermostability at the expense of extensibility due to mutually exclusive mechanisms. Such major challenges have recently been addressed by using noncovalent cross-linking of reversible multiple hydrogen-bonds (H-bonds) that widely exist in biological materials, such as silk and muscle. Recent decades have witnessed the development of many tailor-made high-performance H-bond cross-linked polymeric materials. Here, recent advances in H-bond cross-linking strategies are reviewed for creating high-performance polymeric materials. H-bond cross-linking of polymers can be realized via i) self-association of interchain multiple H-bonding interactions or specific H-bond cross-linking motifs, such as 2-ureido-4-pyrimidone units with self-complementary quadruple H-bonds and ii) addition of external cross-linkers, including small molecules, nanoparticles, and polymer aggregates. The resultant cross-linked polymers normally exhibit tunable high strength, large extensibility, improved thermostability, and healable capability. Such performance portfolios enable these advanced polymers to find many significant cutting-edge applications. Major challenges facing existing H-bond cross-linking strategies are discussed, and some promising approaches for designing H-bond cross-linked polymeric materials in the future are also proposed.

Comment: Here is a new progress report in relation with one of our group research topics. Conceptual design of hydrogen-bond cross-linked polymeric materials are discussed, and the authors focus on the UPy unit as a quadruple H-bonding motif.

Eco-friendly transparent poplar-based composites that are stable and flexible at high temperature

Zou, W.*; Sun, D.*; Wang, Z.; Li, R.; Yu, W.; and Zhang, P.* *RSC Adv.* **2019**, *9*, 21566

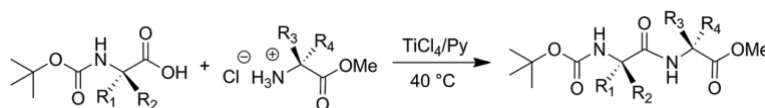


Farmed poplar could meet the human demand for transparent wood-based composites to replace glass, avoiding the consumption of natural forest resources. We removed the lignin of poplar using a potassium hydroxide (KOH) and deionized water solution, the waste black liquor could be converted into compound potassium fertilizer after being neutralized by phosphoric acid. Polyurethane (PU) was then added to the lignin-stripped poplar and hardened, the transparent poplar-based composite (TPC) has stable transparency at high temperatures, and flexibility – it elongates (about 15%) before breaking. These properties could provide more uses in hot environments requiring a flexible shape. The TPC PU provides transmittance of 85%, haze of 83%, and anisotropic light diffraction.

Comment: A rather simple proof of concept about eco-friendly material. I'm not convinced it will be a breakthrough in materials sciences as it is composed of almost 60% of non-recyclable non eco-friendly polyurethanes...

A titanium tetrachloride-based effective methodology for the synthesis of dipeptides

Comande, A.; Greco, M.; Belsito, E. L.; Liguori A.; and Leggio, A.* [RSC Adv. 2019, 9, 22137](#)



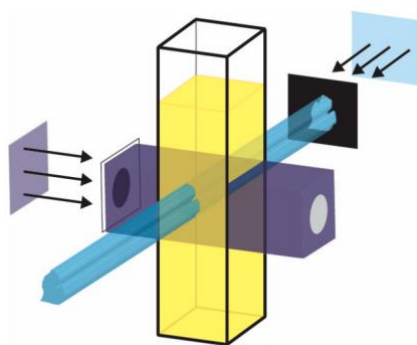
2-6

A series of dipeptide systems have been easily achieved through a TiCl_4 -assisted condensation reaction. The reaction of N-protected amino acids with amino acid methyl esters in pyridine and in the presence of TiCl_4 furnished the corresponding dipeptides with high yields and diastereoselectivity. The reaction was successfully applied to amino acids protected on the α -amino function with different protecting groups. The adopted experimental conditions allowed preserving both the protecting groups on the α -amino function and on the side chain functionalities. Furthermore, the preservation of the stereochemical integrity at the amino acid chiral centres has been verified.

Comment: A good way to efficiently synthesize dipeptides in the lab. One has to notice the maintenance of stereochemical integrity and the yield (>75%). My main concern is about the scalability to industrial process as mentioned in the introduction because the use of titanium salt and pyridine as solvent.

Volumetric Photopolymerization Confinement through Dual-Wavelength Photoinitiation and Photoinhibition

van der Laan, H. L.; Burns, M. A.; Scott, T. F.* [ACS Macro Lett. 2019, 8, 899–904.](#)

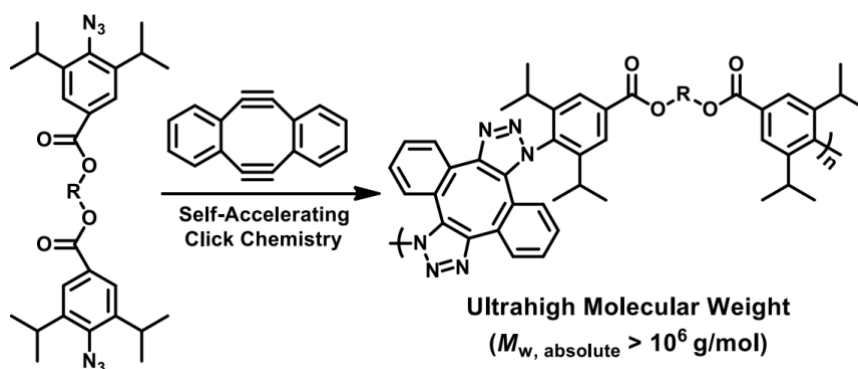


Conventional photolithographic rapid prototyping approaches typically achieve reaction confinement in depth through patterned irradiation of a photopolymerizable resin at a wavelength where the resin strongly absorbs, such that only a very thin layer of material is solidified. Consequently, three-dimensional objects are fabricated by progressive, two-dimensional addition of material, curtailing fabrication rates and necessitating the incorporation of support structures to ensure the integrity of overhanging features. Here, we **examine butyl nitrite as a UV-active photoinhibitor** of blue light-induced photopolymerizations and explore its utilization to confine in depth the region polymerized in a volume of resin. By employing two perpendicular irradiation patterns at blue and near-UV wavelengths to independently effect either polymerization initiation or inhibition, respectively, we enable **three-dimensional photopolymerization patterning in bulk resin**, thereby complementing emergent approaches to volumetric 3D printing.

Comment: If you are interested in 3D printing and the new trending methods (like the paper [Yali presented us](#) a few months ago), this paper describes a fast volumetric printing method where **the inhibitor is orthogonally activated with UV light**. In my opinion, this process limits the shapes that can be accessible but, on the other hand, it is way faster than the tomographic technique that Yali described.

Step-Growth Polymerization Method for Ultrahigh Molecular Weight Polymers

Zhang, L.; Ren, X.; Zhang, Y.; Zhang, K.* [ACS Macro Lett. 2019, 8, 948–954.](#)



The preparation of polymers with an ultrahigh molecular weight ($>10^6 \text{ g/mol}$; UHMW) is always a challenge for homogeneous step-growth polymerization. Herein, a unique homogeneous step-growth polymerization method was developed to prepare various UHMW polymers. In this approach, a **double-strain-promoted azide-alkyne click reaction (DSPAAC)** with a reactive intermediate was used as the polymerization reaction, and *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (DIBOD) and bis-azide compounds with 2,6-diisopropylphenyl azide terminals were used as the monomer pairs. The DSPAAC reaction, with a reactive intermediate, facilitated this polymerization method to efficiently prepare UHMW polymers under convenient, stoichiometrically imbalanced conditions using a slight excess of DIBOD to bis-azide monomer. In addition, the click nature of the DSPAAC reaction facilitated this polymerization method to synthesize UHMW polymers under ambient conditions, requiring no catalysts. The resultant UHMW polymers presented strong fluorescence peaking at 423 nm, good thermal property with the glass transition temperature up to 270 °C, and good mechanical property with Young's modulus above 1 GPa.

Comment: Using click chemistry to synthesize polymers by step-growth polymerization is not new. I have never seen, however, an example with a double-strained alkyne. It does not require any catalysts and, even better, it yields polymers with high molecular weights and good mechanical properties. Therefore, this strategy may become more common in the future.