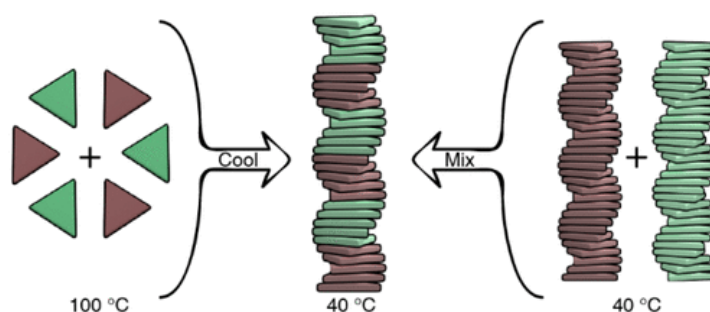


Supramolecular Block Copolymers under Thermodynamic Control

Adelizzi, B.; Aloï, A.; Markvoort, J. A.; Ten Eikelder, M. M. H.; Voets, K. I.; Palmans, R. A. A.; Meijer, E. W.* *J. Am. Chem. Soc.* **2018**, *ASAP*.

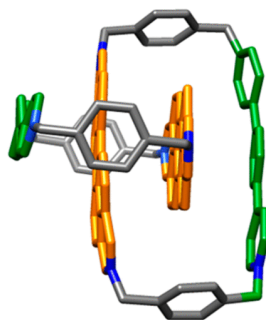


Supramolecular block copolymers are becoming attractive materials in nascent optoelectronic and catalytic technologies. However, their dynamic nature precludes the straightforward tuning and analysis of the polymer's structure. Here we report the elucidation on the microstructure of triarylamine triamide-based supramolecular block copolymers through a comprehensive battery of spectroscopic, theoretical, and super-resolution microscopic techniques. Via spectroscopic analysis we demonstrate that the direct mixing of preassembled homopolymers and the copolymerization induced by slow cooling of monomers lead to the formation of the same copolymer's architecture. The small but pronounced deviation of the experimental spectra from the linear combination of the homopolymers' spectra hints at the formation of block copolymers. A mass balance model is introduced to further unravel the microstructure of the copolymers formed, and it confirms that stable multiblock supramolecular copolymers can be accessed from different routes. The multiblock structure of the supramolecular copolymers originates from the fine balance between favorable hydrogen-bonding interactions and a small mismatch penalty between two different monomers. Finally, we visualized the formation of the supramolecular block copolymers by adapting a recently developed super-resolution microscopy technique, interface point accumulation for imaging in nanoscale topography (iPAINT), for visualizing the architectures formed in organic media. Combining multiple techniques was crucial to unveil the microstructure of these complex dynamic supramolecular systems.

Comment: I think that most of the working people on triarylamine projects should already have read this article but, in case, I put it in the literature of the week. This article investigates the thermodynamic equilibrium of a mixed self-assembled triarylamine structure. To manage that, they also used a technique that Andreas has already presented us during the group meeting: super-resolution spectroscopy. I wonder: if we succeed in controlling precisely the self-assembly and find a way to "freeze it", can we use the triarylamine polymer structure to codify information?

Towards a Charged Homo[2]catenane Employing Diazaperopyrenium Homophilic Recognition

Gong, X.; Zhou, J.; Hartlieb, J. K.; Miller, C.; Peng, L.; Farha, K. O.; Hupp, T. J.; Young, M. R.; Wasielewski, R. M.*; Stoddart, J. F.* *J. Am. Chem. Soc.* **2018**, *ASAP*

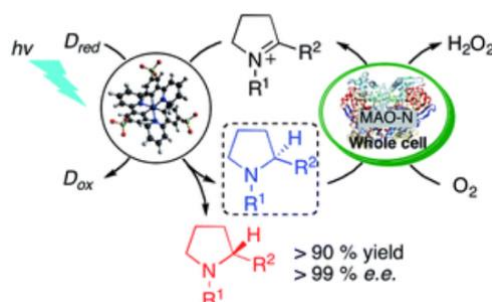


An octacationic diazaperopyrenium (DAPP^{2+})-based homo[2]catenane (**DAPPHC** $^{8+}$), wherein no fewer than eight positive charges are associated within a mechanically interlocked molecule, has been produced in 30% yield under ambient conditions as a result of favorable homophilic interactions, reflecting a delicate balance between strong π - π interactions and the destabilizing penalty arising from Coulombic repulsions between DAPP^{2+} units. This **DAPPHC** $^{8+}$ catenane is composed of two identical mechanically interlocked tetracationic cyclophanes, namely DAPPBox^{4+} , each of which contains one DAPP^{2+} unit and one extended viologen (ExBIPY^{2+}) unit, linked together by two *p*-xylylene bridges. The solid-state structure of the homo[2]catenane demonstrates how homophilic interactions play an important role in the formation of **DAPPHC** $^{8+}$, in which the mean ring planes of the two DAPPBox^{4+} cyclophanes are oriented at about 60° with respect to each other, with a centroid-to-centroid separation of 3.7 Å between the mean planes of the outer ExBIPY^{2+} and inner DAPP^{2+} units, and 3.6 Å between the mean planes of the two inner DAPP^{2+} units. We show that irradiation of the **DAPPHC** $^{8+}$ catenane at 330 nm in acetonitrile solution results in simultaneous energy and electron transfer. The latter occurs from the inner DAPP^{2+} dimer to the outer ExBIPY^{2+} unit, leading to the generation of a temporary charge-separated state within a rigid and robust homo[2]catenane. Compared to DAPPBox^{4+} , both forward- and back-electron transfer in **DAPPHC** $^{8+}$ occur with faster rates, owing to the closer proximity between the electron donor and acceptor in the homo[2]catenane than in the separated cyclophane.

Comment: Interesting paper on the synthesis of catenanes. Their synthetic strategy is surprising because they used two DAPP^{2+} units working as driving force to form a charge-dense catenane, in fact the strong π - π interactions help to balance the energy arising from Coulombic repulsions. Their multi-charge interconnected structure could be interesting in the future to construct a more complex architecture with high charge densities.

Enantioselective Synthesis of Amines by Combining Photoredox and Enzymatic Catalysis in a Cyclic Reaction Network

Guo, X.; Okamoto, Y.; Schreier, M. R.; Ward, T. R.*; Wenger, O. S.* [Chem. Sci. 2018, Advance Article](#).

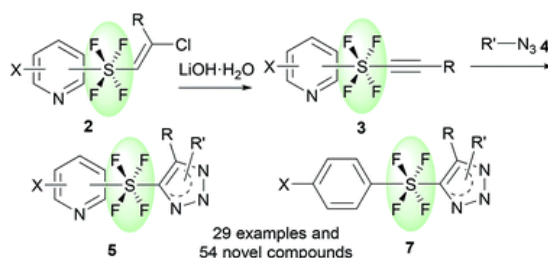


Visible light-driven reduction of imines to enantioenriched amines in aqueous solution is demonstrated for the first time. **Excitation** of a new water-soluble variant of the widely used **[Ir(ppy)₃]** (ppy = 2-phenylpyridine) photosensitizer in the presence of a cyclic imine affords a highly reactive α -amino alkyl radical that is intercepted by hydrogen atom transfer (HAT) from ascorbate or thiol donors to afford the corresponding amine. The enzyme **monoamine oxidase** (MAO-N-9) **selectively catalyzes the oxidation of one of the enantiomers to the corresponding imine**. Upon **combining the photoredox and biocatalytic processes** under continuous photo-irradiation, enantioenriched amines are obtained in excellent yields. To the best of our knowledge, this is the first demonstration of a concurrent photoredox- and enzymatic catalysis leading to a light-driven asymmetric synthesis of amines.

Comment: As it is accurately said in the conclusion, this article is a “proof-of-concept”, meaning that for the first time this approach has been described and is working. Unfortunately, it is still limited to a small number of imines because of the nature of the enzyme (MAO-N). Moreover, a lot of potential problems remain present if one would like to expand the library of molecules to reduce by using this methodology. Indeed, there is often a mutual inhibition between the photosensitizer and the enzyme, hence it is necessary to compartmentalise these systems (in this paper, the authors used a cell but it required the presence of water as a solvent). Nevertheless, I think it could be interesting to keep an eye on the progress in this promising field.

An Eccentric Rod-like Linear Connection of Two Heterocycles: Synthesis of Pyridine *trans*-Tetrafluoro- λ^6 -Sulfanyl Triazoles

Das, P.; Niina, K.; Hiromura, T.; Tokunaga, E.; Saito, N.; Shibata, N.* [Chem. Sci. 2018, Advance Article](#).

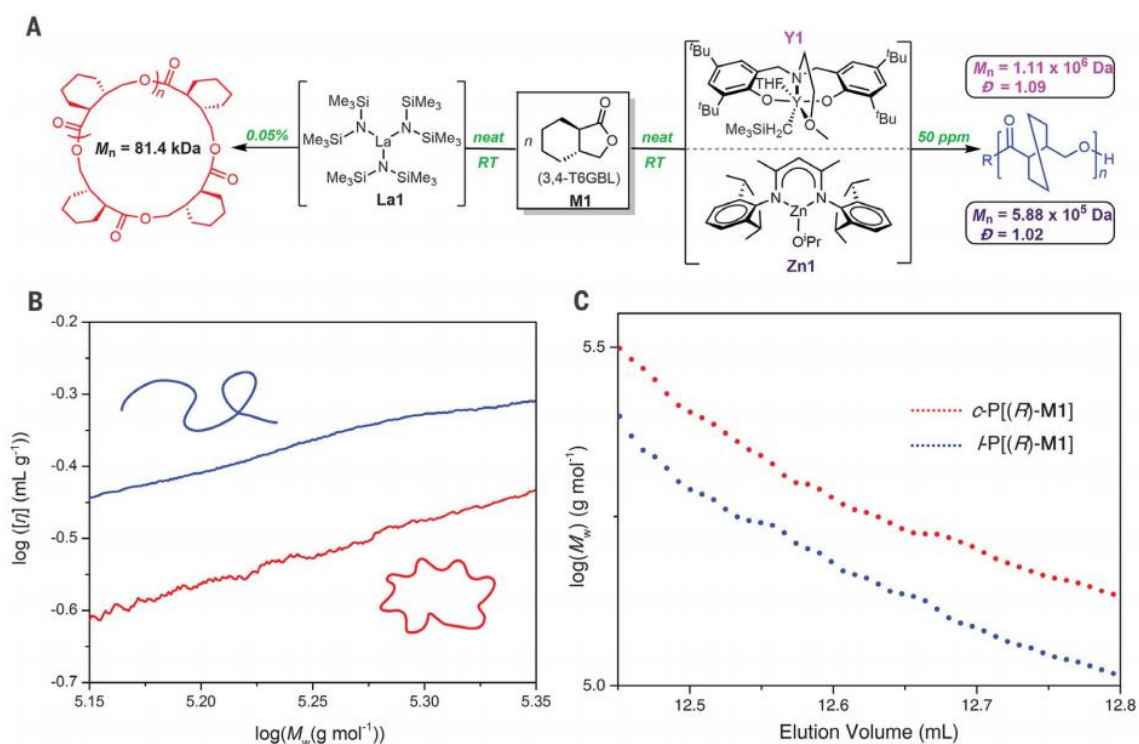


The *trans*-tetrafluoro- λ^6 -sulfane (**SF₄**) group has been utilized as a unique **three-dimensional building block** for the **linear connection of two independent N-heterocycles, pyridines and triazoles**. The linearly connected heterocyclic compounds were synthesized by thermal Huisgen 1,3-dipolar cycloaddition between previously unknown pyridine SF₄-alkynes and readily available azides, providing a series of rod-like SF₄-connected N-heterocycles in good to excellent yields. X-ray crystallographic analysis of the target products revealed the *trans*-geometry of the SF₄ group, which linearly connects two independent N-heterocycles. This research will open the field of chemistry of SF₄-connected heterocyclic compounds.

Comment: I think that this abstract is an excellent summary of the potential of the SF₄ group. In the future, it may be useful to keep this building block in mind if you are interested in the elaboration of complex architectures. However, its synthesis requires specific equipment, particularly during the chloro-fluorination step.

A Synthetic Polymer System with Repeatable Chemical Recyclability

Zhu, J.-B.; Watson, E. M.; Tang, J.; Chen E. Y.-X. [*Science*, 2018, 360, 398–403.](#)

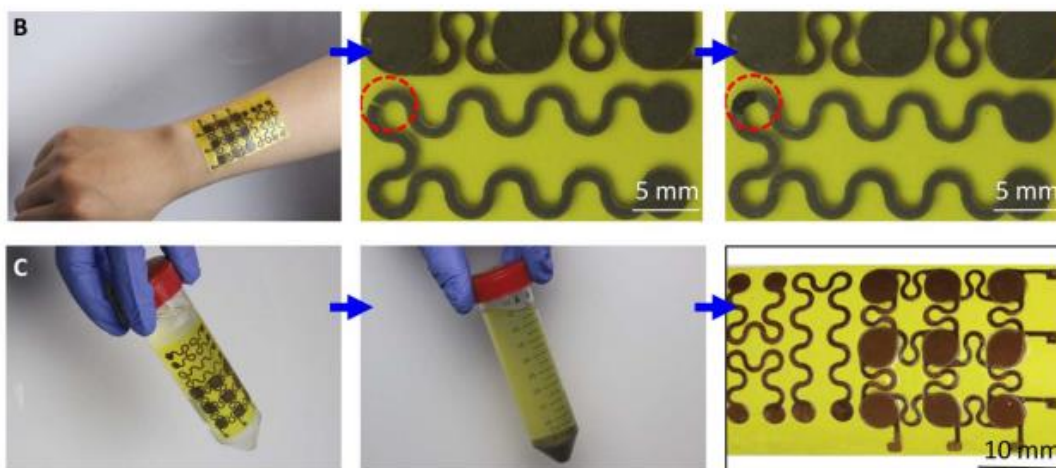


The development of chemically recyclable polymers offers a solution to the end-of-use issue of polymeric materials and provides a closed-loop approach toward a **circular materials economy**. However, polymers that can be easily and selectively depolymerized back to monomers typically require low-temperature polymerization methods and also lack physical properties and mechanical strengths required for practical uses. We introduce a polymer system based on **γ -butyrolactone (GBL)** with a trans-ring fusion at the α and β positions. Such trans-ring fusion renders the commonly considered as nonpolymerizable GBL ring readily polymerizable at room temperature under solvent-free conditions to yield a high-molecular weight polymer. The polymer has enhanced thermostability and can be repeatedly and quantitatively recycled back to its monomer by thermolysis or chemolysis. Mixing of the two enantiomers of the polymer generates a **highly crystalline supramolecular stereocomplex**.

Comment: The authors declare quantitative reversibility of GBL-based plastics at industrially appropriate conditions (120 °C, ZnCl_2). Taking into account the relatively low producing price proposed, the approach looks particularly promising. However, a less expensive catalyst would be required.

Rehealable, Fully Recyclable, and Malleable Electronic Skin Enabled by Dynamic Covalent Thermoset Nanocomposite

Zou, Z.; Zhu, C.; Li, Y.; Lei, X.; Zhang, W; Xiao, J. [*Sci. Adv.* 2018, 4, eaaq0508.](#)

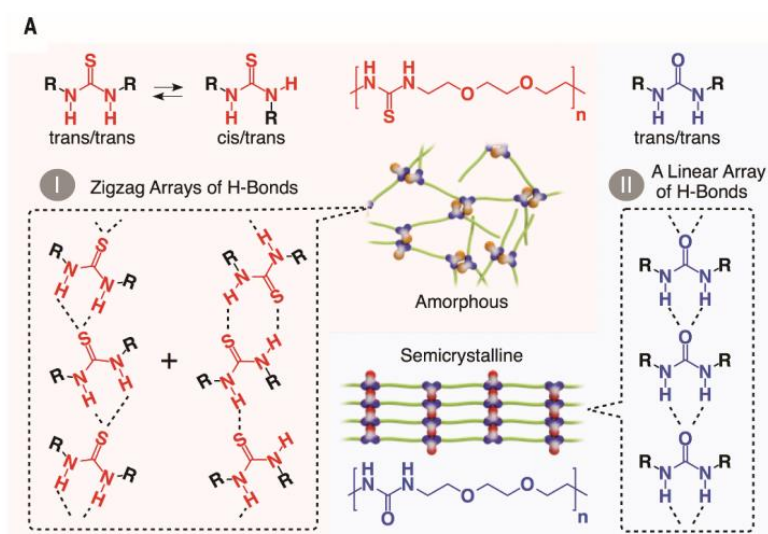


Electronic skin (e-skin) mimicking functionalities and mechanical properties of natural skin can find broad applications. **We report the first dynamic covalent thermoset-based e-skin**, which is connected through robust covalent bonds, rendering the resulting devices good chemical and thermal stability at service condition. By doping the dynamic covalent thermoset with conductive silver nanoparticles, we demonstrate a robust yet rehealable, fully recyclable, and malleable e-skin. **Tactile, temperature, flow, and humidity sensing capabilities** are realized. The e-skin can be rehealed when it is damaged and can be fully recycled at room temperature, which has rarely, if at all, been demonstrated for e-skin. After rehealing or recycling, the e-skin regains mechanical and electrical properties comparable to the original e-skin. In addition, malleability enables the e-skin to permanently conform to complex, curved surfaces without introducing excessive interfacial stresses. These properties of the e-skin yield an economical and eco-friendly technology that can find broad applications in robotics, prosthetics, health care, and human-computer interface.

Comment: Fully recyclable e-skin with 3 types of the sensors. I appreciated the relatively simple chemistry of the elastomers.

Mechanically Robust, Readily Repairable Polymers via Tailored Noncovalent Cross-linking

Yanagisawa, Y.; Nan, Y.; Okuro, K.; Aida, T. [Science 2018, 359, 72-76.](#)

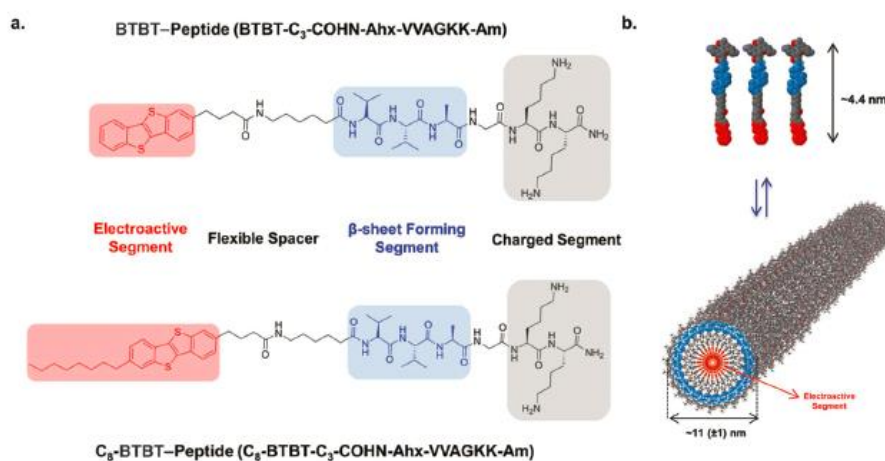


Expanding the range of healable materials is an important challenge for sustainable societies. Noncrystalline, **high-molecular-weight polymers** generally form mechanically robust materials, which, however, are **difficult to repair** once they are fractured. This is because their polymer chains are heavily entangled and diffuse too sluggishly to unite fractured surfaces within reasonable time scales. Here we report that **low-molecular-weight polymers, when cross-linked by dense hydrogen bonds, yield mechanically robust yet readily repairable materials**, despite their extremely slow diffusion dynamics. A key was to use thiourea, which anomalously forms a **zigzag hydrogen-bonded array** that does not induce unfavorable crystallization. Another key was to incorporate a structural element for activating the exchange of hydrogen-bonded pairs, which enables the fractured portions to rejoin readily upon compression.

Comment: The most inventive setup to quantify a self-healing process I have ever seen.

The Design and Fabrication of Supramolecular Semiconductor Nanowires Formed by Benzothienobenzothiophene (BTBT)-Conjugated Peptides

Khalily, M. A.; Usta, H.*; Ozdemir, M.; Bakan, G.; Dikecoglu, F. B.; Edwards-Gayle, C.; Hutchinson, J. A.; Hamley, I. W.; Dana, A.; Guler, M. O.* [Nanoscale 2018, Advance Article](#)

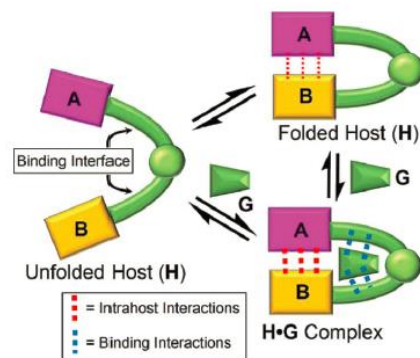


π -Conjugated small molecules based on a [1]benzothieno[3,2-*b*]benzothiophene (BTBT) unit are of great research interest in the development of solution-processable semiconducting materials owing to their excellent charge-transport characteristics. However, the BTBT π -core has yet to be demonstrated in the form of electro-active one-dimensional (1D) nanowires that are self-assembled in aqueous media for potential use in bioelectronics and tissue engineering. Here we report the design, synthesis, and self-assembly of benzothienobenzothiophene (BTBT)-peptide conjugates, the BTBT-peptide (BTBT-C₃-COHN-Ahx-VVAGKK-Am) and the C₈-BTBT-peptide (C₈-BTBT-C₃-COHN-Ahx-VVAGKK-Am), as β -sheet forming amphiphilic molecules, which self-assemble into highly uniform nanofibers in water with diameters of 11-13(\pm 1) nm and micron-size lengths. Spectroscopic characterization studies demonstrate the J-type π - π interactions among the BTBT molecules within the hydrophobic core of the self-assembled nanofibers yielding an electrical conductivity as high as $6.0 \times 10^{-6} \text{ S cm}^{-1}$. The BTBT π -core is demonstrated, for the first time, in the formation of self-assembled peptide 1D nanostructures in aqueous media for potential use in tissue engineering, bioelectronics and (opto)electronics. The conductivity achieved here is one of the highest reported to date in a non-doped state.

Comment: It's a nice work. The electrical conductivity of the two nanofiber films were well investigated.

Intramolecularly Enhanced Molecular Tweezers with Unusually Strong Binding for Aromatic Guests in Unfavorable Solvents

Xing, X.; Zhao, Y.* [*Org. Biomol. Chem.* **2018**, Advance Article.](#)

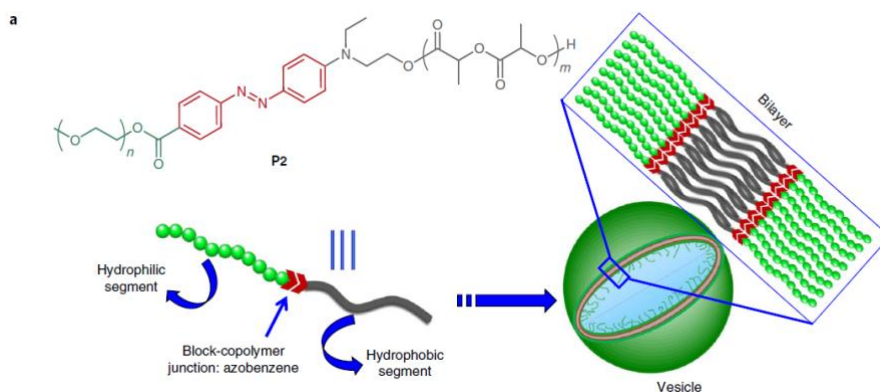


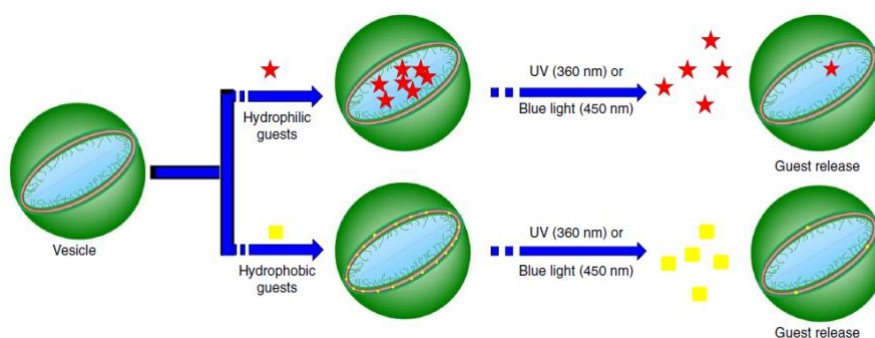
Molecular tweezers using aromatic interactions for binding normally work best in polar instead of nonpolar solvents due to the strong solvophobic effect in the binding. Inspired by biological receptors that utilize "delocalized binding interactions" remote from the binding interface to strengthen guest-binding, we constructed molecular tweezers that have a reversed solvent effect. As the direct aromatic binding interactions were weakened by nonpolar solvent, guest-triggered intrahost interactions between two strategically placed carboxylic acids became stronger and contributed to the binding.

Comment: The intrahost interaction between guest and host leads to a reversed solvent effect. It would be more interesting if the molecular tweezers were functionalized with light-responsive groups and could release the guest.

Dynamic Actuation of Glassy Polymersomes through Isomerization of a Single Azobenzene Unit at the Block Copolymer Interface

Molla, M.; Rangadurai, P.; Antony, L.; Swaminathan, S.; Pablo, J.; Thayumanavan, S.* [*Nat. Chem.* **2018**, *10*, 659-666.](#)



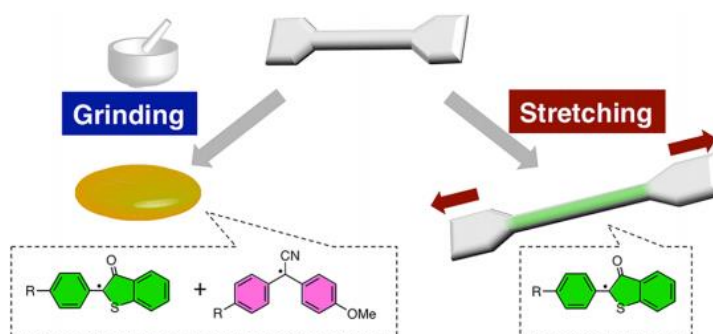


Nature has engineered exquisitely responsive systems where molecular-scale information is transferred across an interface and propagated over long length scales. Such systems rely on multiple interacting, signalling and adaptable molecular and supramolecular networks that are built on dynamic, non-equilibrium structures. Comparable synthetic systems are still in their infancy. Here, we demonstrate that the light-induced actuation of a molecularly thin interfacial layer, assembled from a hydrophilic- azobenzene -hydrophobic diblock copolymer, can result in a reversible, long-lived perturbation of a robust glassy membrane across a range of over 500 chemical bonds. We show that the out-of-equilibrium actuation is caused by the photochemical *trans*–*cis* isomerization of the azo group, a single chemical functionality, in the middle of the interfacial layer. The principles proposed here are implemented in water-dispersed nanocapsules, and have implications for on-demand release of embedded cargo molecules.

Comment: A very interesting study showing how the continuous *cis-trans* isomerization of azobenzene causes the perturbation of a robust glassy membrane, which results in an increasing penetration of capsule molecules through the membrane. The computer-assisted molecular modelling of the non-equilibrium system is worth a detailed look because not many studies in this field are accompanied with such a detailed simulations nor contain information about how to find appropriate parameters for the simulated structures. Of course, Prof. Thayumanavan's group has been combining his work with simulations for quite a while and has good experience with it.

Multicolor Mechanochromic Polymer Blends that Can Discriminate between Stretching and Grinding

Ishizuki, K.; Aoki, D.; Goseki, R.; Otsuka, H.* [ACS Macro Lett. 2018, 7, 556–560.](#)



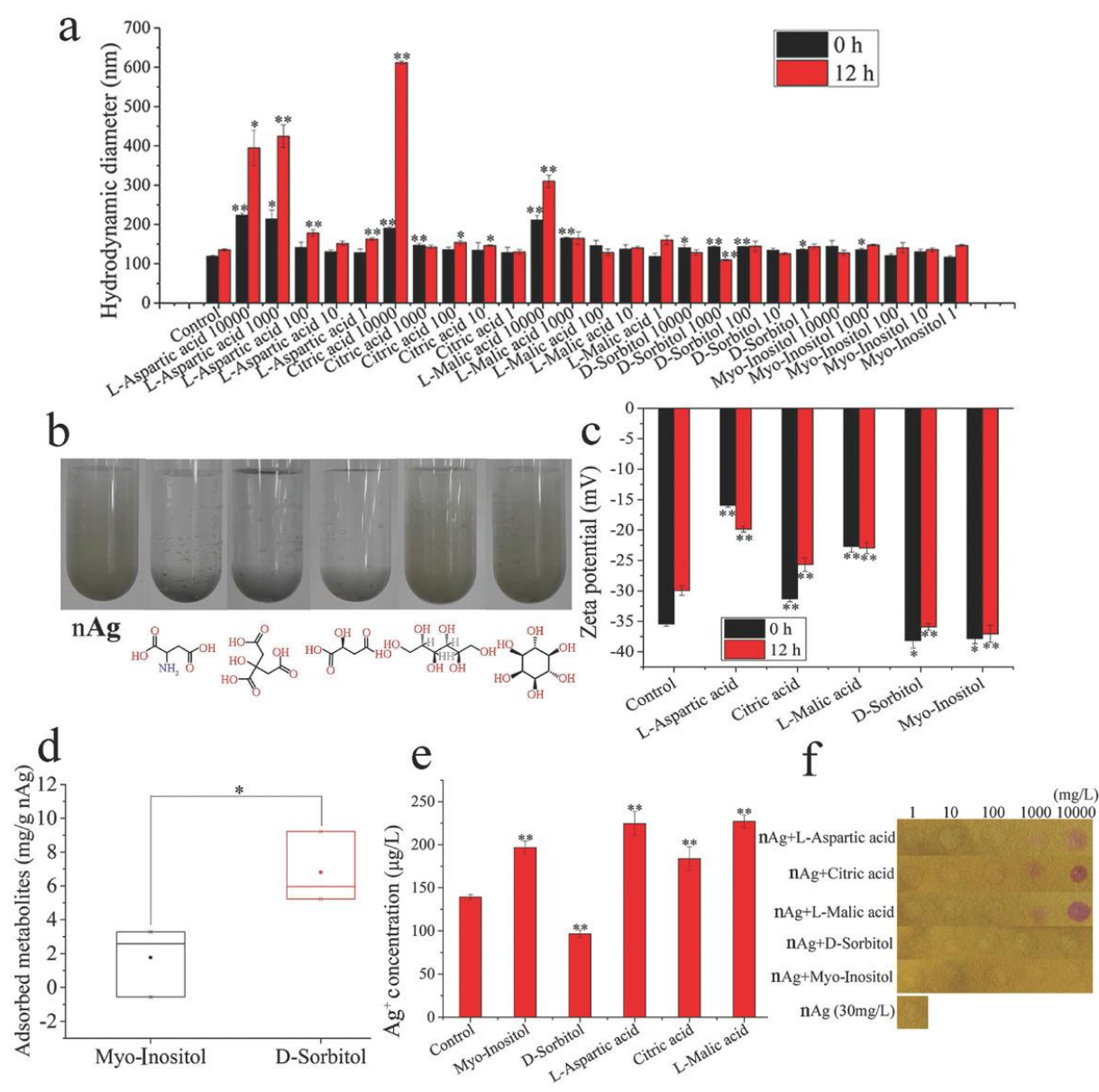
Mechanochromic polymers, which react to mechanical force by changing color, are expected to find applications in smart materials such as damage sensors. Although numerous types of mechanochromic polymers have been reported so far, developing mechanochromic polymers that can recognize different mechanical stimuli remains a formidable challenge. Materials that not only change their color in response to a mechanical stimulus but also detect its nature should be of great importance for practical applications. In this paper, we report our preliminary findings on

multicolor mechanochromic polymer blends that **can discriminate between two different mechanical stimuli, i.e., stretching and grinding**, by simply blending two mechanochromic polymers with different architectures. The rational design and blending of two mechanochromic polymers with radical-type mechanochromophores embedded separately in positions adjacent to soft or hard domains made it possible to achieve multicolor mechanochromism in response to different stimuli. Electron paramagnetic resonance and solid-state UV–vis measurements supported the mechanism proposed for this discrimination.

Comment: The discrimination between the two types of mechanical force applied to the material is achieved only by the design of the structure. A green mechanochromic molecule is embedded in the soft domains, whereas a pink mechanochromic molecule is embedded in the hard domains. The latter are only sensitive to the shearing stress applied when grinding, whereas the soft domains are sensitive to both grinding and tensile stress.

Screening Small Metabolites from Cells as Multifunctional Coatings Simultaneously Improves Nanomaterial Biocompatibility and Functionality

Sun A. Q.; Ban Z.; Mu L.; Hu X. Q.* [Science Advances 2018, 1800341](#)

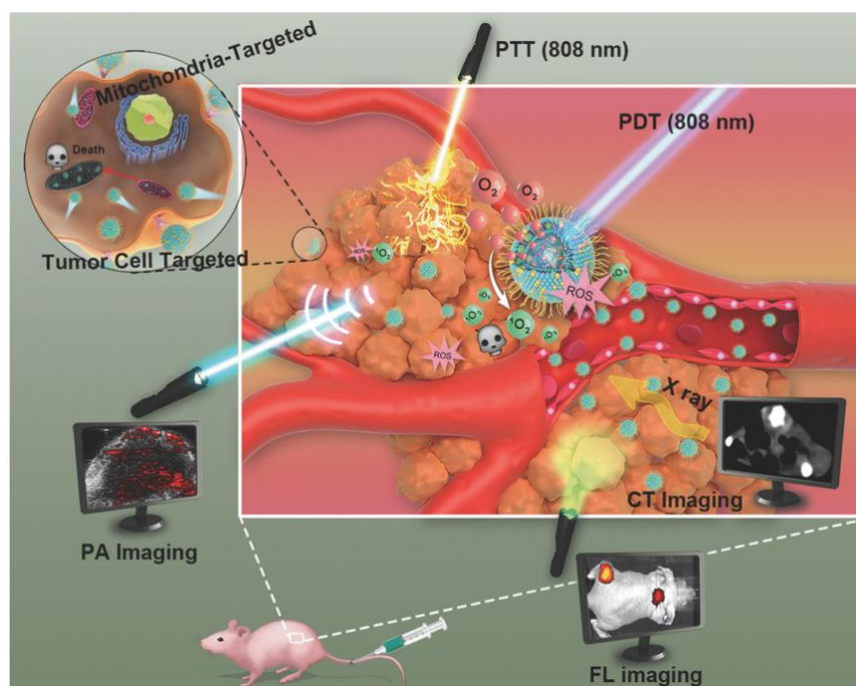


Currently, nanomaterials face a dilemma due to their advantageous properties and potential risks to human health. Here, a strategy to improve both nanomaterial biocompatibility and functionality is established by screening small metabolites from cells as nanomaterial coatings. A metabolomics analysis of cells exposed to nanosilver (nAg) integrates volcano plots (t-tests and fold change analysis), partial least squares-discriminant analysis (PLS-DA), and significance analysis of microarrays (SAM) and identifies six metabolites (l-aspartic acid, l-malic acid, myoinositol, d-sorbitol, citric acid, and l-cysteine). The further analysis of cell viability, oxidative stress, and cell apoptosis reveals that d-sorbitol markedly reduces nAg cytotoxicity. Subsequently, small molecule loading, surface oxidation, and ionic release experiments support d-sorbitol as the optimal coating for nAg. Importantly, d-sorbitol loading improves the duration of the antibacterial activity of nAg against *Escherichia coli* and *Staphylococcus aureus*. The biocidal persistence of nAg-sorbitol is extended beyond 9 h, and the biocidal effects at 12 h are significantly higher than those of naked nAg. This work proposes a new strategy to improve the biocompatibility and functionality of nAg simultaneously by screening small metabolites from cells as nanomaterial functional coatings, a method that can be applied to mitigate the side effects of other nanomaterials.

Comment: Many methods have been explored to reduce the nanotoxicity. Unfortunately, the biocompatibility of nanomaterials were in most cases accompanied by reduced functionality. For instance, chemical modifications would reduce photocatalytic activity. Therefore, a universal strategy to improve nanomaterial biocompatibility and functionality simultaneously is urgently needed, as both properties determine the ability to commercialize nanomaterials.

Mitochondria-Targeted Artificial “Nano-RBCs” for Amplified Synergistic Cancer Phototherapy by a Single NIR Irradiation

Zhang, L.; Wang, D.*; Yang, K.; Sheng, D.; Tan, B.; Wang, Z.; Chen, Y.* [*Science Advances*. 2018, 1800049.](#)

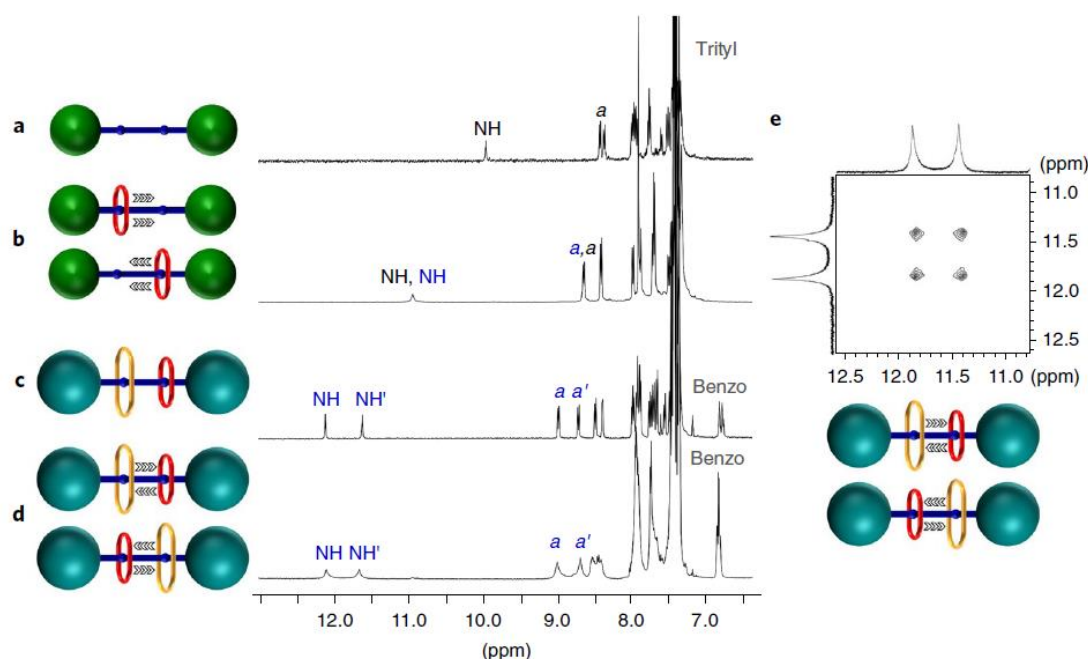


Phototherapy has emerged as a novel therapeutic modality for cancer treatment, but its low therapeutic efficacy severely hinders further extensive clinical translation and application. This study reports amplifying the phototherapeutic efficacy by constructing a near-infrared (NIR)-responsive multifunctional nanoplatform for synergistic cancer phototherapy by a single NIR irradiation, which can concurrently achieve mitochondria-targeting phototherapy, synergistic photothermal therapy (PTT)/photodynamic therapy (PDT), self-sufficient oxygen-augmented PDT, and multiple-imaging guidance/monitoring. Perfluorooctyl bromide based nanoliposomes are constructed for oxygen delivery into tumors, performing the functions of red blood cells (RBCs) for oxygen delivery ("Nano-RBC" nanosystem), which can alleviate the tumor hypoxia and enhance the PDT efficacy. The mitochondria-targeting performance for enhanced and synergistic PDT/PTT is demonstrated as assisted by nanoliposomes. In particular, these "Nano-RBCs" can also act as the contrast agents for concurrent computed tomography, photoacoustic, and fluorescence multiple imaging, providing the potential imaging capability for phototherapeutic guidance and monitoring. This provides a novel strategy to achieve high therapeutic efficacy of phototherapy by the rational design of multifunctional nanoplatforms with the unique performances of mitochondria targeting, synergistic PDT/PTT by a single NIR irradiation (808 nm), self-sufficient oxygen-augmented PDT, and multiple-imaging guidance/monitoring.

Comment: In this work, for the first time, the rational design and construction of a multifunctional nanoplatform for amplified phototherapy has been developed. The system achieves mitochondria-targeting phototherapy, synergistic PTT/PDT by a single NIR irradiation (808 nm), self-sufficient oxygen-augmented PDT, and multiple-imaging guidance/monitoring.

Ring-through-ring Molecular Shuttling in a Saturated [3]rotaxane

Zhu, K.;* Baggi, G.; Loeb, S.* [Nat.Chem. 2018, 10, 625-630.](#)



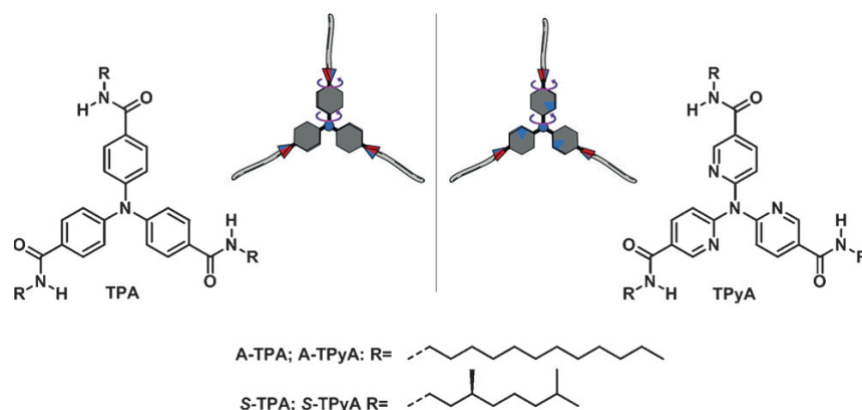
Mechanically interlocked molecules such as rotaxanes and catenanes comprise two or more components whose motion relative to each other can be controlled. A [2]rotaxane molecular shuttle, for example, consists of an axle bearing two recognition sites and a single macrocyclic

wheel that can undergo a to-and-fro motion along the axle-shuttling between the recognition sites. The ability of mechanically interlocked molecules to undergo this type of large-amplitude change is the core mechanism behind almost every interlocked molecular switch or machine, including sophisticated mechanical systems such as a molecular elevator and a peptide synthesizer. Here, as a way to expand the scope of dynamics possible at the molecular level, we have developed a molecular shuttling mechanism involving the exchange of rings between two recognition sites in a saturated [3]rotaxane (one with no empty recognition sites). This was accomplished by passing a smaller ring through a larger one, thus achieving ring-through-ring molecular shuttling.

Comment: Although it seems that this discovery is a quite simple work and not that significant, it might really bring some intriguing aspects to the design of new topologies in MIM. For example, is it possible to use this shuttling system towards nano-weaving if some kind of polymers with the ability to form knots are attached to the two rings?

Unravelling the Pathway Complexity in Conformationally Flexible N-Centered Triarylamine Trisamides

Adelizzi, B.; Filot, I. A. W.; Palmans, A. R. A.*; Meijer, E. W.* [Chem. Eur. J. 2017, 23, 6103.](#)

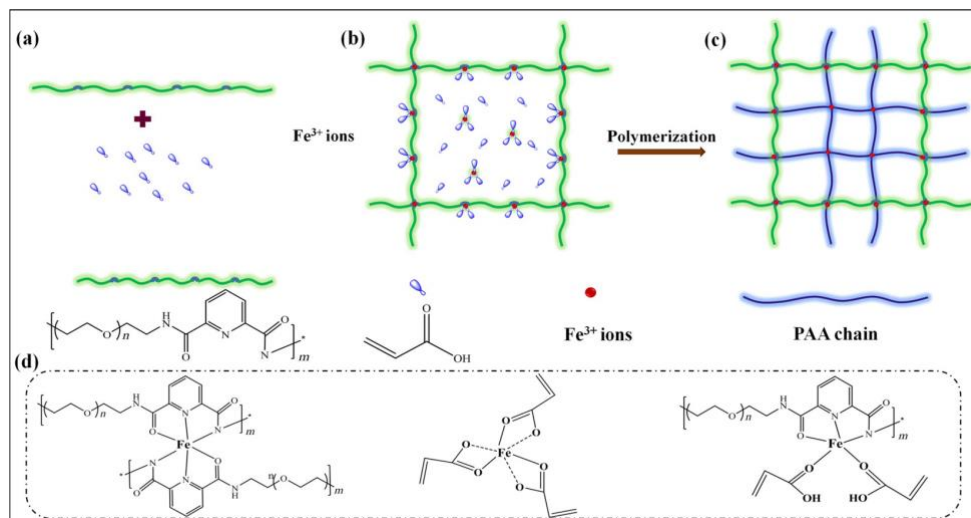


Two families of C₃-symmetrical triarylamine-trisamides comprising a triphenylamine- or a tri(pyrid-2-yl)amine core are presented. Both families self-assemble in apolar solvents via cooperative hydrogen-bonding interactions into helical supramolecular polymers as evidenced by a combination of spectroscopic measurements, and corroborated by DFT calculations. The introduction of a stereocenter in the side chains biases the helical sense of the supramolecular polymers formed. Compared to other C₃-symmetrical compounds, a much richer self-assembly landscape is observed. Temperature-dependent spectroscopy measurements highlight the presence of two self-assembled states of opposite handedness. One state is formed at high temperature from a molecularly dissolved solution via a nucleation–elongation mechanism. The second state is formed below room temperature through a sharp transition from the first assembled state. The change in helicity is proposed to be related to a conformational switch of the triarylamine core due to an equilibrium between a 3:0 and a 2:1 conformation. Thus, within a limited temperature window, a small conformational twist results in an assembled state of opposite helicity.

Comment: They describe an interesting change in the helicity of a triarylamine based supramolecular system. The switch is achieved just by a change in the temperature. But these results should also be interpreted with regards of a recent paper in [Nature](#) of the same group in which a partial different explanation and description of this phenomena is given.

A Conductive Self-Healing Double Network Hydrogel with Toughness and Force Sensitivity

Liu, S; Li, K; Hussain, I; Oderinde, O; Yao, F; Zhang, J; Fu, G,* *Chem. Eur. J.* **2018**, *24*, 6632.

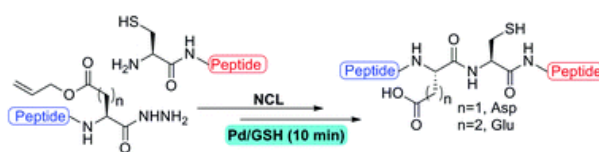


Mechanically tough and electrically conductive self-healing hydrogels may have broad applications in wearable electronics, health-monitoring systems, and smart robotics in the following years. Herein, a new design strategy is proposed to synthesize a dual physical cross-linked polyethylene glycol/poly(acrylic acid) (PEG/PAA) double network hydrogel, consisting of ferric ion cross-linked linear chain extensions of PEG (2,6-pyridinedicarbonyl moieties incorporated into the PEG backbone, PEG- H_2pdca) as the first physical network and a PAA- Fe^{3+} gel as the second physical network. Metal-ion coordination and the double network structure enable the double network hydrogel to withstand up to 0.4 MPa tensile stress and 1560% elongation at breakage; the healing efficiency reaches 96.8% in 12 h. In addition, due to dynamic ion transfer in the network, the resulting hydrogels exhibit controllable conductivity ($0.0026\text{--}0.0061\text{ S cm}^{-1}$) and stretching sensitivity. These functional self-healing hydrogels have potential applications in electronic skin. It is envisioned that this strategy can also be employed to prepare other high-performance, multifunctional polymers.

Comment: An interesting supramolecular material with good self-healing properties and controllable conductivity.

Palladium Mediated Deallylation in Fully Aqueous Conditions for Native Chemical Ligation at Aspartic and Glutamic Acid Sites

Jbara, M.; Eid, E.; Brik, A.* *Org. Biomol. Chem.*, **2018**, Advance Article

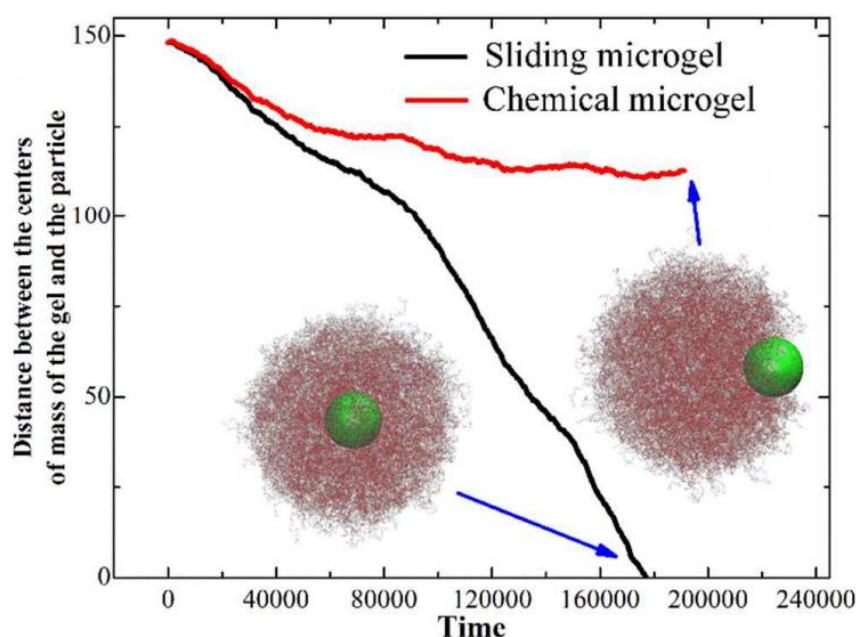


An efficient native chemical ligation approach at Asp and Glu sites is reported applying a hydrazide precursor, as a peptide thioester, and allyl protection at the side chain of Asp and Glu. The allyl protection was efficiently removed, after the ligation step, using the water-soluble palladium complex $[\text{Pd}(\text{allyl})\text{Cl}]_2$ and glutathione within a few minutes under fully aqueous conditions.

Comment: I'm not very familiar with NCL experimentation, so I'll ask our specialists: what would you think about their method guys, is this really as relevant as they present it?

Adaptive Structure of Gels and Microgels with Sliding Cross-Links: Enhanced Softness, Stretchability and Permeability

Gavrilov, A. A.; Potemkin, I.* [Soft Matter 2018, ASAP.](#)



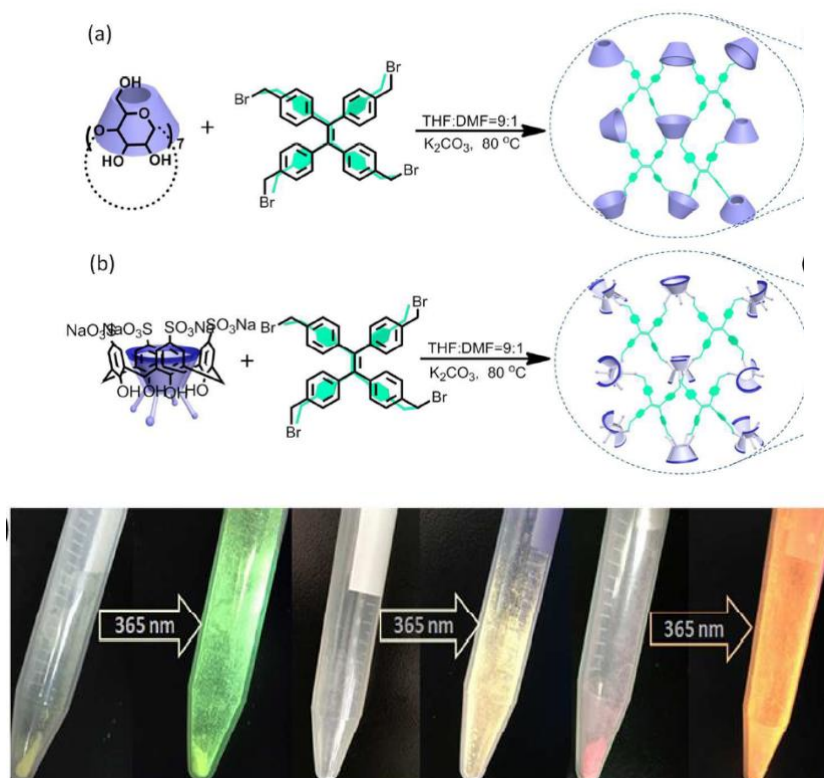
We propose an experimentally-inspired model of gels and microgels with sliding cross-links, and use this model to study the mechanical and structural properties with molecular dynamics simulations. In the model, the gels and microgels are made of linear polymer chains with threaded rings capable of sliding along the chains and bulky end-groups keeping the rings threaded mimic polyrotaxanes; **they are covalently linked to each other not through the backbones but through the rings**. Both gels and microgels are shown to be much softer in the regime of intermediate and large deformations and also much stretchable than the topologically equivalent chemical counterparts. The physical reason for that is the mobility of the cross-links which leads to the formation of long, longitudinally oriented “subchains” between cross-linked rings upon uniaxial deformation. The microgels are tested for adsorption on a solid flat surface and for interaction with colloidal particles of different sizes. We demonstrate that the sliding microgel is subjected to stronger flattening on the surface than the chemical one. **Enforced penetration of solid particles into the sliding microgel without breaking of covalent bonds is predicted** even if the size of the particles is comparable or larger than the mesh size of the chemical microgel and smaller than the size of polyrotaxane. **This penetration is accompanied by the disappearance of the trace (cavity):** the microgel is characterized by adaptive porosity tunable to the guest-object.

Comment: The system simulated in the present work is different than the polyrotaxane-based gel studied in the team because of the nature of the crosslinks, as explained in the summary.

However, it is expected that similar tendencies are to be observed. The most interesting result, in my opinion, is about the permeability of nanoparticles through the network. Nanoparticles can penetrate more deeply inside the “sliding microgel” than in a chemically crosslinked one because of the adaptative mesh size; to the best of my knowledge, no experimental work has studied this effect.

Tunable Photo-luminescence Behaviors of Macrocycles Containing Polymer Networks in Solid-state

Zhao, Q.; Liu, Y.* [Chem. Commun. 2018, ASAP.](#)

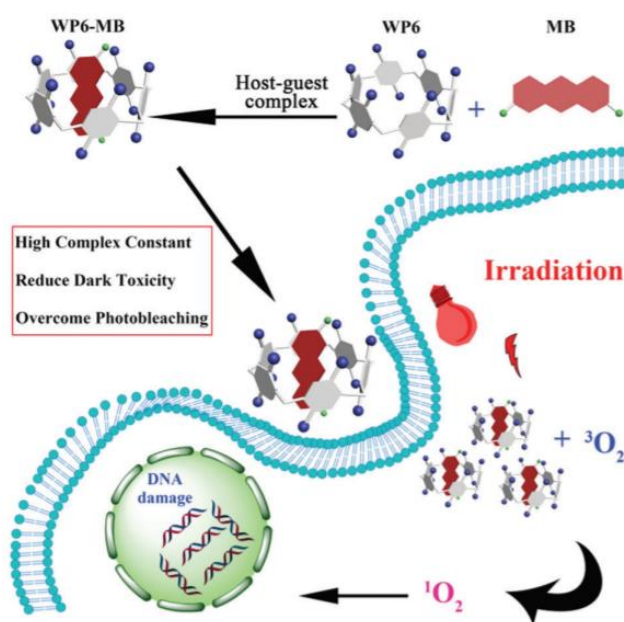


Two porous polymers were synthesized by tetraphenylethylene (TPE) crosslinked β -cyclodextrins (β -CD) and sulfonatocalix[4]arene (SC4A). Owing to the FRET process from the TPE to encapsulated fluorophores, those polymers provide universal platforms for the fabrication of photo-luminescence tunable organic solid materials.

Comment: Two macrocycles (β -cyclodextrins and sulfonatocalix[4]arene) are separately introduced into the tetraphenylethylene polymer. These two polymers could encapsulate some specific guest dyes, leading to the formation of tunable photo-luminescence. This strategy provides a novel method to construct tunable photo-luminescence solid materials.

A Supramolecular Photosensitizer System Based on the Host–guest Complexation between Water-soluble Pillar[6]arene and Methylene Blue for Durable Photodynamic Therapy

Yang, K.; Wen, J.; Chao, S.; Liu, J.; Yang, K.; Pei, Y.; Pei, Z.* [Chem. Commun. 2018, ASAP.](#)

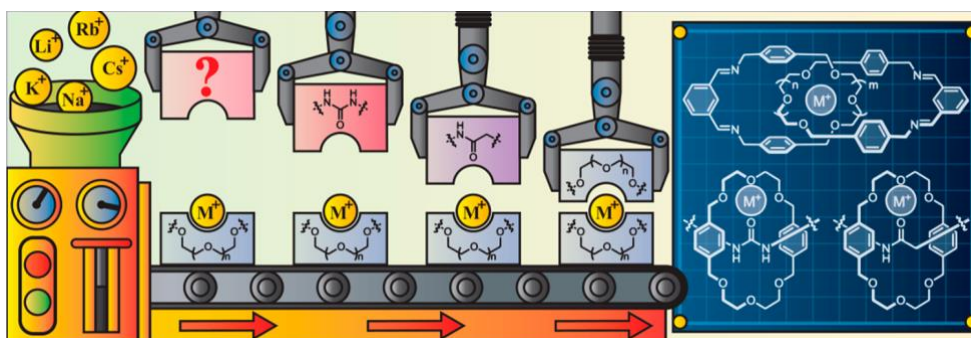


A supramolecular photosensitizer system WP6–MB was synthesized based on water-soluble pillar[6]arene and the photosensitizer methylene blue (MB) via host–guest interaction. MB can complex with WP6 directly with a high complex constant without further modification. In particular, WP6–MB can reduce the dark toxicity of MB remarkably. Furthermore, it can efficiently overcome photobleaching and extend the time for singlet oxygen production of MB upon light irradiation, which is significant for durable photodynamic therapy.

Comment: A very interesting host-guest system, which could perform as photosensitizer to reduce the dark toxicity of MB and protect MB from photobleaching.

Using Alkali Metal Ions To Template the Synthesis of Interlocked Molecules

Inthasot, A.; Tung, S.-T.; Chiu, S.-H.* [Acc. Chem. Res. ASAP.](#)



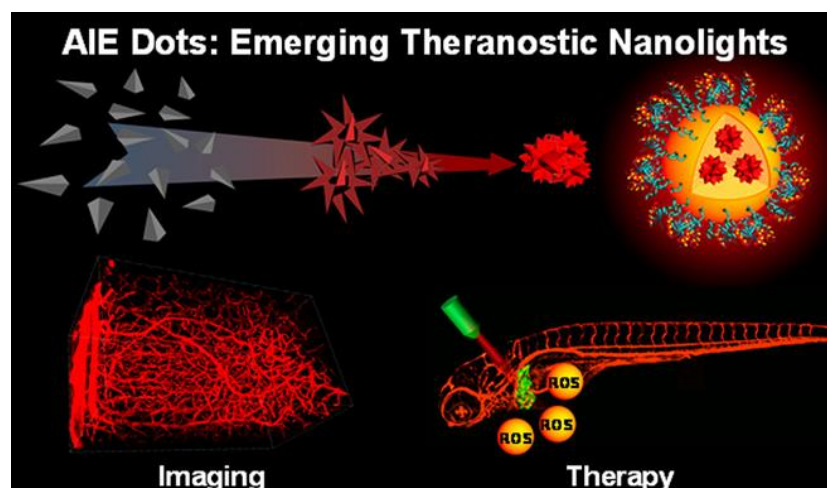
In 1987, Pedersen, Cram, and Lehn were awarded the Nobel Prize in Chemistry to honor their achievements in, among other things, the selective recognition of alkali metal ions by synthetic hosts. Almost three decades later, the 2016 Nobel Prize went to Stoddart, Sauvage, and Feringa for the development of artificial molecular machines, in which interlocked molecules play a significant role. Surprisingly, although many rotaxane- and catenane-based molecular machines

have been constructed using various templating approaches, alkali metal ions, which are good templates for crown ether synthesis, have only rarely been applied as templates for the assembly of these interlocked molecules. This paucity of examples is probably due to the less well defined coordination numbers and geometries in the complexation of alkali metal ions to common oxygen-containing ligands, resulting in much weaker metal–ligand interactions and less predictable structures for their complexes compared with those formed between transition metal ions and common pyridine-containing ligands. Nevertheless, the ease of removing alkali metal ions from interlocked compounds and their much lower toxicity compared with that of transition metal ions are attractive features that have inspired their use as templates in the synthesis of interlocked molecules. About a decade ago, we began investigating the feasibility of using alkali metal ions to template the formation of catenanes and rotaxanes, with the hope of developing facile, broadly applicable, green, and efficient methods for their construction. We noticed that the interactions between oxygen-containing ligands and alkali metal ions can be strengthened by minimizing the effects of competing interactions from solvent molecules and counteranions. Thus, to increase the solubility of the metal ion salts in less polar solvents (e.g., CH_2Cl_2 , CHCl_3) and minimize ion pairing, we chose tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB), a weakly coordinating anion, as the counteranion for the alkali metal ions applied as templates. Our strategy has been based on the association of simple and general recognition units: (i) the orthogonal arrangement of two oligo(ethylene glycol) chains around an alkali metal ion and (ii) the encircling of a single urea/amide unit by an oligo(ethylene glycol)-containing macrocycle in the presence of a templating alkali metal ion. The former recognition system has allowed the facile construction of many interesting interlocked structures, including cyclic [2]catenane trimers and tetramers; the latter has provided several rotaxanes, including some incorporating monomers of practically important (macro)molecules (e.g., peptides, polymers) and some that behave as switches with unique functions (e.g., catalysis, gelation). The components in these recognition systems possess high flexibility in terms of their structures and the choice of suitable alkali metal ion templates. This Account tells the story of the concept behind this alkali metal ion-templating approach as well as its elaboration, scope, and recent advances. We hope to convince the reader that alkali metal ions are powerful templates for assembling interlocked structures and compounds and also to demonstrate the range of possibilities that they provide for future endeavors.

Comment: An innovative method to prepare interlocked molecules using cheaper and safer reagents. After all, it's like a return in the past with the first examples of crown ethers used with alkali metals.

Aggregation-Induced Emission (AIE) Dots: Emerging Theranostic Nanolights

Feng, G.; Liu, B.* [Acc. Chem. Res. ASAP.](#)



Theranostic nanolights refer to luminescent nanoparticles possessing both imaging and therapeutic functions. Their shape, size, surface functions, and optical properties can be precisely manipulated through integrated efforts of chemistry, materials, and nanotechnology for customized applications. When localized photons are used to activate both imaging and therapeutic functions such as photodynamic or photothermal therapy, these theranostic nanolights increase treatment efficacy with minimized damage to surrounding healthy tissues, which represents a promising noninvasive nanomedicine as compared to conventional theranostic approaches.

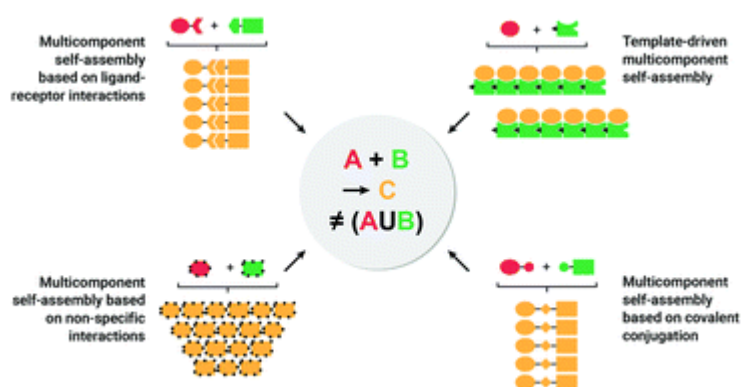
As one of the most promising theranostic nanolights, organic dots with aggregation-induced emission (AIE dots) are biocompatible nanoparticles with a dense core of AIE fluorogens (AIEgens) and protective shells, whose sizes are in the range of a few to tens of nanometers. Different from conventional fluorophores that suffer from aggregation-caused quenching (ACQ) due to π - π stacking interaction in the aggregate state, AIEgens emit strongly as nanoaggregates due to the restriction of intramolecular motions. Through precise molecular engineering, AIEgens could also be designed to show efficient photosensitizing or photothermal abilities in the aggregate state. Different from ACQ dyes, AIEgens allow high loading in nanoparticles without compromised performance, which makes them the ideal cores for theranostic nanolights to offer high brightness for imaging and strong photoactivities for theranostic applications.

In this Account, we summarize the recent advance of AIE dots and highlight their great potential as theranostic nanolights in biomedical applications. Starting from the design of AIEgens, the fabrication of AIE dots and their bioimaging applications are discussed. The exceptional advantages of superbrightness, high resistance to photobleaching, lack of emission intermittency, and excellent biocompatibility have made them reliable cross platform contrast agents for different imaging techniques such as confocal microscopy, multiphoton fluorescence microscopy, super-resolution nanoscopy, and light-sheet ultramicroscopy, which have been successfully applied for cell tracking, vascular disease diagnosis, and image-guided surgery. The integration of therapeutic functions with customized AIEgens has further empowered AIE dots as an excellent theranostic platform for image-guided phototherapy. Of particular interest is AIE photosensitizer dots, which simultaneously show bright fluorescence and high photosensitization, yielding superior performance to commercial photosensitizer nanoparticles in image-guided therapy. Further development in multiphoton excited photodynamic therapy has offered precise treatment with up to 5 μm resolution at 200 μm depth, while chemiexcited photodynamic therapy has completely eliminated the limitation of penetration depth to realize power-free imaging and therapy. With this Account, we hope to stimulate more collaborative research interests from different fields of chemistry, materials, biology, and medicine to promote translational research of AIE dots as the theranostic nanolights.

Comment: Yes, theranostics again. It seems that half of the papers from ACS nano deal with theranostics and even when I check my other journals I find some. More particularly, I enjoyed the part about the chemiexcited photodynamic therapy.

Multicomponent Self-assembly as a Tool to Harness new Properties from Peptides and Proteins in Material Design

Okesola, B. O.; Mata, A.* [*Chem. Soc. Rev.*, **2018**, *47*, 3721-3736](#)

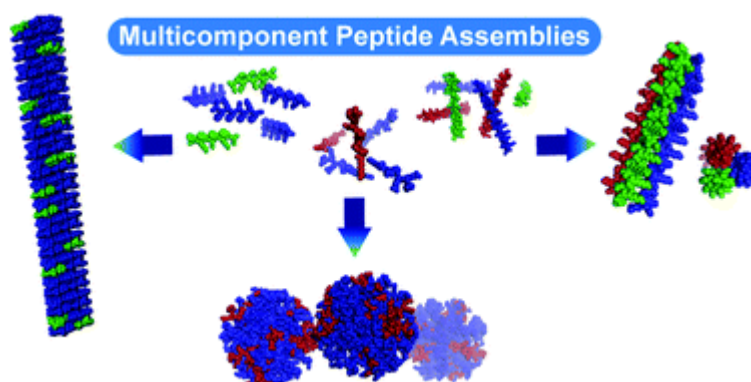


Nature is enriched with a wide variety of complex, synergistic, and highly functional protein-based multicomponent assemblies. As such, nature has served as a source of inspiration for using multicomponent self-assembly as a platform to create highly ordered, complex, and dynamic protein and peptide-based nanostructures. Such an assembly system relies on the initial interaction of distinct individual building blocks leading to the formation of a complex that subsequently assembles into supramolecular architectures. This approach not only serves as a powerful platform for gaining insight into how proteins co-assemble in nature but also offers huge opportunities to harness new properties not inherent in the individual building blocks. In the past decades, various multicomponent self-assembly strategies have been used to extract synergistic properties from proteins and peptides. This review highlights the updates in the field of multicomponent self-assembly of proteins and peptides and summarizes various strategies, including covalent conjugation, ligand–receptor interactions, templated/directed assembly and non-specific co-assembly, for driving the self-assembly of multiple proteins and peptide-based building blocks into functional materials. In particular, we focus on peptide- or protein-containing multicomponent systems that, upon self-assembly, enable the emergence of new properties or phenomena. The ultimate goal of this review is to highlight the importance of multicomponent self-assembly in protein and peptide engineering, and to advocate its growth in the fields of materials science and nanotechnology.

Comment: Not just easy to read, I also really liked how the authors summed up the examples they used and their discussion points in tables 1 and 2.

Multicomponent Peptide Assemblies

Raymond, D. M.; Nilsson, B. L.* [*Chem. Soc. Rev.*, **2018**, *47*, 3659-3720](#)

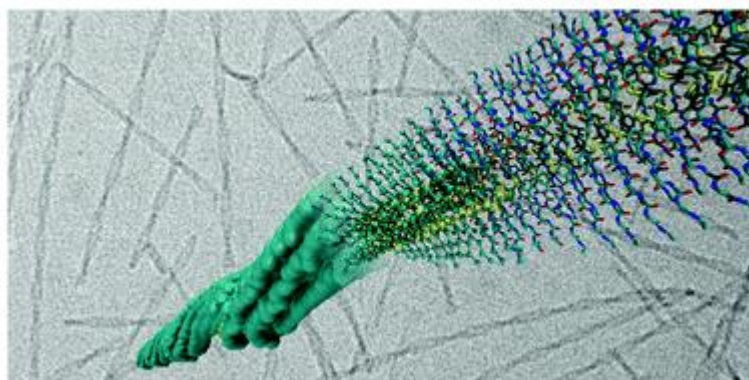


Self-assembled peptide nanostructures have been increasingly exploited as functional materials for applications in biomedicine and energy. The emergent properties of these nanomaterials determine the applications for which they can be exploited. It has recently been appreciated that nanomaterials composed of multicomponent coassembled peptides often display unique emergent properties that have the potential to dramatically expand the functional utility of peptide-based materials. This review presents recent efforts in the development of multicomponent peptide assemblies. The discussion includes multicomponent assemblies derived from short low molecular weight peptides, peptide amphiphiles, coiled coil peptides, collagen, and β -sheet peptides. The design, structure, emergent properties, and applications for these multicomponent assemblies are presented in order to illustrate the potential of these formulations as sophisticated next-generation bio-inspired materials.

Comment: Longer to read than the others, this review may be a complementary inspiration source coupled with the previous ones for our members of the peptide projects.

Molecular Simulations of Self-assembling Bio-inspired Supramolecular Systems and their Connection to Experiments

Frederix, P. W. J. M.;* Patmanidis, I.; Marrink, S. J.* [*Chem. Soc. Rev.* **2018**, *47*, 3470-3489](#)



In bionanotechnology, the field of creating functional materials consisting of bio-inspired molecules, the function and shape of a nanostructure only appear through the assembly of many small molecules together. The large number of building blocks required to define a nanostructure combined with the many degrees of freedom in packing small molecules has long precluded molecular simulations, but recent advances in computational hardware as well as software have made classical simulations available to this strongly expanding field. Here, we review the state of the art in simulations of self-assembling bio-inspired supramolecular systems. We will first discuss progress in force fields, simulation protocols and enhanced sampling techniques using recent examples. Secondly, we will focus on efforts to enable the comparison of experimentally accessible observables and computational results. Experimental quantities that can be measured by microscopy, spectroscopy and scattering can be linked to simulation output either directly or indirectly, *via* quantum mechanical or semi-empirical techniques. Overall, we aim to provide an overview of the various computational approaches to understand not only the molecular architecture of nanostructures, but also the mechanism of their formation.

Comment: Andreas gave us a presentation about computation that focused on multistep synthesis prediction. If you liked it and wonder what can be done at the next levels, this review gives an overview of what and how is possible to predict peptides supramolecular assemblies. Thankfully, the review is written for a larger readership than just people in the field, but it may still be complicated to follow from time to time and needs some side searches on the discussed systems.

Direct Synthesis of Covalently Self-Assembled Peptide Nanogel from Tyrosine-Rich Peptide Monomer and Its Biomineralized Hybrids

Min, K.-I.; Kim, D.-H.; Lee, H.-J.; Lin, L.; Kim, D.-P.* *Angew. Chem. Int. Ed.* **2018**, *57*, 5630-5634

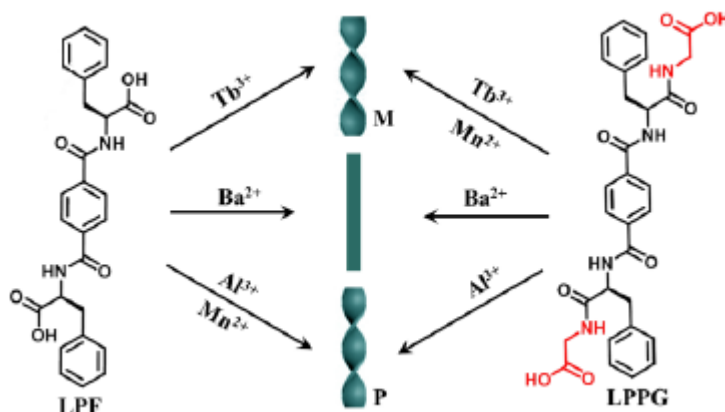


There has been significant progress in the self-assembly of biological materials but the one-step covalent self-assembly of peptide for well-defined nanostructures is still in its infancy. Inspired by the biological functions of tyrosine, a covalently assembled fluorescent peptide nanogel is developed by a ruthenium-mediated, **one-step photo-crosslinking of tyrosine-rich short peptides under the visible light within 6 minutes**. The covalently assembled peptide nanogel is stable in various organic solvents and different pH levels, unlike those made from vulnerable non-covalent assemblies. The semipermeable peptide nanogel with a high density of redox-active tyrosine acts as a novel nano-bioreactor, allowing the formation of uniform metal-peptide hybrids by selective biomineralization under UV irradiation. As such, this peptide nanogel could be useful in the design of novel nanohybrids and peptidosomes possessing functional nanomaterials.

Comment: “Keep it simple” they said, so they did. I was quite impressed when I saw that such a small and simple peptide would lead to such ultrafast covalent self-assembly. I personally still have some difficulties to see the applications, but I find the proof of concept elegant.

Metal-Ion-Mediated Supramolecular Chirality of L-Phenylalanine Based Hydrogels

Wang, F.; Feng, C.-L.* *Angew. Chem. Int. Ed.*, **2018**, *57*, 5655-5659

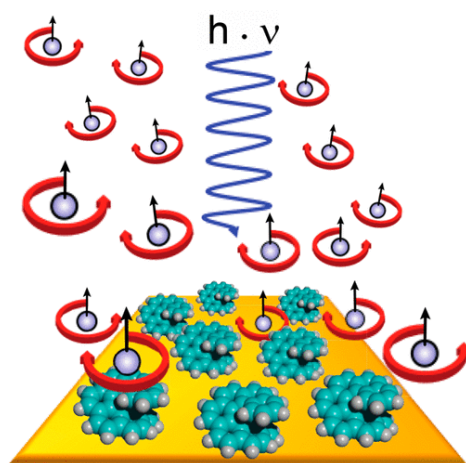


For chiral hydrogels and related applications, one of the critical issues is how to control the chirality of supramolecular systems in an efficient way, including easy operation, efficient transfer of chirality and so on. Herein, supramolecular chirality of L-phenylalanine based hydrogels can be effectively controlled by using a broad range of metal ions. The degree of twisting (twist pitch) and the diameter of the chiral nanostructures can also be efficiently regulated. These are ascribed to the synergic effect of hydrogen bonding and metal ion coordination. This study may develop a methodology to design a new class of electronically, optically, and biologically active materials.

Comment: The authors present in this article the screening of the metal effect on the supramolecular assembly of two close peptide systems. If the full characterization is classic (but efficient), their SEM images truly are impressive.

Chirality-Dependent Electron Spin Filtering by Molecular Monolayers of Helicenes

Kettner, M.; Maslyuk, V. V.; Nürenberg, D.; Seibel, J.; Gutierrez, R.; Cuniberti, G.; Ernst, K.-H.*; Zacharias, H.* [*J. Phys. Chem. Lett.* **2018**, *9*, 2025.](#)

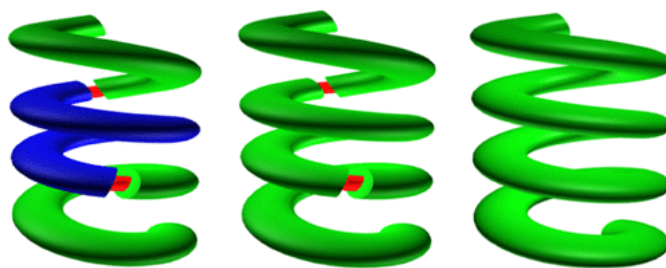


The interaction of low-energy photoelectrons with well-ordered monolayers of enantiopure helical heptahelicene molecules adsorbed on metal surfaces leads to a preferential transmission of one longitudinally polarized spin component, which is strongly coupled to the helical sense of the molecules. Heptahelicene, composed of only carbon and hydrogen atoms, exhibits only a single helical turn but shows excess in longitudinal spin polarization of about $P_z = 6$ to 8% after transmission of initially balanced left- and right-handed spin polarized electrons. Insight into the electronic structure, that is, the projected density of states, and the spin-dependent electron scattering in the helicene molecule is gained by using spin-resolved density functional theory calculations and a model Hamiltonian approach, respectively. **Our results support the semiclassical picture of electronic transport along a helical pathway under the influence of spin-orbit coupling induced by the electrostatic molecular potential.**

Comment: I am being a bit selfish with this paper because I think most of you will not find it of particular interest. But it is a simple and easy to understand paper about **spin-filtering**. Their main experimental characterization is what I still consider the gold standard in the field. If you have any interest in the matter, the *paper is short enough and not too technical* so I recommend it.

Making Molecular and Macromolecular Helical Tubes: Covalent and Noncovalent Approaches

Liu, C.-Z.; Yan, M.; Wang, H.; Zhang, D.-W.; Li, Z.-T.* [*ACS Omega* 2018, 3, 5165.](#)



Aromatic foldamers possess well-defined cavity that can be stabilized by discrete intramolecular interactions including hydrogen bonding, solvophobicity, electrostatic repulsion, or coordination. Long foldamers can form **dynamic deep helical tubular architectures** that are not only structurally attractive but also useful hosts for guest encapsulation, chirality induction, delivery, and catalysis. This kind of helical tubular structures can be formed by single molecules or macromolecules or by connecting short-folded or helical segments through noncovalent or covalent forces. **This perspective summarizes the recent advances on the construction of helical tubes and their properties and functions.**

Comment: Before anything: you can always break the rules and report papers from journals that are not in our list! This is a short review containing some examples, rules, and design principles towards the construction of large helical structures. There are notably implications in ion transport, spintronics, encapsulation and more, but mostly I enjoyed the sheer beauty of the chemical design.