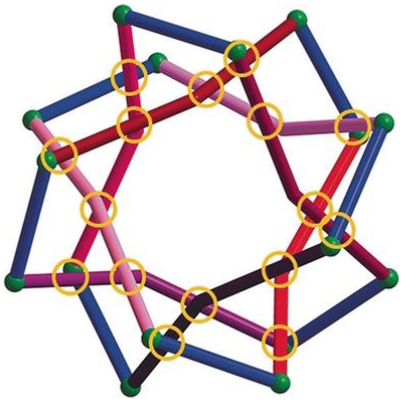
Comment on “Coordination-Driven Self-Assembly of a Molecular Knot Comprising Sixteen Crossings”

Leigh, D. A.*; Lemonnier, J-F.; Woltering, S. L. *Angew. Chem. Int. Ed.* **2018**, *57*, ASAP.

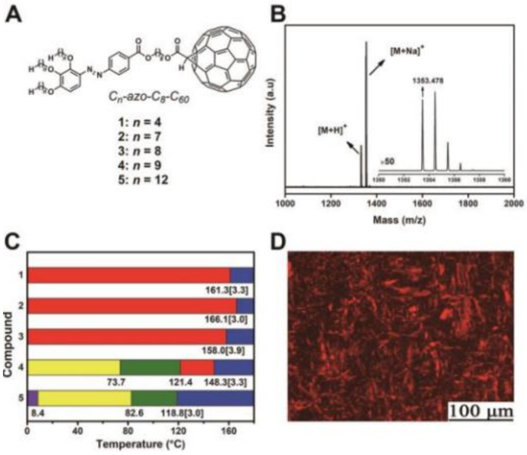


The remarkable metalla-knot obtained by Kim, Jung, Chi and colleagues is an 8_{18} knot, a metalla-knot that comprises eight crossings, not sixteen. It is the first knot to be synthesized having the 8_{18}topology. Like several previous molecular knots, it adopts a conformation that does not correspond to the reduced form of the knot and has additional persistent nugatory crossings.

Comment: Inspiring article on the way to characterized and determined the topology of a molecular knot. Leigh and al showed that the metalla-knot obtained by Kim, Jung, Chi and colleagues is an 8^{18} knot, a metalla-knot that comprises eight crossings, not sixteen. This error is due by the fact that the molecular knot can adopted a conformation that does not correspond to the reduced form of the knot and has additional persistent nugatory crossings.

Unique Supramolecular Liquid Crystal Phases with Different Two-Dimensional Crystal Layers

Hu, Y.; Wu, K. Y. ; Zhu, T. ; Shen, P. ; Zhou, Y. ; Li, X. ; Wang, C. L. ; Tu, Y. ; Li, C. Y..*
Angew. Chem. Int. Ed. ASAP.

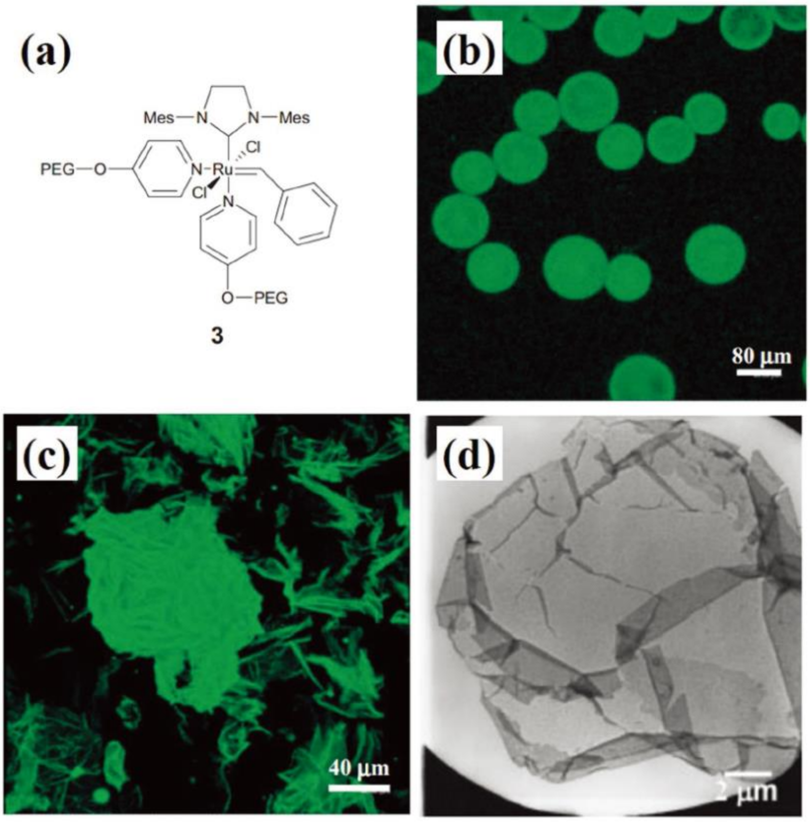


We report here a series of tetrablock-mimic azobenzene-containing fullerene dyads that form phase segregated two-dimensional (2D) crystal constructed supramolecular liquid crystals (LCs). The unique double-, triple- and quadruple-layer packing structure of fullerenes in 2D crystals leads to different smectic supramolecular LC phases, and novel LC phase transitions are observed due to the change of fullerene packing layer number in 2D crystals. Interestingly, by combining the LC properties with 2D crystals, these materials show excellent electron mobility in the order of 10^{-3} $cm^2V^{-1}s^{-1}$, despite their relatively low fullerene content. Our results provide a novel method to manipulate 2D crystal layer thickness, with promising applications in optoelectronic devices.

Comment: Interesting paper reporting a series of azobenzene-containing fullerene dyads which gives a 2D crystal of supramolecular LC phases with different fullerene packing layer thickness. This article could be interesting for Alexis by the fact that they introduce molecular machines (even if in this paper the azobenzene is only used as a mesogene) in liquid crystal and characterized the entire phases of the liquid crystal with several techniques that he could led to use (AFM, SAXS, SCLC).

Nanoparticle Assembly at Liquid–Liquid Interfaces: From the Nanoscale to Mesoscale

Shi, S.; Russell, T. P.* *Adv. Mater.* **2018.** 1800741.

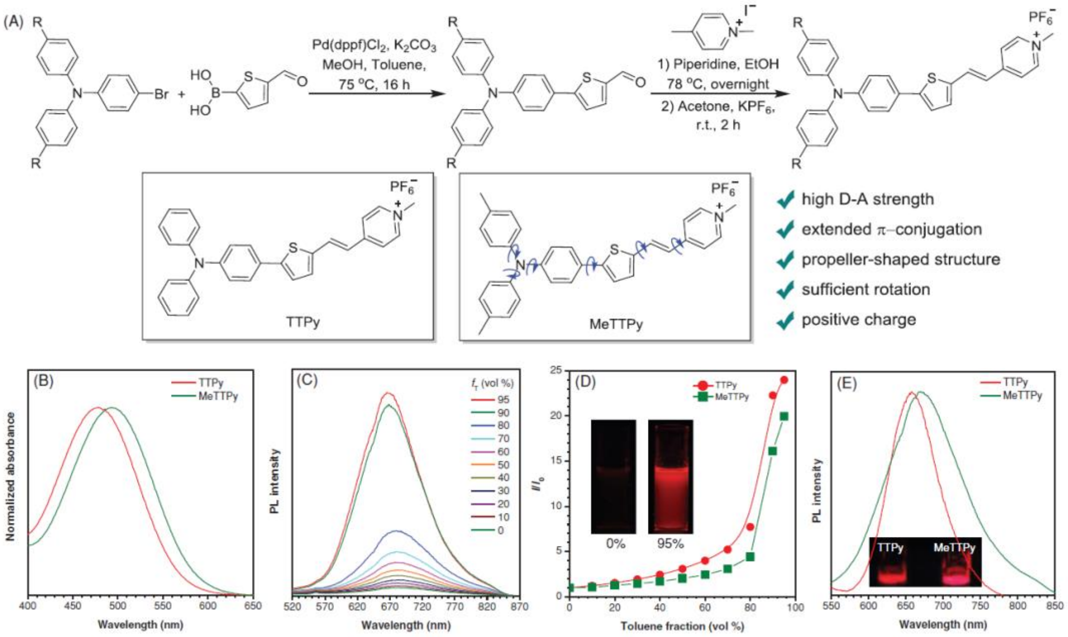


In the past few decades, novel syntheses of a wide range of nanoparticles (NPs) with well-defined chemical composition and structure have opened tremendous opportunities in areas ranging from optical and electronic devices to biomedical markers. Controlling the assembly of such well-defined NPs is important to effectively harness their unique properties. The assembly of NPs at liquid–liquid interfaces is becoming a central topic both in surface and colloid science. Hierarchical structures, including 2D films, 3D capsules, and structured liquids, have been generating significant interest and are showing promise for physical, chemical, and biological applications. Here, a brief overview of the development of the self-assembly of NPs at liquid–liquid interfaces is provided, from theory to experiment, from synthetic NPs to bio-nanoparticles, from water–oil to water–water, and from “liquid-like” to “solid-like” assemblies.

Comment: This review introduces the nanoparticle self-assembly at liquid-liquid interface via different mechanisms. I choose it because some examples in this paper are similar with my research project. Especially, the self-assembly could be cross-linked upon addition of a catalyst. If you are also curious about this kind of research, read it.

Highly Efficient Photosensitizers with Far-Red/Near-Infrared Aggregation-Induced Emission for in Vitro and in Vivo Cancer Theranostics

Wang, D.; Lee, M. M. S.; Shan, G.; Kwok, R. T. K.; Lam, J. W. Y.; Su, H.*; C, Y.*; Tan, B. Z.* *Adv. Mater.* **2018**, 1802105.

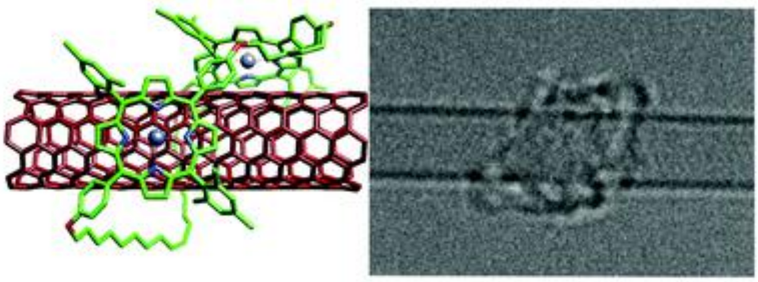


Fluorescence-imaging-guided photodynamic therapy has emerged as a promising protocol for cancer theranostics. However, facile preparation of such a theranostic material for simultaneously achieving bright emission with long wavelength, high-performance reactive oxygen species (ROS) generation, and good targeting-specificity of cancer cells, is highly desirable but remains challenging. In this study, a novel type of far-red/near-infrared-emissive fluorescent molecules with aggregation-induced emission (AIE) characteristics is synthesized through a few steps reaction. These AIE luminogens (AIEgens) possess simple structures, excellent photostabilities, large Stokes shifts, bright emission, and good biocompatibilities. Meanwhile, their ROS generation is extremely efficient with up to 90.7% of ROS quantum yield, which is far superior to that of some popularly used photosensitizers. Importantly, these AIEgens are able to selectively target and ablate cancer cells over normal cells without the aid of any extra targeting ligands. Rather than using laser light, one of the presented AIEgens (MeTTPy) shows a remarkable tumor-targeting photodynamic therapeutic effect by using an ultralow-power lamp light (18 mW cm^{-2}). This study thus not only extends the applications scope of AIEgens, but also offers useful insights into designing a new generation of cancer theranostics.

Comment: Two AIEgens containing TAA are masterly designed, one of which can be used as high-performance reactive oxygen species. It is promising alternatives for cancer theranostics.

Interfacing Porphyrins and Carbon Nanotubes through Mechanical Links

de Juan-Fernández, L.; Münich, P. W.; Puthiyedath, A.; Nieto-Ortega, B.; Casado, S.; Ruiz-González, L.; Pérez, E. M.*; Guldi, D. M.* *Chem. Sci.* **2018**, *9*, 6779–6784.

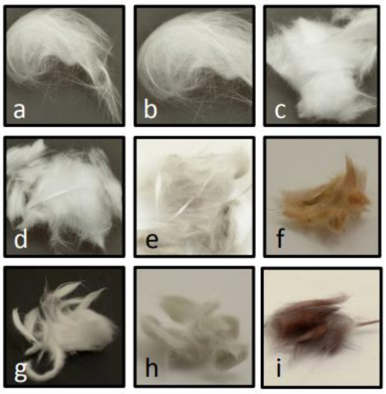


We describe the synthesis of rotaxane-type species composed of **macrocyclic porphyrin rings mechanically interlocked with SWCNT threads**. The formation of mechanically interlocked SWCNTs (MINTs) proceeds with chiral selectivity, and was confirmed by spectroscopic and analytical techniques and adequate control experiments, and corroborated by high-resolution electron microscopy. From a thorough characterization of the MINTs through UV-vis-NIR absorption, fluorescence, Raman, and transient absorption spectroscopy we analyse in detail the electronic interactions of the porphyrins and the SWCNTs in the ground and excited states.

Comment: The type of interactions in hybrid systems of porphyrins and carbon nanotubes is crucial for the elaboration of optoelectronic devices. Here, the authors report the mechanical threading of a porphyrin-containing macrocycle around a carbon nanotube, which may give rise to new properties caused by the proximity of the porphyrin and the CNT. They thoroughly characterized this molecular machine, and the images from high-resolution electron microscopy are impressive.

Glass Wool: A Novel Support for Heterogeneous Catalysis

Elhage, A.; Wang, B.; Marina, N.; Marin, M. L.; Cruz, M.; Lanterna, A. E.*; Scaiano, J. C.* *Chem. Sci.* **2018**, *9*, 6844–6852.

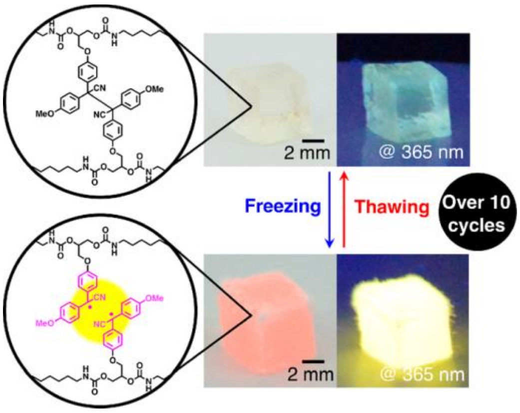


Heterogeneous catalysis presents significant advantages over homogeneous catalysis such as ease of separation and reuse of the catalyst. Here we show that a very inexpensive, manageable and widely available material – glass wool – can act as a catalyst support for a number of different reactions. **Different metal and metal oxide nanoparticles**, based on Pd, Co, Cu, Au and Ru, were deposited on glass wool and used as heterogeneous catalysts for a variety of thermal and photochemical organic reactions including reductive de-halogenation of aryl halides, reduction of nitrobenzene, Csp^3–Csp^3 couplings, N–C heterocycloadditions (click chemistry) and Csp–Csp^2 couplings (Sonogashira couplings). The use of glass wool as a catalyst support for important organic reactions, particularly C–C couplings, opens the opportunity to develop economical heterogeneous catalysts with excellent potential for flow photo-chemistry application.

Comment: I am always fascinated when research is based on a daily-life product. Here, as you can read, it is about glass wool, used as a support for heterogeneous catalysis. **Their results are promising** so we might see this kind of material become more interesting in the future!

Freezing-Induced Mechanoluminescence of Polymer Gels

Kato, S.; Ishizuki, K.; Aoki, D.; Goseki, R.; Otsuka, H.* *ACS Macro Lett.* **2018**, *7*, 1087−1091.

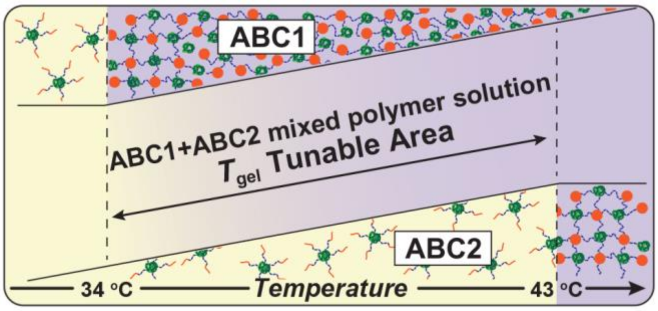


Mechanochromism can be triggered by different mechanical stimuli, such as tension, compression, shearing, and sonication. Freezing a polymer gel also induces mechanical stress on the polymer network. Herein, **freezing-induced mechanoluminescence is demonstrated for the first time** by introduction of a tetraarylsuccinonitrile moiety as a light-emitting mechanochromophore at the cross-linking points of a polymer network, in which the mechanical stress induces not only a color change but also light emission. The detailed mechanism and characteristics of this freezing-induced mechanoluminescence were quantitatively evaluated by **electron paramagnetic resonance spectroscopy**.

Comment: The authors describe an interesting phenomenon for the first time. They achieve luminescence from a polymer as a consequence of a mechanical stress induced by freezing the sample.

Precisely Tunable Sol−Gel Transition Temperature by Blending Thermoresponsive ABC Triblock Terpolymers

Onoda, M.; Tamate, R.; Akimoto, A. M.; Hall, C. C.; Ueki, T.*; Lodge, T. P.*; Yoshida, R.* *ACS Macro Lett.* **2018**, *7*, 950−955.

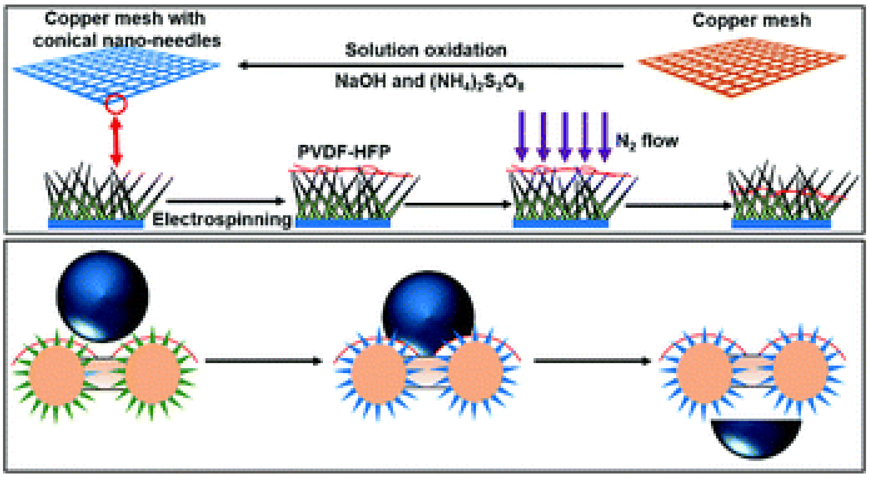


Here, **we report a facile methodology to control the sol−gel transition temperature (T_{gel}) of a physically crosslinked hydrogel by blending two kinds of ABC triblock terpolymers**. Well-defined triblock terpolymers including thermosensitive N-isopropylacrylamide (NIPAAm), ABC1, and ABC2, were prepared by sequential reversible addition−fragmentation chain transfer polymerization. The chemical structure as well as the molecular weight of the A and B blocks for both polymers are identical, whereas the C blocks are different. The C block of ABC1 (C1) is a statistical copolymer of NIPAAm with hydrophobic n-butyl acrylate (BA), while that of ABC2 (C2) is a PNIPAAm homopolymer. Independently prepared ABC triblock terpolymer solutions exhibit well-defined sol−gel transitions. The T_{gel} of ABC1 is lower than that of ABC2 since hydrophobic BA is copolymerized into block C1. Remarkably, the T_{gel} varies linearly within this temperature range by simply blending the two polymers, while the resultant gel strength (∼G') remains almost unchanged. Therefore, the T_{gel} can be precisely adjusted by the mixing ratio of the two polymers. This method for straightforward manipulation of T_{gel} has great potential for various soft material applications such as biomaterials for tissue engineering, drug delivery systems, and injectable gels.

Comment: The sol-gel transition temperature is an important parameter for soft materials. Achieving a good control of it could drastically increase the applications of these materials. Here the authors present a way to manipulate the T_{gel} for a triblock terpolymer.

Janus Porous Membrane with Conical Nano-Needle Channel for Rapid Unidirectional Water Transport

Wang, Z.; Li, Y.; Li, S.*; Guo, J.*; Zhang, S. *Chem.Commun.*, **2018**, Advance Article.

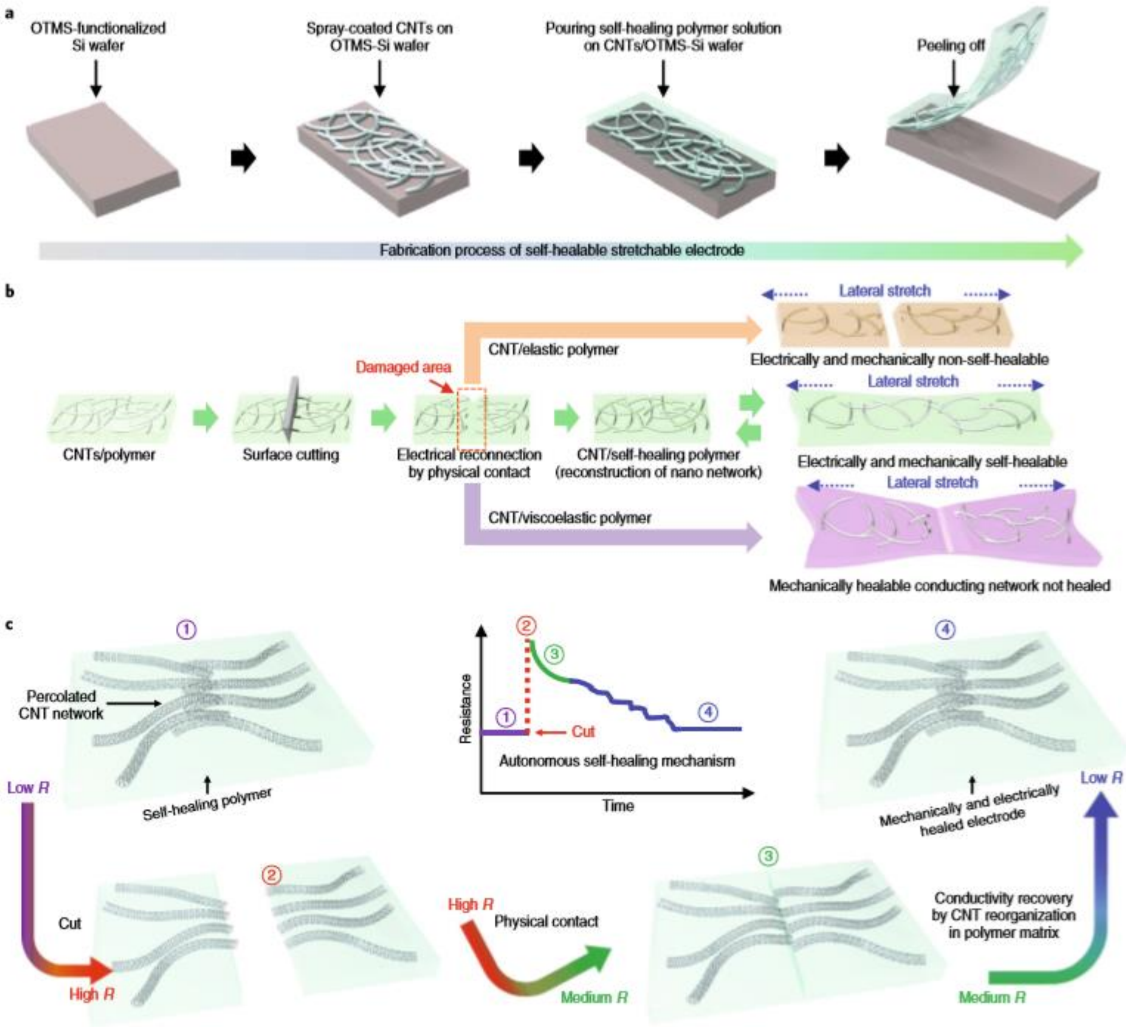


The **pierced nanowire Janus porous membrane** possesses piercing conical nano-needles, which not only form the transport channel to **enhance unidirectional water transport**, but also **reduce the energy barrier of water transport** by changing the way of water transport from droplet to film.

Comment: This article is quite interesting because the authors are using Janus particles to obtain a useful membrane. Even if the article remains quite short, it still allows us to gain practical knowledge on the physics of microfluidic.

An Integrated Self-healable Electronic Skin System Fabricated *Via* Dynamic Reconstruction of a Nanostructured Conducting Network

Son, D.; Kang, J.; Orestis, V.; Kim, Y.; Matsuhisa, N.; Oh, Y. Jin.; To, WF. J.; Mun, J.; Katsumata, T.; Francisco, M. Jooyeun, H.; Ulrike, K.; Lee, Y.; Yun, Y.; Jeffrey, T.; Bao, Z.*
Nat. Nanotechnol. 2018, ASAP.

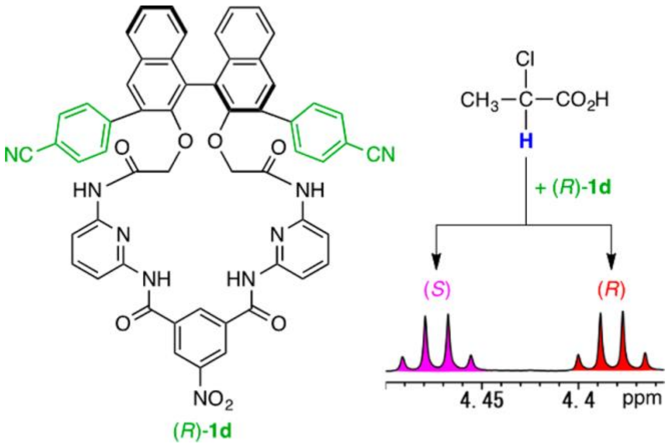


Electronic skin devices capable of monitoring physiological signals and displaying feedback information through closed-loop communication between the user and electronics are being considered for next-generation wearables and the 'Internet of Things'. Such devices need to be ultrathin to achieve seamless and conformal contact with the human body, to accommodate strains from repeated movement and to be comfortable to wear. Recently, self-healing chemistry has driven important advances in deformable and reconfigurable electronics, particularly with self-healable electrodes as the key enabler. Unlike polymer substrates with self-healable dynamic nature, the disrupted conducting network is unable to recover its stretchability after damage. Here, **we report the observation of self-reconstruction of conducting nanostructures when in contact with a dynamically crosslinked polymer network**. This, combined with the self-bonding property of self-healing polymer, allowed subsequent heterogeneous multi-component device integration of interconnects, sensors and light-emitting devices into a single multi-functional system. This first autonomous self-healable and stretchable multi-component electronic skin paves the way for future robust electronics.

Comment: Prof. Bao's most famous research perhaps is her highly sensitive, transparent and stretchable artificial skin, which was inspired by the combination of electronic devices and polymers. In this paper, the authors combine the supramolecular self-healing polymer with 1D nano-structured networks to obtain nanomaterial/polymer composite electrodes. Their multi-functional self-healable electronic skin is really interesting.

Cross-Coupling Approach to an Array of Macrocyclic Receptors Functioning as Chiral Solvating Agents

Tadashi, E.*; Takayuki, Yamasaki. Sagiri, W.; Mahoko, H.; Kazuto, T. *J. Org. Chem.2018. ASAP.*

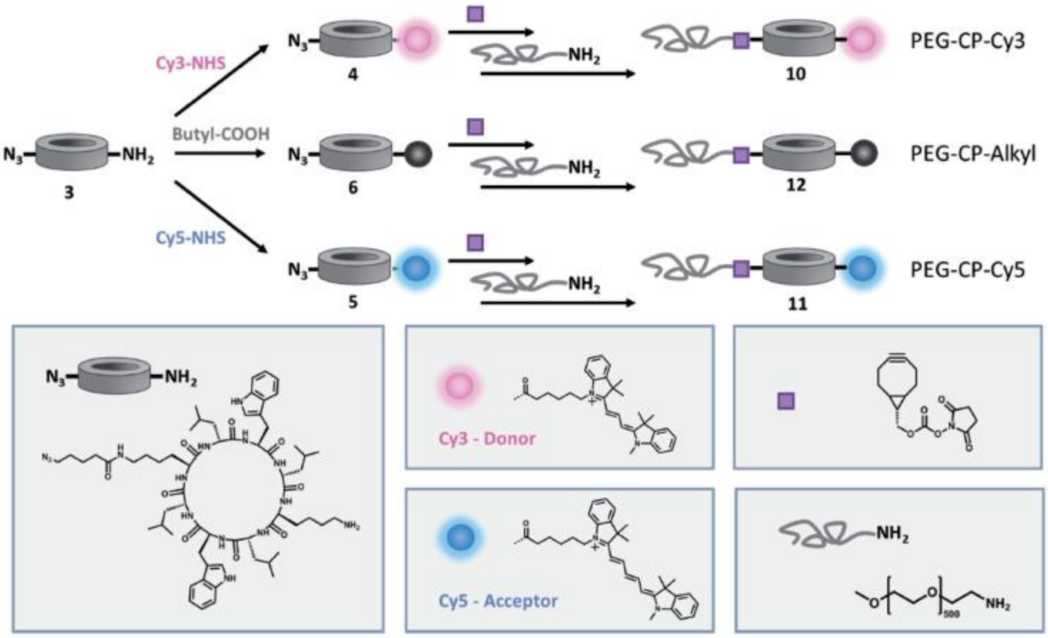


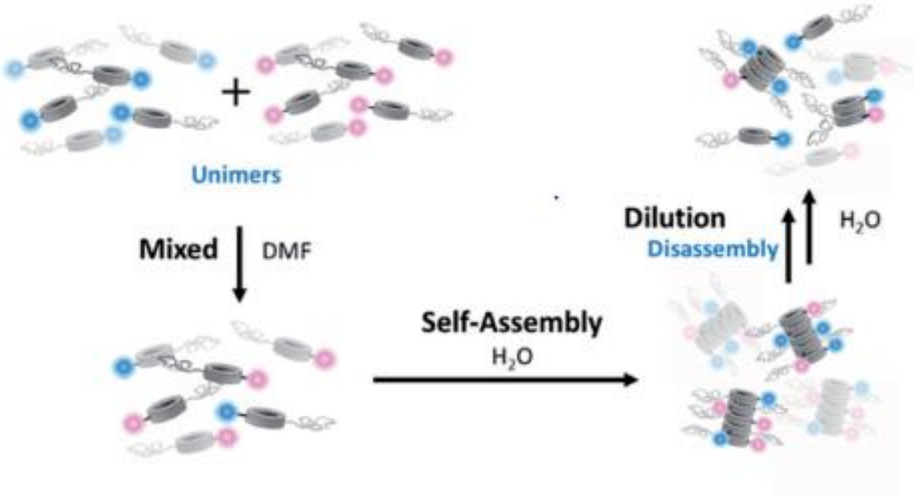
Chiral macrocyclic receptors 1 with multiple hydrogenbonding sites in the cavity were synthesized and used as NMR chiral solvating agents (CSAs). The Suzuki−Miyaura cross-coupling reaction gave rapid access to a series of variants 1b−p of unsubstituted parent compound 1a. Among them, 1d with the 4-cyanophenyl group at the 3,3-positions of the binaphthyl moiety was the most excellent CSA for a benchmark analyte compound, 2-chloropropionic acid (CPA); both of the quartet and doublet signals of CPA were split most completely in $CDCl_3$. Binding constants (Ka) determined in $CDCl_3$ by NMR titrations indicated that (R)-1d was the most enantioselective (Ka(S)/Ka(R) = 5.4). Interestingly, the Ka value of (R)-1d for (S)-CPA (5900) was greater than that of (R)-1a for (S)-CPA (3080), which strongly suggests an attractive interaction between the 4-cyanophenyl group of (R)-1d and (S)-CPA. The X-ray crystal structure of 1d indicates that one of the two H atoms meta to the cyano group is directed toward the cavity. DFT calculations suggested that this H atom of the 4-cyanophenyl group of (R)-1d forms a weak hydrogen bond with the Cl atom of (S)-CPA (C−H···Cl−C hydrogen bond).

Comment: This paper could be proposed as a method to obtain a macrocyle on the strator of the molecular motor. And the multiple hydrogen-bond containning chiral macrocyclic receptor have potential to construct hydrogen bond-based supramolecular materials

Probing the Dynamic Nature of Self-Assembling Cyclic Peptide–Polymer Nanotubes in Solution and in Mammalian Cells

Rho, J. Y.; Brendel, J. C.; MacFarlane, L. R.; Mansfield, E. D.; Peltier, R.; Rogers, S.; Perrier, S.* *Adv. Funt. Mater* **2018** *24*, 1704569.



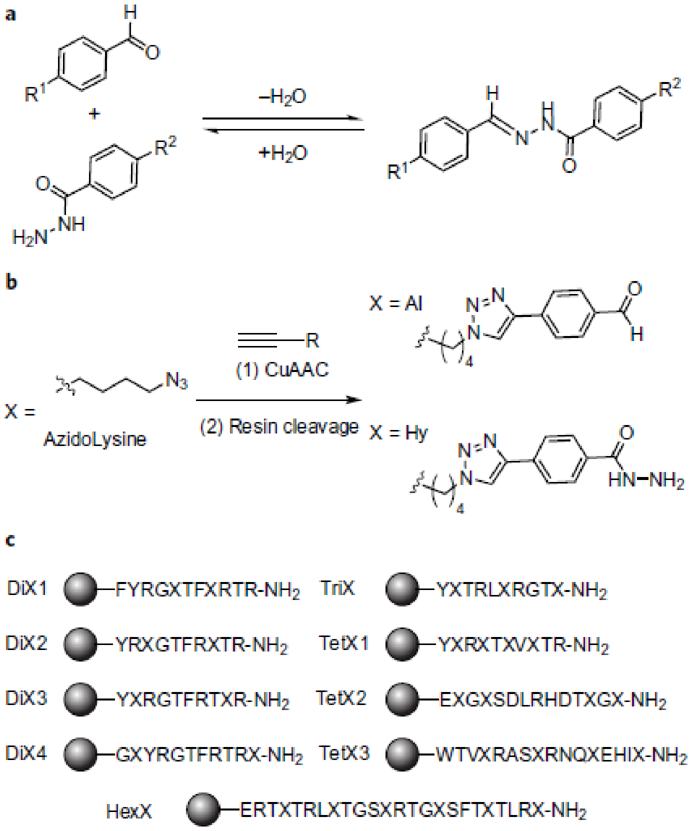


Self-assembling cyclic peptide–polymer nanotubes have emerged as a fascinating supramolecular system, well suited for a diverse range of biomedical applications. Due to their well-defined diameter, tunable peptide anatomy, and ability to disassemble in situ, they have been investigated as promising materials for numerous applications including biosensors, antimicrobials, and drug delivery. Despite this continuous effort, the underlying mechanisms of assembly and disassembly are still not fully understood. In particular, **the exchange of units between individual assembled nanotubes has been overlooked so far**, despite its knowledge being essential for understanding their behavior in different environments. To investigate the dynamic nature of these systems, cyclic peptide–polymer nanotubes are synthesized, conjugated with complementary dyes, which undergo a Förster resonance energy transfer (FRET) in close proximity. Model conjugates enable to demonstrate not only that their self-assembly is highly dynamic and not kinetically trapped, but also that the self-assembly of the conjugates is strongly influenced by both solvent and concentration. Additionally, the versatility of the FRET system allows studying the dynamic exchange of these systems in mammalian cells in vitro using confocal microscopy, demonstrating the exchange of subunits between assembled nanotubes in the highly complex environment of a cell.

Comment: In this study, Foster resonance energy transfer was used as a tool to demonstrate the dynamic behavior of self-assembling cyclic peptide-polymer nanotubes in polar and nonpolar environments, which could also apply to our dynamic methyl-cysteine polymer system.

Dynamic Covalent Chemistry Enables Formation of Antimicrobial Peptide Quaternary Assemblies in a Completely Abiotic Manner

Reuther, J. F.; Dees, J. L.; Kolesnichenko, I. V.; Hernandez, E. T.; Ukraintsev, D. V.; Guduru, R.; Anslyn, E. V.* *Nat. Chem.* **2018** *10*, 45.

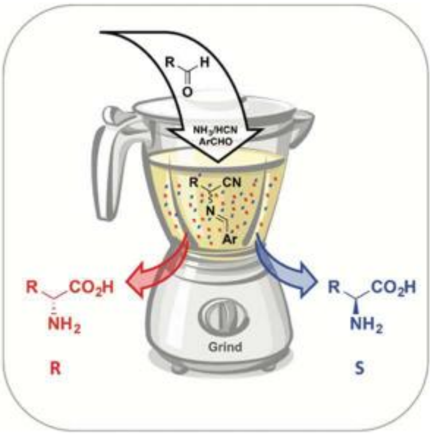


Naturally occurring peptides and proteins often use dynamic disulfide bonds to impart defined tertiary/quaternary structures for the formation of binding pockets with uniform size and function. Although peptide synthesis and modification are well established, controlling quaternary structure formation remains a significant challenge. Here, we report the facile incorporation of aryl aldehyde and acyl hydrazide functionalities into peptide oligomers via solid-phase copper-catalysed azide–alkyne cycloaddition (SP-CuAAC) click reactions. When mixed, these complementary functional groups rapidly react in aqueous media at neutral pH to form peptide–peptide intermolecular macrocycles with highly tunable ring sizes. Moreover, sequence-specific figure-of-eight, dumbbell-shaped, zipper-like and multi-loop quaternary structures were formed selectively. Controlling the proportions of reacting peptides with mismatched numbers of complementary reactive groups results in the formation of higher-molecular-weight sequence-defined ladder polymers. This also amplified antimicrobial effectiveness in select cases. This strategy represents a general approach to the creation of complex abiotic peptide quaternary structures.

Comment: One could also imagine to investigate the effect of a methyl group on cysteines on tertiary/quaternary structures of simple proteins.

The Strecker Reaction Coupled to Viedma Ripening: a Simple Route to Highly Hindered Enantiomerically Pure Amino Acids

Baglai, I.; Leeman, M.; Wurst, K.; Kaptein, B.; Kellogg, R. M.; Noorduin, W. L.* *Chem. Commun.*, **2018**, Advance Article.



The Strecker reaction is broadly used for the preparation of α-amino acids. However, control of enantioselectivity remains challenging. We here couple the **Strecker reaction to Viedma ripening** for the **absolute asymmetric synthesis of highly sterically hindered α-amino acids**. As proof-of-principle, the enantiomerically pure α-amino acids tert-leucine and 1-adamantylglycine were obtained.

Comment: A remarkable work allowing us to obtain enantiomerically pure α-amino acids. This paper may be useful for Yali and her future peptides teammates. The main assertion of this article is that there are "**two strategies** [...] **to obtain enantioselectivity** by means of an asymmetric Strecker reaction [...] **both approaches** still require **protecting groups and chiral reagents** that **need to be removed** after the reaction". However, the method exposed requires the crystallisation of the amide synthesised. If the amide cannot be crystallised, then it becomes necessary to introduce an imine in the system and to remove it, thus reducing the interest of this approach.