Supramolecular Electropolymerization

Ellis, K. T.; Galerne, M.; Armao IV, J. J.; Osypenko, A. ; Martel, D. ; Maaloum, M. ; Fuks, G. ; Moulin, E. ; Gavat, O. ; Giuseppone, N. * <u>Angew. Chem. Int. Ed. ASAP.</u>.



Gaining control over supramolecular polymerization mechanisms is of high fundamental interest to understand self-assembly and self-organization processes at nanoscale. It is also expected to significantly impact the design and improve the efficiency of advanced materials and devices. Up to now, supramolecular polymerization has been shown to take place from unimers in solution, mainly by variations of temperature or of concentration. Here we show that supramolecular nucleation-growth of triarylamine monomers can be triggered by electrochemistry in various solvents. The involved mechanism offers new opportunities to precisely address in space and time the nucleation of supramolecular polymers at an electrode. To illustrate the potential of this methodology, we grow and orient supramolecular nanowires over several tens of micrometers in between different types of commercially available electrodes submitted to a single DC electric field, reaching a precision unprecedented in the literature.

Comment: What a fantastic article! Every human (or similar) should read this work, breathtaking! To be a bit more serious, congrats to all the authors of the paper and especially to Melodie for her obstinacy. Damien trying to be serious; do ask him questions about the paper since he enjoyed so much, apparently.

Substrate-Induced Self-Assembly of Cooperative Catalysts

Manuna, S. P.; Ragazzon, G.; Dupont, J.; Ren, C.; Chen, J.; Prins, J. L.* <u>Angew. Chem. Int.</u> <u>Ed. ASAP.</u>



Biomacromolecular nanotubes play important physiological roles in transmembrane ion/molecule channeling, intracellular transport and inter-cellular communications. While

genetically encoded protein nanotubes are predominant in vivo, the in vitro construction of biomimetic DNA nanotubes has attracted intense interest with the rise of structural DNA nanotechnology. The abiotic use of DNA assembly provides a powerful bottom-up approach for the rational construction of complex materials with arbitrary size and shape at the nanoscale. More specifically, a typical DNA nanotube can be assembled either with parallel-aligned DNA duplexes or by closing DNA tile lattices. These artificial DNA nanotubes can be tailored and site-specifically modified to realize biomimetic functions including ionic or molecular channeling, bioreactors, drug delivery and biomolecular sensing. In this Minireview, we aim to summarize recent advances in design strategies, including the characterization and applications of biomimetic DNA nanotubes.

Comment: Interesting article about an out of equilibrium structure driven by the consumtion of ATP. The system promotes the formation of a supramolecular cooperative catalyst which can induce the formation of the out of equilibrium structure. This system could be compared with the micellar molecular motor and could be adapted to the triarylamine to modulate the self-assembled structure.

Dynamic Covalent Hydrazone Supramolecular Polymers toward Multiresponsive Self-Assembled Nanowire System

Kim, K.-S.; Cho, H. J.; Lee, J.; Ha, S.; Song, S. G.; Kim, S.; Yun, W. S.; Kim, S. K.; Huh, J.*; Song, C.* *Macromolecules* **2018**, *51*, 8278.



Stimuli-responsive polymeric systems are of considerable interest due to their potential applications in environment-adaptive technologies such as smart surfaces. Traditionally, such systems can be constructed either by dynamic noncovalent (supramolecular) or dynamic covalent chemistry, but the use of both chemistries in one system may offer unique opportunities for structural diversity and various controllability. Herein, we report that hydrazone-pyridinum conjugates, which can be dynamically exchanged by transimination, assemble to form one-dimensional nanowires due to direct intermolecular interactions (without metal-ion coordination). The self-assembly process can be controlled not only by dynamic covalent chemistry but also by pH adjustment. The hydrazone-pyridinum conjugates are transformed to merocyanine-type dyes of distinctive negative solvatochromism via deprotonation, which also affects their self-assembly. Such a dual control of the dynamic molecular assembly will provide unique way to develop diverse smart nanomaterials with multistimuli-responsiveness.

Comment: The authors report here one way to tune material using dynamic covalent bonds. Indepth analysis and theoretical discussions are to be mentioned.

Dynamic Cross-Linking of Polyethylene via Sextuple Hydrogen Bonding Array

Tellers, J.; Canossa, S.; Pinalli, R.; Soliman, M.; Vachon, J.*; Dalcanale, E.* <u>Macromolecules</u> 2018, *51*, 7680.



Multiple hydrogen bonding motifs are promising tools for polymer functionalization to obtain adaptable networks combining advantages of permanently cross-linked systems with processability of thermoplastics. Here we describe the use of a new multiple hydrogen bonding motif to impart increased tensile strength, stiffness, barrier properties, and a plateau modulus after melting to functional polyolefins, while retaining adaptability of the polymer network. The cross-linked nature of these polymers was elucidated by thermal and mechanical analysis, revealing a raised glass transition and rheology similar to permanently cross-linked polymer matrices. The apolar polymer matrix was found to stabilize the new hydrogen bonding motif at elevated temperatures. The resulting polymer showed thermal resistance superior to ureidopyrimidone (UPy) motif functionalized materials, the most commonly employed synthetic multiple hydrogen bonding motif to date.

Comment: An interesting self-dimerizing sextuple hydrogen-bonding motif showing very good mechanical properties. The synthesis is easy: one pot reaction and a short work-up.

Paper Origami-Inspired Design and Actuation of DNA Nanomachines with Complex Motions

Zhou, L.; Marras, A. E.; Huang, C.-M.; Castro, C. E.*; Su, H.-J.* *Small* **2018**, *6*, 1802580. 1802580.



Significant progress in DNA nanotechnology has accelerated the development of molecular machines with functions like macroscale machines. However, the mobility of DNA self-assembled nanorobots is still dramatically limited due to challenges with designing and controlling nanoscale systems with many degrees of freedom. Here, an origami-inspired method to design transformable DNA nanomachines is presented. This approach integrates stiff panels formed by bundles of double-stranded DNA connected with foldable creases formed by single-stranded DNA. To demonstrate the method, a DNA version of the paper origami mechanism called a waterbomb base (WBB) consisting of six panels connected by six joints is constructed. This nanoscale WBB can follow four distinct motion paths to transform between five distinct configurations including a flat square, two triangles, a rectangle, and a fully compacted trapezoidal shape. To achieve this, the sequence specificity of DNA base-pairing is leveraged for the selective actuation of joints and the ion-sensitivity of base-stacking interactions is employed for the flattening of joints. In addition, higher-order assembly of DNA WBBs into reconfigurable arrays is achieved. This work establishes a foundation for origami-inspired design for next generation synthetic molecular robots and reconfigurable nanomaterials enabling more complex and controllable motion.

Comment: I think it's a nice example of bio-nanomachines, as I like origami too. With (a lot) more work, we could think of drug encapsulation in those nanorobot and selective delivery as the motion is controllable.

Carbocation Catalysed Ring Closing Aldehyde–Olefin Metathesis

Ni, S.; Franzén, J.* Chem. Commun., 2018, Advance Article.



A highly efficient aldehyde–olefin metathesis catalysed by the carbocation, 4phenylphenyl-diphenylmethylium ion, has been developed. This protocol is characterized by high yields, low catalyst loading (down to 2 mol%), good functional group compatibility and mild reaction conditions.

Comment: This short article details the elaboration of a new approach in the metathesis if aldehyde and olefin. The principle sounds easy and the process seems efficient. Unfortunately, the abstract may mislead you. Indeed, the "**highly efficient metathesis**" usually shows an **80% yield**, with a maximum of 86%. Moreover, the terms "good functional group compatibility" is also not very accurate. Only 20 examples have been tested and some of them even present low yield, around 26-40%. Finally, because of the carbocation nature of the catalyst, it is impossible to use any nucleophile functionality without protecting it beforehand.

Facile Preparation of Phospholipid–Amorphous Calcium Carbonate Hybrid Nanoparticles: Toward Controllable Burst Drug Release and Enhanced Tumor Penetration

Wang, C.; Liu, X.; Chen, S.; Hu, F.; Sun, J.*; Yuan, H.* <u>Chem. Commun.</u>, 2018, Advance Article.



A facile solvent diffusion method was developed to prepare phospholipid–amorphous calcium carbonate (ACC) hybrid nanoparticles via a one-pot approach. The hybrid nanoparticles can specifically realize water-responsive burst drug release in cancer cells and potentiate drug penetration into deep tumor tissues for advanced cancer therapy.

Comment: I have to admit that, at first, I chose this article because of its incredible picture. I would never expect this kind of things in a scientific paper. However, after reading the article, I found it quite interesting. Indeed, the authors made a complete study of their nanoparticles, from the synthesis to the application *in vivo* on mice. They are using a panel of technics to characterize them that is always useful to keep in mind.

On Demand Switching of Polymerization Mechanism and Monomer Selectivity with Orthogonal Stimuli

Peterson, B. M.; Kottisch, V.; Supej, M. J.; Fors, B. P.* ACS Cent. Sci. 2018, 4, 1228.



The development of next-generation materials is coupled with the ability to predictably and precisely synthesize polymers with well-defined structures and architectures. In this regard, the discovery of synthetic strategies that allow on demand control over monomer connectivity during polymerization would provide access to complex structures in a modular fashion and remains a grand challenge in polymer chemistry. In this Article, we report a method where monomer selectivity is controlled during the polymerization by the application of two orthogonal stimuli. Specifically, we developed a cationic polymerization where polymer chain growth is controlled by a chemical stimulus and paired it with a compatible photocontrolled radical polymerization. By alternating the application of the chemical and photochemical stimuli the incorporation of vinyl ethers and acrylates could be dictated by switching between cationic and radical polymerization mechanisms, respectively. This enables the synthesis of multiblock copolymers where each block length is governed by the amount of time a stimulus is applied, and the quantity of blocks is determined by the number of times the two stimuli are toggled. This new

method allows on demand control over polymer structure with external influences and highlights the potential for using stimuli-controlled polymerizations to access novel materials.

Comment: A good first step towards one-pot sequence-controlled polymer synthesis. Even if the dispersity is not the best, it still is relatively good (1.11). They used their previously-published cationic polymerization and then tuned the catalysis to work in the same conditions for radical polymerization, so it is not a completely new system or polymerization reaction system but it is still quite a feat.

Expanding the Chemical Space of Biocompatible Fluorophores: Nanohoops in Cells

White, B. M.; Zhao, Y.; Kawashima, T. E.; Branchaud, B. P.; Pluth, M. D.*; Jasti, R.* <u>ACS</u> <u>Cent. Sci. 2018, 4, 1173.</u>



The design and optimization of fluorescent molecules has driven the ability to interrogate complex biological events in real time. Notably, most advances in bioimaging fluorophores are based on optimization of core structures that have been known for over a century. Recently, new synthetic methods have resulted in an explosion of nonplanar conjugated macrocyclic molecules with unique optical properties yet to be harnessed in a biological context. Herein we report the synthesis of the first aqueous-soluble carbon nanohoop (i.e., a macrocyclic slice of a carbon nanotube prepared via organic synthesis) and demonstrate its bioimaging capabilities in live cells. Moreover, we illustrate that these scaffolds can be easily modified by well-established "click" chemistry to enable targeted live cell imaging. This work establishes the nanohoops as an exciting new class of macrocyclic fluorophores poised for further development as novel bioimaging tools.

Comment: As they say in the introduction, it is incredible that we are still using in biology coloring agents discovered a long time ago and that most of the different dyes are just structural modifications of these old coloring agents. Here is a dye inspired by CNTs with a completely different structure from the old ones and hopefully some completely different imaging limitations.

Organoids: The Body Builders

Eisenstein, M.* Nat. Meth. 2018, 15, 19.



Inside every stem cell is an organ waiting to happen-biologists have known this for generations. But only recently have they learned how readily that potential can be unlocked in culture. With relatively minimal coaxing, researchers around the world are now converting stem cells into organized threedimensional (3D) 'organoid' assemblies that mimic the structure and function of organs ranging from the colon to the brain. "The power that these cells have after hundreds of millions of years of evolution to build a higher-order structure is just incredible," says Hans Clevers, a leader in the field, based at the Hubrecht Institute in the Netherlands. Many researchers stumbled upon these capabilities through a process they describe as 'chance' or 'serendipity'. For example, Madeline Lancaster's cerebral organoids were born from a happy accident while cultivating mouse neural stem cells as a postdoc in Jürgen Knoblich's lab at the Institute of Molecular Biology in Austria. "We had some leftover reagents for making the cells stick to the dish, but these had probably gone bad because the cells didn't stick," says Lancaster. "Instead, they formed these really interesting spherical 3D structures." When she transferred these spheres to a solid substrate, they formed simple cortical structures with virtually no further intervention. Of course, these primitive assemblies are only starting points, and researchers in this field are working hard to make organoid production more robust, reproducible and representative of in vivo tissues. But the rewards have already been considerable, with early efforts clearly demonstrating the power of organoids as tools for developmental biology, disease research and regenerative medicine.

Comment: The abstract was very lack-luster (2 lines) so this was the introduction of the review/summary on this method. This is quite far from our research field; however, I feel like it is something that you ought to know about. Stem cells have always been a remarkable potential source of advancements in biology and knowing that we are getting close to "growing" organs –or tumors– to study them, it seems like an important topic to follow. Furthermore, Nature Methods has chosen this method to be their method of the year.

Peroxisome-targeted Supramolecular Nanoprobes Assembled with Pyrenelabelled Peptide Amphiphiles

Kim, I.; Bang, W. Y.; Kim, S.; Jin, S. M.; Hyun, J. Y.; Han, E. H. *; Lee, E.*; <u>*Chem. Asian J.*</u> 2018, *Accepted Article*



Despite the versatile metabolic functions of peroxisomes such as lipid synthesis and fatty acid oxidation and their relevance to genetically inherited diseases, namely, peroxisome biogenesis disorders and peroxisomal enzyme deficiency, there is not much research on peroxisome-targeting therapeutics. Herein we present supramolecular nanostructured probes based on the self-assembly of peptide amphiphiles (PAs) having peroxisome-targeting ability in mammalian cells. The PA was designed to include the peroxisome-targeting tripeptide (SKL) and a fluorescent dye (pyrene). It was revealed that the presence of the SKL-appended carboxyl terminal group of PA, the extent of α -helical nature of the peptide block, and the fibrillar morphology of nano-assemblies affected the targeting efficiency of PA supramolecular nanoprobe. The simple modification of PAs by the peroxisome-targeting strength prediction showed an enhanced peroxisome specificity, as expected. This work provides important insights into designing subcellular organelle-targeting nanoparticles for next-generation nanomedicines. A peroxisome-targetable supramolecular nanoprobe was prepared based on the aqueous self-assembly of peptide amphiphiles containing SKL-COOH, which can be recognized by the peroxisome targeting signal receptor type 1 of the peroxisome membrane.

Comment: It's a nice work aiming to find applications of peptide amphiphiles self-assembly in targeting cell.

Tunable Fluorescence from a Responsive Hyperbranched Polymer with Spatially Arranged Fluorophore Arrays

Cao, X.; Gan, W.; Shi, Y.; Xu, H.; Gao, H *; Chem. Asian J. 2018, Accepted Article



In the present study, a water-soluble hyperbranched polymer platform that contained a Förster resonance energy transfer (FRET) array and exhibited varied fluorescence in response to solvent, light, and CN- anion stimuli was constructed. The use of chain-growth copper-catalyzed azide-alkyne cycloaddition polymerization (CuAACP) enabled accurate control of the ratio and distance of three incorporated fluorophores, coumarin (Cou), nitrobenzoxadiazole (NBD), and photoswitchable spiropyran (SP), that could be reversibly transformed into the red-emitting merocyanine (MC) state. Within the FRET system, the energy flow from Cou to MC was significantly enhanced by the introduction of NBD as a central fluorophore relay. Moreover, the energy-transfer efficiency was increased by changing the solvent from tetrahydrofuran to more

polar water; this was accompanied by a clear color change and fluorescence behavior. These correlations of polymer composition and solvent polarity to the FRET efficiency were finally applied to the effective detection of CN⁻ anion; thus demonstrating a function of this polymer as a CN⁻ sensor. Chameleon-like nanoparticles: A water-soluble hyperbranched polymer platform that contained a Förster resonance energy transfer (FRET) array and exhibited varied fluorescence in response to light, solvent, and CN⁻ anion stimuli was constructed (see figure). The use of click chemistry polymerization enabled accurate control of the ratio and distance of three incorporated fluorophores for sensor applications.

Comment: Hyperbranched polymers form chameleon-like nanoparticles that can be used as a CN⁻ sensor.

A Chemoselective Strategy for Late-Stage Functionalization of Complex Small Molecules with Polypeptides and Proteins

Cohen D. T.; Cohen C.; Fadzen C. M.; Mijalis A. J.; Hie L.; Johnson K. D.; Shriver Z.; Plante O.; Miller S. J.; Buchwald S. L.; Pentelute B. L.* *Nat. Chem.* **2018**, ASAP.



Conjugates between proteins and small molecules enable access to a vast chemical space that is not achievable with either type of molecule alone; however, the paucity of specific reactions capable of functionalizing proteins and natural products presents a formidable challenge for preparing conjugates. Here we report a strategy for conjugating electron-rich (hetero)arenes to polypeptides and proteins. Our bioconjugation technique exploits the electrophilic reactivity of an oxidized selenocysteine residue in polypeptides and proteins, and the electron-rich character of certain small molecules to provide bioconjugates in excellent yields under mild conditions. This conjugation chemistry enabled the synthesis of peptide-vancomycin conjugates without the prefunctionalization of vancomycin. These conjugates have an enhanced in vitro potency for resistant Gram-positive and Gram-negative pathogens. Additionally, we show that a 6 kDa affibody protein and a 150 kDa immunoglobulin-G antibody could be modified without diminishing bioactivity.

Comment: The research of developing new strategy for the conjugation between proteins and small molecules is always a hot and useful topic.

Light-Driven Molecular Trap Enables Bidirectional Manipulation of Dynamic Covalent Systems

Kathan, M.; Eisenreich, F.; Jurissek, C.; Dallmann, A.; Gurke, J.; Hecht, S.* Nat. Chem. 2018,

a 313 nm Ar S OH 10, 1031. 660 nm Ar S OH 11'A/H NHR

+ H₂NR, H

+ H₂O

III_{A/H}

NHR

Ш

(5.0

Tauto

Conde

IV'_{A/H}

IV' (23.0)

III' (13.7) IV_{A/H}

313 nm

ŇH₀R

(0.0)



Comment: It's a new methodology for manipulating the outcome of a reversible chemical reaction.

Oscillations, travelling fronts and patterns in a supramolecular system

b

(23.9)

Taute

(8.8)

(15.6)

Leira-Iglesias, J.; Tassoni, A.; Adachi, T.; Stich, M.; Hermans, T. M.* <u>Nat. Nanotechnol. 2018</u>, <u>ASAP</u>.



Supramolecular polymers, such as microtubules, operate under non-equilibrium conditions to drive crucial functions in cells, such as motility, division and organelle transport. In vivo and in vitro size oscillations of individual microtubules (dynamic instabilities) and collective oscillations4 have been observed. In addition, dynamic spatial structures, like waves and polygons, can form in non-stirred systems. Here we describe an artificial supramolecular polymer made of a perylene diimide derivative that displays oscillations, travelling fronts and centimetre-scale self-organized patterns when pushed far from equilibrium by chemical fuels. Oscillations arise from a positive feedback due to nucleation–elongation–fragmentation, and a negative feedback due to sizedependent depolymerization. Travelling fronts and patterns form due to self-assembly induced density differences that cause system-wide convection. In our system, the species responsible for the nonlinear dynamics and those that self-assemble are one and the same. In contrast, other reported oscillating assemblies formed by vesicles, micelles or particles rely on the combination of a known chemical oscillator and a stimuliresponsive system, either by communication through the solvent (for example, by changing pH), or by anchoring one of the species covalently (for example, a Belousov–Zhabotinsky catalyst). The design of self-oscillating supramolecular polymers and large-scale dissipative structures brings us closer to the creation of more life-like materials that respond to external stimuli similarly to living cells, or to creating artificial autonomous chemical robots.

Comment: Using the small molecules to rationally design the self-oscillating supramolecular polymers, providing us a way to smarter materials and artificial chemical robots. The next steps from this research should be to add functionality. Just as Job Boekhoven wrote "the forces generated by oscillating structures could serve as an artificial cytosketelon that induces the division of a phospholipid vesicle, thus coupling the division of artificial cell to an externally fuelled clock".

Bacteria photosensitized by intracellular gold nanoclusters for solar fuel production

Zhang, H.; Liu1, H.; Tian, Z.; Lu, D.; Yu, Y.; Cestellos-Blanco, S.; Sakimoto, K. K.; Yang, P. *Nat. Nanotechnol.* **2018**, *ASAP*.



The demand for renewable and sustainable fuel has prompted the rapid development of advanced nanotechnologies to effectively harness solar power. The construction of photosynthetic biohybrid systems (PBSs) aims to link preassembled biosynthetic pathways with inorganic light absorbers. This strategy inherits both the high light-harvesting efficiency of solid-state semiconductors and the superior catalytic performance of whole-cell microorganisms. Here, we introduce an intracellular, biocompatible light absorber, in the form of gold nanoclusters (AuNCs), to circumvent the sluggish kinetics of electron transfer for existing PBSs. Translocation of these AuNCs into non-photosynthetic bacteria enables photosynthesis of acetic acid from CO2. The AuNCs also serve as inhibitors of reactive oxygen species (ROS) to maintain high bacterium viability. With the dual advantages of light absorption and biocompatibility, this new generation of PBS can efficiently harvest sunlight and transfer photogenerated electrons to cellular metabolism, realizing CO_2 fixation continuously over several days.

Comment: This paper may provide a new way to get renewable energy by using a biological method. It is quite important to get both the light-harvesting efficiency and catalytic performance, and this work achieve both of them.

Gold-Catalyzed Conversion of Lignin to Low Molecular Weight Aromatics



A heterogeneous catalyst system, employing Au nanoparticles (NPs) and Li–Al (1 : 2) layered double hydroxide (LDH) as support, showed excellent activity in aerobic oxidation of the benzylic alcohol group in β -O-4 linked lignin model dimers to the corresponding carbonyl products using molecular oxygen under atmospheric pressure. The synergistic effect between Au NPs and the basic Li–Al LDH support induces further reaction of the oxidized model compounds, facilitating facile cleavage of the β -O-4 linkage. Extension to oxidation of γ -valerolactone (GVL) extracted lignin and kraft lignin using Au/Li–Al LDH under similar conditions produced a range of aromatic monomers in high yield. Hydrolysis of the Au/Li–Al LDH oxidized lignin was found to increase the degree of lignin depolymerization, with monomer yields reaching 40% for GVL extracted lignin. Based on these results, the Au/Li–Al LDH + O₂ catalyst system shows potential to be an environmentally friendly means of depolymerizing lignin to low molecular weight aromatics under mild conditions.

Comment: As you may all know by now, we will eventually have an issue with chemicals prepared from fossil fuels. One solution would be to synthesize new platform molecules from biobased resources, lignin being one of them. The problem is, it is a hard task to depolymerize it, and even more under eco-friendly conditions. In this paper, the authors present a new system that leads to high yields (compared to what currently exists) and that is not so harmful to the environment.

A Programmable and Biomimetic Photo-Actuator: A Composite of a Photo-Liquefiable Azobenzene Derivative and Commercial Plastic Film



Many interesting deformations in nature enlighten us to develop novel mechanical systems. Here, a helical gripper was inspired by the predation motion of pythons. It grasped an object by twisting around it, which is different from conventional claw-shape grippers. To mimic this helical deformation, a soft photo-actuator was fabricated by compositing one photo-liquefiable azobenzene derivative and low-density polyethylene (LDPE) film in a specific route. The actuator was programmed to complete a reversible spiralization and despiralization motion. Upon photoirradiation, the azobenzene derivative transformed directly from **crystal to isotropic liquid** at room temperature, and the microcosmic volume changes were elegantly transferred into the fabricated bilayer films to bring about a large macroscopic deformation. The photoinduced spiral ribbons show controllable handedness and pitches, in correlation with the light intensity and the pretreatment way. It is the flexibility of the soft actuator and the strength of the helical deformation makes it possible to simulate the helical motion of pythons' predation. The actuator can grasp a **variety of objects with different sizes and shapes** showing its reliability. The bilayer actuators are **easily fabricated, manipulative and recyclable**, promising their applications as high-performance photomechanical devices.

Comment: And this week again, without any surprise, an article about a photomechanical response in an azobenzene-containing material. The main point to stress in this example is that the bending is due to the liquefaction of the azobenzene layer, changing the volume of one face of the strip. Concerning the mechanical response, the authors compare it to the predation motion of pythons because it can adapt its grasp to a variety of objects with different shapes.

Dual-Programmable Shape-Morphing and Self-Healing Organohydrogels Through Orthogonal Supramolecular Heteronetworks

Zhao, Z.; Zhuo, S.; Fang, R.; Zhang, L.; Zhou, X.; Xu, Y.; Zhang, J.; Dong, L. J. Liu, M.* <u>Adv.</u> <u>Mater. 2018</u>, 1804435.



Programmable materials that can change their inherent shapes or properties are highly desirable due to their promising applications. However, among various programmable shape-morphing materials, the single control route allows temporary states to recover the unchangeable former state, thus lacking the sophisticated programmability for their shape-encoding behaviors and mechanics. Herein, dual-programmable shape-morphing organohydrogels featuring supramolecular heteronetworks are developed. In the system, the metallo-supramolecular hydrogel framework and micro-organogels featuring semicrystalline comb-type networks independently respond to different stimuli, thereby providing orthogonal dual-switching mechanics and ultrahigh mechanical strength. The supramolecular heteronetworks also possess excellent self-healing properties. More notably, such orthogonal supramolecular heteronetworks demonstrate hierarchical shape morphing performance that far exceeds conventional shape-morphing materials. Utilizing this dual programming strategy of the orthogonal supramolecular heteronetworks, the material's permanent shape can be manipulated in a step-wise shape morphing process, thereby realizing sophisticated shape changes with a high degree of freedom. The organohydrogels can act as a biomimetic smart device for the on-demand control of unidirectional liquid transport. Based on these characteristics, it is anticipated that the supramolecular organohydrogels may serve as adaptive programmable materials for a variety of applications.

Comment: It is a unique shape-morphing system constructed by the emulsion-polymerization strategy. This material possesses several distinct shapes under different conditions, which makes sense. And another novel point is the introduction of silica nanoparticles, which maintains the hydrogel framework and homogenizes the distribution of stress under tense condition.

Rational Construction of Highly Tunable Donor-Acceptor Materials Based on a Crystalline Host-Guest Platform

Zhang, D.-S.; Gao, Q.; Chang, Z.*; Liu, X.- T; Zhao. B.; Xuan, Z.; Hu, T.-L.; Zhang, Y.-H.; Zhu, J.; Bu, X.-H.* <u>Adv. Mater. **2018**</u>, 1804602.



Organic donor-acceptor systems have attracted much attention due to their various potential applications. However, the rational construction and modulation of highly ordered donor-acceptor systems could be a challenge due to the complicated self-assembly process of donor and acceptor species. Considering the well-defined arrangement of species at the molecule level, a crystalline host-guest system could be an ideal platform for the rational construction of donor-acceptor systems. Herein, it is shown how the rational construction of highly tunable donor-acceptor materials can be achieved based on a crystalline host-guest platform. Within the well-established metal-organic framework NKU-111 as the crystalline host enabled by the relatively stable coordination-directed assembly, the introduction and arrangement of guest molecules in the crystals allow the rational construction of the NKU-111⊃guest donor-acceptor system. The donor-acceptor interaction in the systems can be readily modulated with different guest molecules, which can be justified by the well-demonstrated guest-dependent characteristics. Accordingly, the NKU-111⊃guest reveals highly tunable donor-acceptor properties such as charge-transfer-based emissions and electrical conductivity. This work indicates the potential of crystalline host-guest systems as an ideal platform for systematic investigations of donor-acceptor materials.

Comment: It is a novel crystalline host-guest system based on a MOF platform. The modulable charge-transfer was achieved via introducing different guest molecules.

Leaving Groups as Traceless Topological Modifiers for the Synthesis of Topologically Isomeric Polymer Networks

Gu, Y.; Schauenburg, D.; Bode, J. W.*; Johnson, J. A.* J. Am. Chem. Soc. 2018, 140, 14033-14037.



The chemical and topological structure of polymer networks can seldom be orthogonally controlled. For example, novel network topologies are often accessed via the direct incorporation of supramolecular assemblies into the network structure, introducing potentially undesirable chemical components. Here, we address this deficiency by programming topology into network precursors through the incorporation of self-assembly motifs in leaving groups, which become "traceless topological modifiers." Our method enables us to control polymer network topology using self-assembled structures as templates that are not themselves incorporated into the network. We demonstrate this strategy using a model network formed through potassium acyltrifluoroborate (KAT) ligation. Two four-arm polyethylene glycol (PEG)-based star polymers prepared with either O-ethyl or O-octyl carbamoyl hydroxylamine chain ends serve as network precursors, where differences in chain end hydrophobicity produce different self-assembly states in solution. Addition of a bis-KAT reagent to these star polymers induces amide bond formation and concomitant expulsion of the ethyl or octyl traceless topological modifiers, producing topologically isomeric PEG gels with identical chemical compositions yet vastly different physical properties. This work highlights the impact of topology on polymer network properties and provides a new strategy, traceless topological modification, for polymer network design.

Comment: The authors have found a very elegant way to control the topology of topologically isomeric networks in a traceless manner. To do so, they make use of carefully chosen leaving groups that will template the network before self-assembly. Using an incremental approach, they can use this method to finely tune the network topology. I like papers that make you wonder how come no one has thought about that before.

Neighboring Component Effect in a Tri-stable [2]Rotaxane

Wang, Y.; Cheng, T.; Sun, J.; Liu, Z.; Frasconi, M.; Goddard, W. A. III; Stoddart, J. F.* <u>J.</u> <u>Am. Chem. Soc. **2018**, 140, 13827-13834.</u>



The redox properties of cyclobis(paraquat-pphenylene) cyclophane (CBPQT⁴⁺) render it a uniquely variable source of recognition in the context of mechanically interlocked molecules, through aromatic donor-acceptor interactions in its fully oxidized state (CPBQT⁴⁺) and radicalpairing interactions in its partially reduced state (CBPQT²⁽⁺⁺)). Although it is expected that the fully reduced neutral state (CBPQT⁽⁰⁾) might behave as a π -donating recognition unit, resulting in a dramatic change in its binding properties when compared with the other two redox states, its role in rotaxanes has not yet been investigated. To address this challenge, we report herein the synthesis of a tri-stable [2]rotaxane in which a CBPQT⁴⁺ ring is mechanically interlocked with a dumbbell component containing five recognition sites_ (i) a bipyridinium radical cation (BIPY⁽⁺⁾) located centrally along the axis of the dumbbell, straddled by (ii) two tetrafluorophenylene units linked to (iii) two triazole rings. In addition to the selective recognition between (iv) the CBPQT⁴⁺ ring and the triazole units, and (v) the CBPQT2⁽⁺⁺⁾ ring and the reduced BIPY⁽⁺⁺⁾ unit in the dumbbell component, investigations in solution have now confirmed the presence of additional non-covalent bonding interactions between the CBPQT⁽⁰⁾ ring, acting as a donor in its neutral state, and the two tetrafluorophenylene acceptors in the dumbbell component. The unveiling of this piece of molecular recognition in a [2]rotaxane is reminiscent of the existence in much simpler, covalently linked, organic molecules of neighboring group participation (anchimeric assistance giving way to transannular interactions) in small-, medium-, and large-membered rings.

Comment: In this paper, the authors use the classical "blue-box" on a rotaxane but this time they investigate the fully reduced state. Interestingly, the reduced ring can interact with a fluorinated aromatic ring in the rotaxane whereas in solution this interaction is too weak to be observed (the binding constant is too low to be measured). This work shows the effect of the neighbors which in this case favors this interaction. It shows a new fundamental application (I love this expression) of mechanical bonding.

Dynamic Self-correcting Nucleophilic Aromatic Substitution

Ong, W. J.; Swager, T. M. Nat. Chem. 2018, 10, 1023.



Dynamic covalent chemistry, with its ability to correct synthetic dead-ends, allows for the synthesis of elaborate extended network materials in high yields. However, the limited number of reactions amenable to dynamic covalent chemistry necessarily confines the scope and functionality of materials synthesized. Here, we explore the dynamic and self-correcting nature of nucleophilic aromatic substitution (S_NAr), using *ortho*-aryldithiols and *ortho*-aryldifluorides that condense to produce redox-active thianthrene units. We demonstrate the facile construction of two-, three- and four-point junctions by reaction between a dithiol nucleophile and three different model electrophiles that produces molecules with two, three and four thianthrene moieties, respectively, in excellent yields. The regioselectivity observed is driven by thermodynamics; other connections form under kinetic control. We also show that the same chemistry can be extended to the synthesis of novel ladder macrocycles and porous polymer networks with Brunauer–Emmett–Teller surface area of up to 813 m² g⁻¹.

Comment: Dynamic covalent chemistry based on nucleophilic aromatic substitution (S_NAr) . That's how you exploit serendipity, seriously. Also, although in the paper they draw the mechanism, you should try by yourselves for fun and have a thought if you would consider it likely or not.

Substituent Effects and Mechanism in a Mechanochemical Reaction

Barbee, M. H.; Kouznetsova, T.; Barrett, S. L.; Gossweiler, G. R.; Lin, Y.; Rastogi, S. K.; Brittain, W. J.; Craig, S. L. *J. Am. Chem. Soc.* **2018**, *140*, 12746.



We report the effect of substituents on the force-induced reactivity of a spiropyran mechanophore. Using single molecule force spectroscopy, force-rate behavior was determined for a series of spiropyran derivatives substituted with H, Br, or NO₂ para to the breaking spirocyclic C–O bond. The force required to achieve the rate constants of ~10 s⁻¹ necessary to observe transitions in the force spectroscopy experiments depends on the substituent, with the more electron withdrawing substituent requiring less force. Rate constants at 375 pN were determined for all three derivatives, and the force-coupled rate dependence on substituent identity is well explained by a Hammett linear free energy relationship with a value of $\rho = 2.9$, consistent with a highly polar transition state with heterolytic, dissociative character. The methodology paves the way for further application of linear free energy relationships and physical organic methodologies to mechanochemical reactions, and the characterization of new force probes should enable additional, quantitative studies of force-coupled molecular behavior in polymeric materials.

Comment: It is not the first time that a SP ends up under an AFM force probe. Nevertheless, I like their polymer approach. I was somehow disappointed that the "mechanism" part was not really ending the on-going discussion on cleavage or concerted mechanism. But I suspect that it is a purely semantic question.