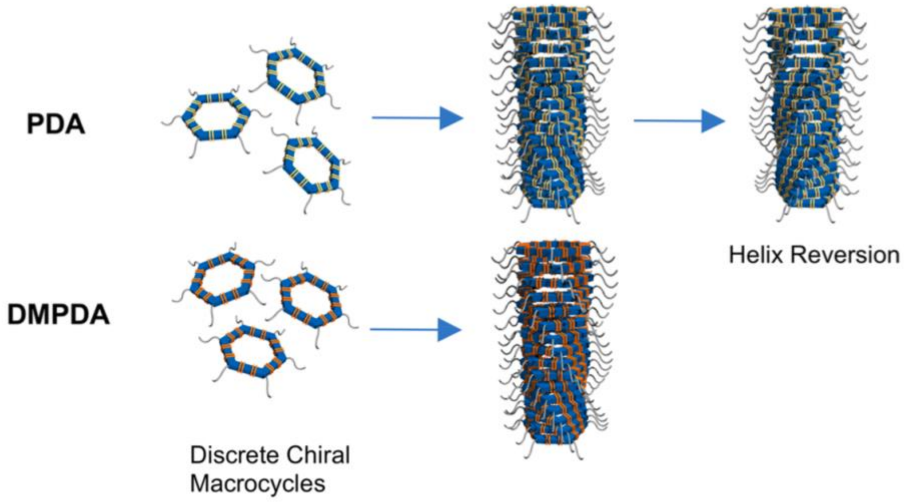
Pathway Complexity in the Stacking of Imine-Linked Macrocycles Related to Two-Dimensional Covalent Organic Frameworks

Wang, S.; Chavez, A. D.; Thomas, S.; Li, H.; Flanders, N. C.; Sun, C.; Strauss, M. J.; Chen, L. X.; Markvoort, A. J.; Brédas, J.-L.; Dichtel, W. R.* *Chem. Mater.* **2019**, *31*, 7104–7111.

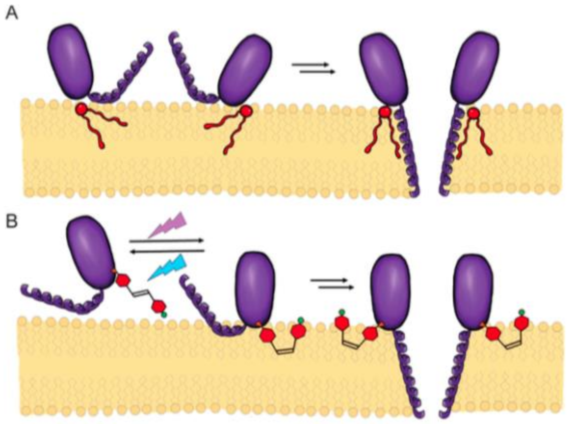


Interlayer interactions play an important role in the formation of two-dimensional covalent organic frameworks (2D COFs), yet the effects of monomer structure on COF formation, crystallinity, and susceptibility to exfoliation are not well understood. Here we probe these effects by studying the stacking behavior of imine-linked macrocycles that represent discrete models of 2D COFs. Specifically, macrocycles based on terephthaldehyde (PDA) or 2,5-dimethoxyterephthaldehyde (DMPDA) stack upon cooling molecularly dissolved solutions. Both macrocycles assemble cooperatively with similar ΔH_e values of −97 kJ/mol and −101 kJ/mol, respectively, although the DMPDA macrocycle assembly process showed a more straightforward temperature dependence. Density functional theory calculations of the stacking of PDA macrocycles suggested two stable configurations that were close in energy. Circular dichroism spectroscopy performed on macrocycles bearing chiral side chains revealed a helix reversion process for the PDA macrocycles that was not observed for the DMPDA macrocycles. **Given the structural similarity of these monomers, these findings demonstrate that the stacking processes associated with nanotubes derived from these macrocycles, as well as for the corresponding COFs, are complex and susceptible to kinetic traps, casting doubt on the relevance of thermodynamic arguments for improving materials quality.** Rather, a deeper understanding of the mechanism of supramolecular polymerization and its interplay with polymerization and error correction during COF synthesis is needed for improved control of the crystallinity and morphology of these emerging materials.

Comment: Although I am not a fan of COFs, the elegance of this macrocycle has to be enough to make it to the literature of the week. In all seriousness, ΔH_e values of −97 kJ/mol and −101 kJ/mol for a structure that does not involve H-bonding is fascinating. In addition, such large structures *can* self-assemble into long fibers, again, mainly by geometrical factors!

Reversible Photocontrolled Nanopore Assembly

Mutter, N. L.; Volarić, J.; Szymański, W.; Feringa, B. L.; Maglia, G. *J. Am. Chem. Soc.* **2019**, *141*, 14356–14363.

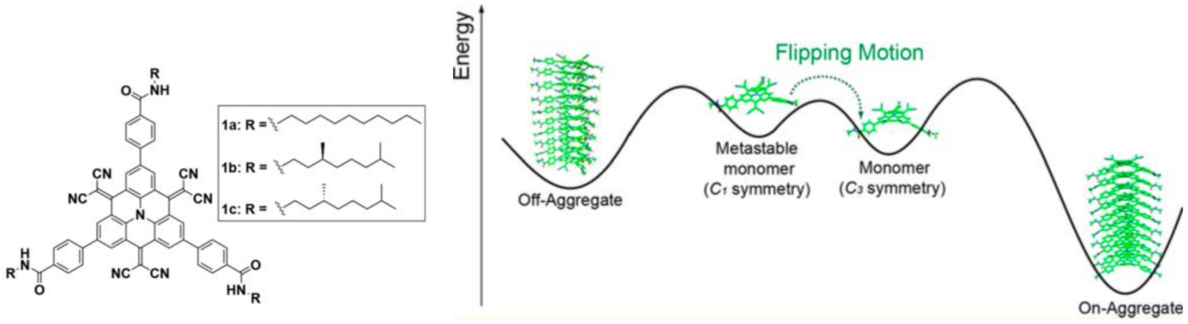


Self-assembly is a fundamental feature of biological systems, and control of such processes offers fascinating opportunities to regulate function. Fragaceatoxin C (FraC) is a toxin that upon binding to the surface of sphingomyelin-rich cells undergoes a structural metamorphosis, leading to the assembly of nanopores at the cell membrane and causing cell death. In this study we attached photoswitchable azobenzene pendants to various locations near the sphingomyelin binding pocket of FraC with the aim of remote controlling the nanopore assembly using light. **We found several constructs in which the affinity of the toxin for biological membranes could be activated or deactivated by irradiation, thus enabling reversible photocontrol of pore formation.** Notably, one construct was completely inactive in the thermally adapted state; it however induced full lysis of cultured cancer cells upon light irradiation. Selective irradiation also allowed isolation of individual nanopores in artificial lipid membranes. Photocontrolled FraC might find applications in photopharmacology for cancer therapeutics and has potential to be used for the fabrication of nanopore arrays in nanopore sensing devices, where the reconstitution, with high spatiotemporal precision, of single nanopores must be controlled.

Comment: Special delivery for Wenzhi: Mainly because here they, correctly, speak of pore formation rather that ion channels and even then they can have nice step-like behavior in the BLM (black layer membrane) experiments.

Flipping Motion To Bias the Organized Supramolecular Polymerization of N-Heterotriangulenes

Dorca, Y.; Cerdá, J.; Aragó, J.*; Ortí, E.*; Sánchez, L.* *Chem. Mater.* **2019**, *31*, 7024–7032.



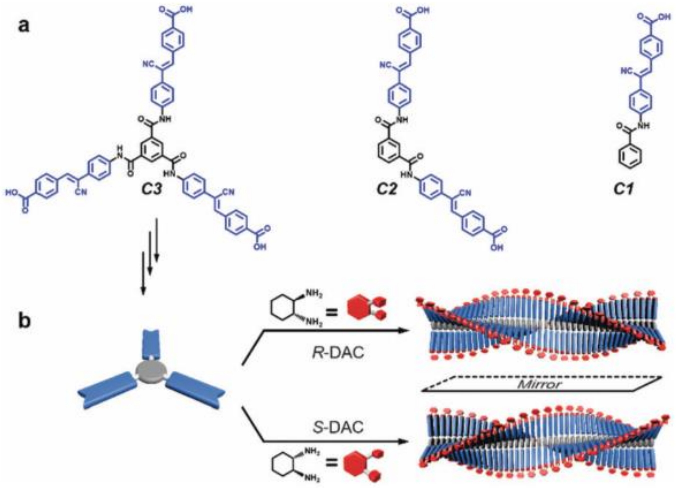
Synergistic experimental and theoretical studies have allowed the disentangling of the possible pathways for the supramolecular polymerization of a series of dicyanovinyl-bridged *N*-

heterotriangulene (NHT) derivatives bearing benzamide units with achiral (**1a**) and chiral (**1b**,**c**) side chains. The synthesis of these bowl-shaped, self-assembling units yields a mixture of monomeric species with C_3- and C_1-symmetry. Both monomeric species are able to self-assemble into different supramolecular aggregates with sufficient stability to coexist in freshly prepared solutions. The dissimilar ratio of the aggregates initially generated results in different spectroscopic features and, more specifically, in the apparition of nonmirror circular dichroism (CD) spectra for chiral **1b** and **1c**. The interconversion at room temperature of the aggregates formed by the C_3- and C_1-symmetry monomeric species is energetically unfavorable due to the steric hindrance between the neighboring dicyanovinyl groups within the aggregate. Heating the aggregates constituted by both monomeric species favors their disassembly and, at the same time, the conversion of the monomeric species with C_1-symmetry into that with C_3-symmetry by a flipping motion of one dicyanovinyl group. Cooling down the solutions back to room temperature leads to the formation of helical-like columnar aggregates based on C_3-symmetry monomers showing specular CD spectra for chiral **1b** and **1c**. The flipping motion at the molecular level described here for the bowl-shaped dicyanovinyl-bridged NHTs **1a**–**c** is, to the best of our knowledge, the only example in which a geometric change in the monomeric species, with no participation of intramolecular noncovalent interactions, is responsible for biasing the pathway complexity that yields two different stable supramolecular architectures from a single self-assembling unit.

Comment: Aside from the very obvious "look, yet another triarylamine that self-assembles", it is yet another example showing how complex these systems can become by minor details such as having more than one "stable" monomeric form.

The Chiral Amine Triggered Self-Assembly of Achiral Emissive Molecules into Circularly Polarized Luminescent Supramolecular Assemblies

Sang, Y.; Yang, D.; Duan, P.; Liu, M.* *Chem. Commun.* **2019**, *55*, 11135–11138.

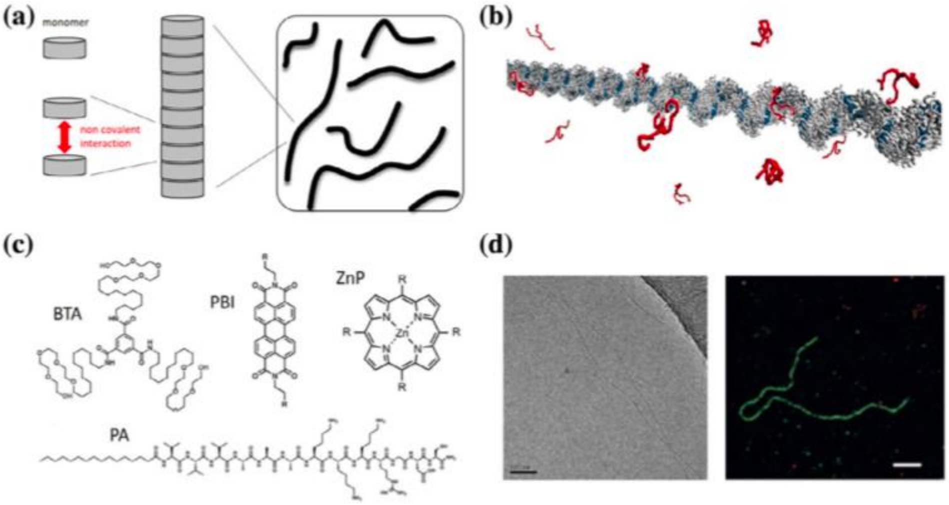


Enantiomeric diaminocyclohexane was found to trigger the self-assembly of achiral monomers into chiral supramolecular assemblies with **strong circularly polarized luminescence**.

Comment: The concept is simple: arrange known AIE in a chiral manner to induce circularly polarized emission. Very simple, very short paper, but I am not so happy about their experimental data: I really wonder if they really have the nice fibers their cartoon wants us to believe.

Molecular Modelling of Supramolecular Polymers

Bochicchio, D.; Pavan, G. M.* *Adv. Phys.* **2018**, *3*, 315–337.

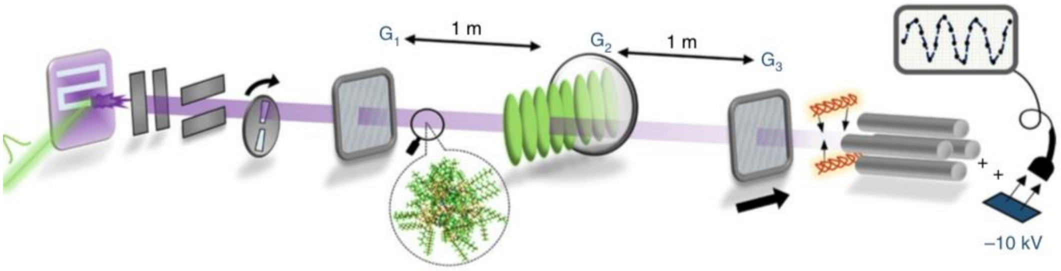


Nature uses self-assembly for building supramolecular materials possessing fascinating properties (self-healing, adaptive, reconfigurable and responsive) that are fundamental for many complex biological functions. Artificial supramolecular polymers, composed of monomers that self-assemble via non-covalent interactions, are attracting increasing interest as platforms for building innovative materials, as these possess similar bioinspired dynamic properties. However, their design still relies on an inefficient/expensive trial-and-error approach. A key question is how to design the monomers to control the properties of the supramolecular polymer. Most often, obtaining from the experiments molecular-level information on how to control these assemblies is prohibitively difficult. Molecular modelling is a fundamental support in this field, allowing investigation of the supramolecular polymer from a privileged point of view and at high-resolution. Such a 'virtual microscope' can provide information on the factors that control supramolecular polymer structure and dynamics, on the monomer–monomer interactions and their cooperativity that are precluded to the experiments, paving the way to structure–property relationships useful to advance the rational design of such materials. **This review discusses the state of the art of molecular modelling and simulation of supramolecular polymers.** The field is advancing quickly. But the detailed insight that can be reached and the continuous technical developments promise that this is only the beginning.

Comment: I am not going to claim anything regarding the quality of this review, but I will state that it is probably one of the few review out there on this subject. And regardless of the poor reputation that computer-based approaches have within the experimental community – and rightly so I should add – if we want to move away from our little "mix, heat, cold-down, voilà there is a fiber" game, computer-based methods will need to play a role. But when?! And how to make these two communities speak the same language…

Quantum Superposition of Molecules Beyond 25 kDa

Fein, Y. Y.; Geyer, P.; Zwick, P.; ka, F. K. X.; Pedalino, S.; Mayor, M.; Gerlich, S.; Arndt, M.* *Nat. Phys.* **2019**, *10*, ASAP.

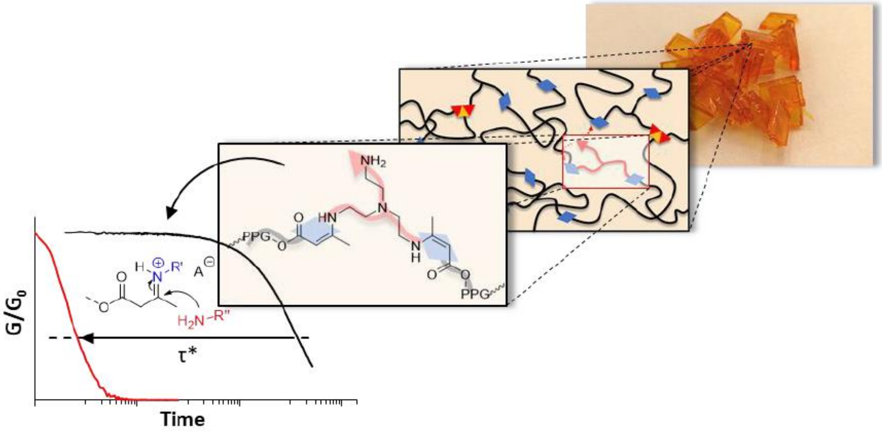


Matter-wave interference experiments provide a direct confirmation of the quantum superposition principle, a hallmark of quantum theory, and thereby constrain possible modifications to quantum mechanics. By increasing the mass of the interfering particles and the macroscopicity of the superposition, more stringent bounds can be placed on modified quantum theories such as objective collapse models. Here, we report interference of a molecular library of functionalized oligoporphyrins with masses beyond 25,000 Da and consisting of up to 2,000 atoms, by far the heaviest objects shown to exhibit matter-wave interference to date. We demonstrate quantum superposition of these massive particles by measuring interference fringes in a new 2-m-long Talbot–Lau interferometer that permits access to a wide range of particle masses with a large variety of internal states. The molecules in our study have de Broglie wavelengths down to 53 fm, five orders of magnitude smaller than the diameter of the molecules themselves. Our results show excellent agreement with quantum theory and cannot be explained classically. The interference fringes reach more than 90% of the expected visibility and the resulting macroscopicity value of 14.1 represents an order of magnitude increase over previous experiments.

Comment: No, I did not go into the details. I just decided to make my “organic chemist” and take home the message: “Hey, quantum mechanics applies to big molecules too” and the little fact that apparently the only limitation for testing bigger systems is a technical one? Fascinating.

Fast processing of highly crosslinked, low-viscosity vitrimers

Taplan, C.; Guerre M.*; Winne J. M.* and Du Prez F. E.*. *Mat. Hor.,* ***2019****, Advance article*



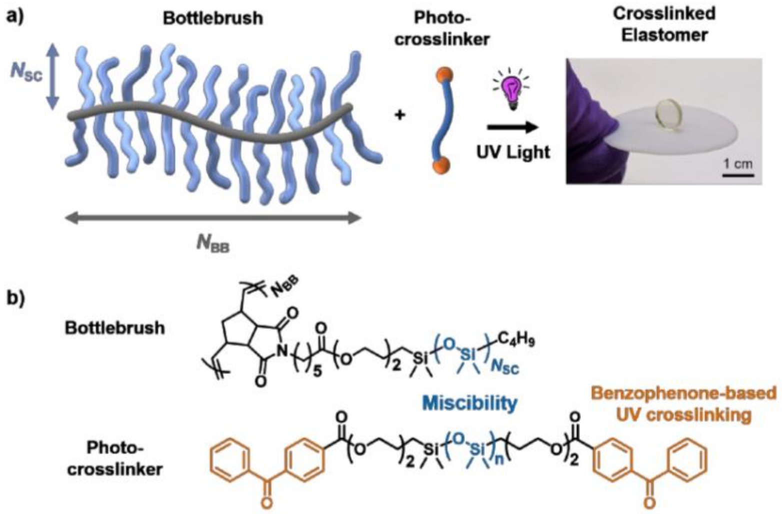
This study describes a rational approach to go beyond the current processability limits of vitrimer materials, with a demonstration of low-viscosity fast processing of highly crosslinked permanent networks. Vitrimers are a recently introduced class of polymer networks with a unique glass-like viscoelastic behavior, in which bond exchange reactions govern the macroscopic material flow.

The restricted chain mobility, only enabled by chemical exchanges, typically limits the use of continuous processing techniques, such as extrusion or injection moulding. Herein, we outline a straightforward material design approach, taking into account both the effect of minor additives on the chemistry of bond rearrangement as well as the macromolecular architecture of the vitrimeric network. These combined effects are demonstrated to work in an additive fashion, culminating in stress relaxation times below 1 s at 150 °C. The observed rapid bond exchanges in permanent networks result in an unprecedented control of the polymer material behavior, where the material flow is still dominated by chemical exchanges, but only marginally limited by the chemical exchange rate, overcoming the challenges encountered so far in continuous processing of highly crosslinked vitrimeric systems.

Comment: Vitrimers are a very hot topic. The authors have achieved here something hard: the repressibility of such materials. It relies on the same chemistry our group is using: the imine (or enamine in their case) condensation. My main remark is about the storage modulus below 1 MPa of the polymer… It is very soft, no surprise it can be reprocessed.

Super-Soft Solvent-Free Bottlebrush Elastomers for Touch Sensing

Reynolds, V. G.; Mukherjee, S.; Xie, R.; Levi, A. E.; Atassi‖, A.; Uchiyama, T.; Wang, H.; Chabinyc, M. L.* and Bates, M. B.* *Mat. Hor.*, **2019**, *Advance article*

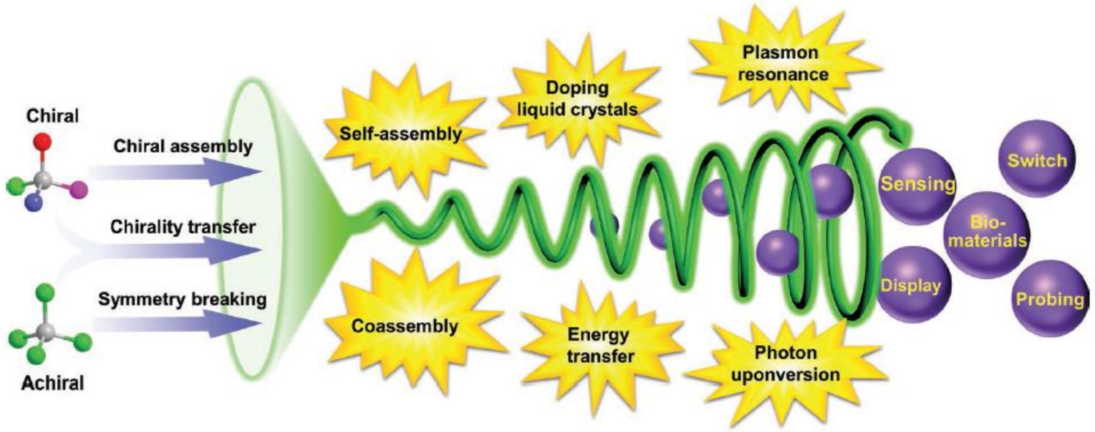


The sensitivity of capacitive pressure sensors is primarily determined by the modulus of a soft dielectric layer that reversibly deforms to produce an electrical signal. Unfortunately, the mechanical properties of conventional linear networks are constrained such that a lower limit on softness translates to poor capacitive pressure sensor performance. Here, we overcome this paradigm by leveraging the intrinsic "super-soft" characteristic of bottlebrush polymers. A simple light-induced crosslinking strategy is introduced to facilitate device fabrication and parallel plate capacitive pressure sensors constructed with these bottlebrush polymer networks exhibit up to a 53× increase in sensitivity compared to traditional material formulations, e.g., Sylgard 184. This combination of contemporary synthetic chemistry and application-driven materials design accentuates the opportunities available at the intersection of science and engineering.

Comment: This article is a hybrid between academic and applied chemistry, which is rare enough to mention it. The main novelty is the use of a bottlebrush network improving the softness of the polymer.

Organic Long-Persistent Luminescence from a Flexible and Transparent Doped Polymer

Sang, Y.; Han, J.; Zhao, T. ; Duan, P.*; Liu, M.* *Adv. Mater.* **2019**, 1900110.

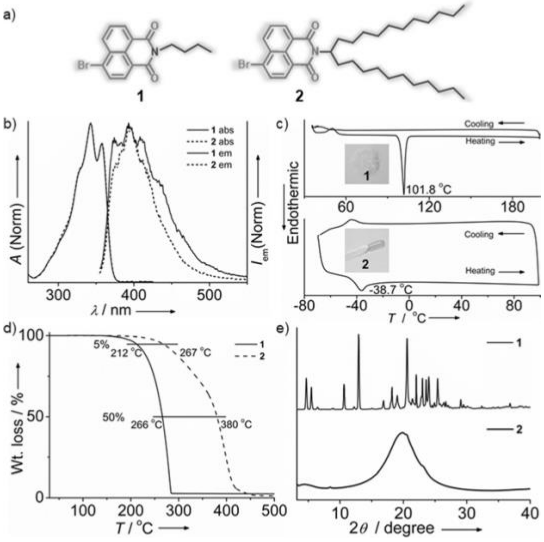


Currently, the development of circularly polarized luminescent (CPL) materials has drawn extensive attention due to the numerous potential applications in optical data storage, displays, back lights in 3D displays, and so on. While the fabrication of CPL-active materials generally requires chiral luminescent molecules, the introduction of the "self-assembly" concept offers a new perspective in obtaining the CPL-active materials. Following this approach, various self-assembled materials, including organic-, inorganic-, and hybrid systems can be endowed with CPL properties. Benefiting from the advantages of self-assembly, not only chiral molecules, but also achiral species, as well as inorganic nanoparticles have potential to be self-assembled into chiral nanoassemblies showing CPL activity. In addition, the dissymmetry factor, an important parameter of CPL materials, can be enhanced through various pathways of self-assembly. Here, the present status and progress of self-assembled nanomaterials with CPL activity are reviewed. An overview of the key factors in regulating chiral emission materials at the supramolecular level will largely boost their application in multidisciplinary fields.

Comment: This review is comprehensive and discusses the requirements and examples of CPL. I am sure that you could get some useful information from it if you are curious about CPL.

Paintable Room-Temperature Phosphorescent Liquid Formulations of Alkylated Bromonaphthalimide

Goudappagouda; Manthanath, A.; Wakchaure, V. C; Ranjeesh, K. C; Das, T.; Vanka, K.; Nakanishi, T.; Babu, S. S.* *Angew. Chem.* **2019**, *131*, 2306-2310.

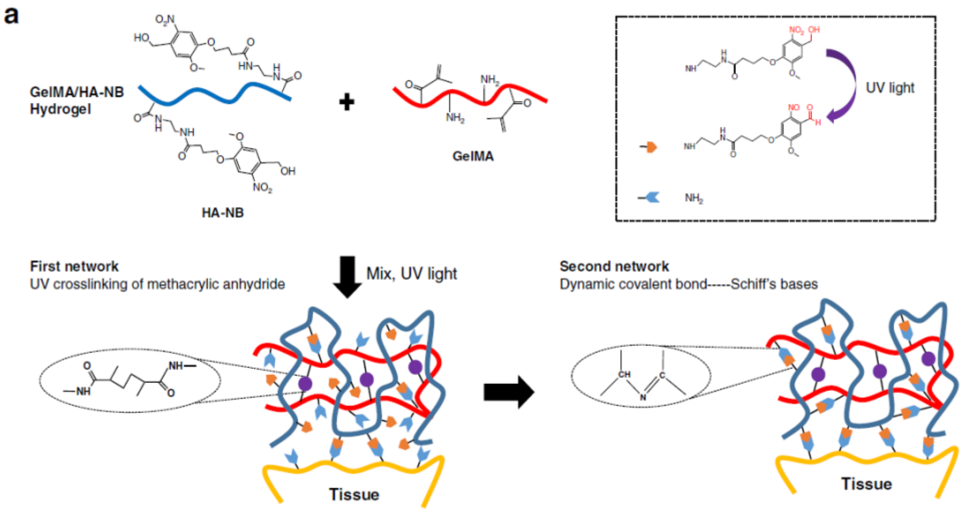


Organic phosphors have been widely explored with an understanding that crystalline molecular ordering is a requisite for enhanced intersystem crossing. In this context, we explored the room-temperature phosphorescence features of a solvent-free organic liquid phosphor in air. While alkyl chain substitution varied the physical states of the bromonaphthalimides, the phosphorescence remained unaltered for the solvent-free liquid in air. As the first report, a solvent-free liquid of a long swallow-tailed bromonaphthalimide exhibits room-temperature phosphorescence in air. Doping of the phosphor with carbonyl guests resulted in enhanced phosphorescence, and hence a large-area paintable phosphorescent liquid composite with improved lifetime and quantum yield was developed.

Comment: Here is a very simple phosphorescent system, of course, there is a reasonable story behind this paper and sufficient evidence is presented. The 50 pages supporting information help to understand the mechanism of this system and also gives me some ideas about my project.

A Strongly Adhesive Hemostatic Hydrogel for The Repair of Arterial and Heart

Hong, Y.; Zhou, F.; Hua, Y.; Zhang, X.; Ni, C.; Pan, D.; Zou, Y. * *Nat Commum.* **2019** *10,* 2060.

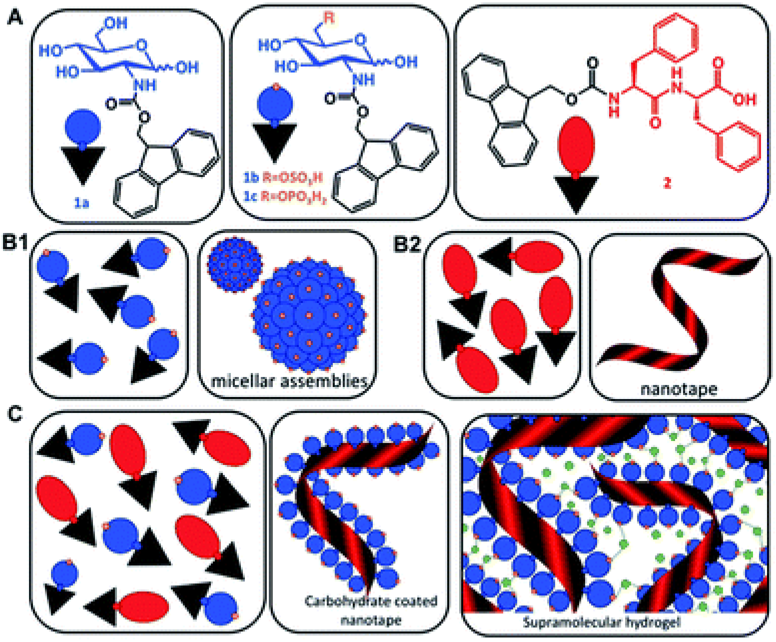


Uncontrollable bleeding is a major problem in surgical procedures and after major trauma. Existing hemostatic agents poorly control hemorrhaging from traumatic arterial and cardiac wounds because of their weak adhesion to wet and mobile tissues. Here we design a photo-reactive adhesive that mimics the extracellular matrix (ECM) composition. This biomacromolecule-based matrix hydrogel can undergo rapid gelling and fixation to adhere and seal bleeding arteries and cardiac walls after UV light irradiation. These repairs can withstand up to 290 mm Hg blood pressure, significantly higher than blood pressures in most clinical settings (systolic BP 60–160 mm Hg). Most importantly, the hydrogel can stop high-pressure bleeding from pig carotid arteries with 4~ 5 mm-long incision wounds and from pig hearts with 6 mm diameter cardiac penetration holes. Treated pigs survived after hemostatic treatments with this hydrogel, which is well-tolerated and appears to offer significant clinical advantage as a traumatic wound sealant.

Comment: This fancy paper is, for me, the insertion of 2 functional crosslink hydrogel. The UV light here plays a dual trigger role: one is the direct photo-polymerization, and another is inducing the imine condensation. The covalent mixture of 2 hydrogels after UV irradiation can increase the mechanical force which it is capable to withstand for the blood pressure. The reversible imine formation provides the hydrogel some dynamic character. The combination of the irreversible crosslinker and the reversible imine dynamic polymer provide us a strongly adhesive hemostatic hydrogel.

Minimalistic Supramolecular Proteoglycan Mimics by Co-assembly of Aromatic Peptide and Carbohydrate Amphiphiles

Brito, A.; Abul-Haija, Y. M.; Da Costa, D. S.; Novoa-Carballal, R.; Reis, R. L.; Ulijn, R. V.;* Pashkuleva, I.* *Chem Sci* **2019** *10*, 2385.

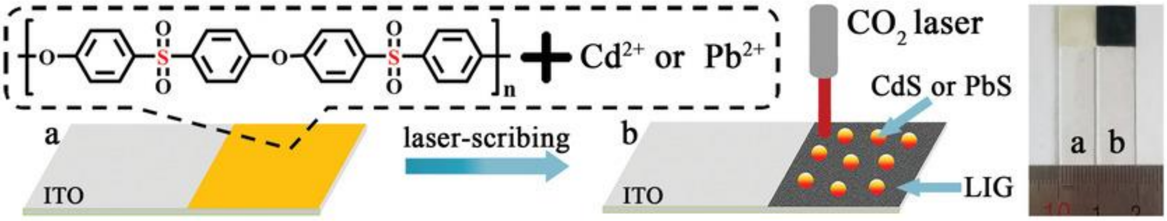


We report the co-assembly of aromatic carbohydrate and dipeptide amphiphiles under physiological conditions as a strategy to generate minimalistic proteoglycan mimics. The resulting nanofibers present a structural, fluorenylmethoxycarbonyl-diphenylalanine (Fmoc-FF) core and a functional carbohydrate (Fmoc-glucosamine-6-sulfate or -phosphate) shell. The size, degree of bundling and mechanical properties of the assembled structures depend on the chemical nature of the carbohydrate amphiphile used. In cell culture medium, these nanofibers can further organize into supramolecular hydrogels. We demonstrate that, similar to proteoglycans, the assembled gels prolong the stability of growth factors and preserve the viability of cultured cells. Our results demonstrate that this approach can be applied to the design of extracellular matrix (ECM) substitutes for future regenerative therapies.

Comment: If you want to scan the literature of dynamic peptide libraries, I would strongly recommend the work from prof. Rein V. Ulijn. His group investigates the supramolecular hydrogels of Fmoc-protected carbonhydrates and amino acids, which are both very simple and employ easily obtained components. Even if this paper here is not about peptide segments, they still discuss how small biological molecules can generate the proteoglycan mimics.

Direct-Laser-Writing of Metal Sulfide-Graphene Nanocomposite Photoelectrode toward Sensitive Photoelectrochemical Sensing

Ge, L.; Hong, Q.; Li, H.; Liu, C.; Li, F.* *Adv. Funct. Mater.* **2019**, *29*, ASAP

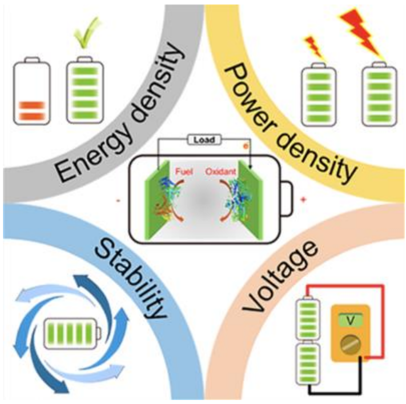


Here, a facile approach for the in situ fabrication of metal sulfide (MS)-graphene (G) nanocomposite, CdS-G and PbS-G, on indium-tin oxide (ITO) glass is demonstrated using a simple and scalable direct-laser-writing method in ambient air. Through the CO_2 laser irradiation of a metal-complex containing polyethersulfone layer on ITO glass, both the crystallization of laser-induced MS (LIMS) and the formation of laser-induced graphene (LIG) are synchronously achieved in one step, giving rise to a laser-induced MS-G nanocomposite photoelectrode, denoted as LI-MS-G@ITO. In such a laser-scribing process, polyethersulfone not only acts as the carbon source to grow LIG but also provides an in situ source of S^{2-} to produce LIMS with the aids of carbothermic reduction of sulfur element in polyethersulfone. The obtained LI-MS-G@ITO inherits the porous network architecture of polyethersulfone-derived LIG, in which the LIMS nanocrystals uniformly decorate the multilayered graphene sheets with good dispersion, presenting a fast and stable photocurrent response with high reproducibility, which, as a proof-of-concept, further facilitates the use of a LI-CdS-G@ITO photoanode as an efficient transducer for photoelectrochemical detection of Cu^{2+} with high sensitivity and selectivity. This work can offer a universal and versatile protocol for the in situ and synchronous fabrication of novel MS-G nanocomposites for sensitive photoelectrochemical analysis.

Comment: Normally, both graphene and metal sulfide (MS) need to be pre-synthesized, and then assembled together, before deposition on an electrode surface. The authors have developed a procedure that greatly simplifies the fabrication of MS-G on ITO surfaces, using a known technique (direct laser writing) which had not yet been applied in this field.

Tackling the Challenges of Enzymatic (Bio)Fuel Cells

Xiao, X.; Xia, H.; Wu, R.; Bai, L.; Yan, L.; Magner, E.; Cosnier, S.; Lojou, E.*; Zhu, Z.*; Liu, A.* *Chem. Rev.* **2019**, *119*, 9509–9558.

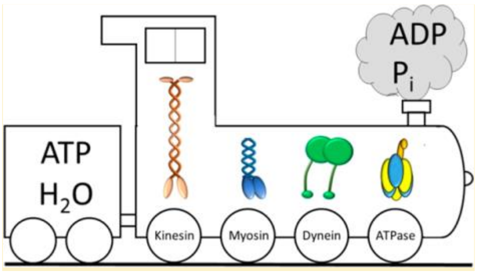


The ever-increasing demands for clean and sustainable energy sources combined with rapid advances in biointegrated portable or implantable electronic devices have stimulated intensive research activities in **enzymatic (bio)fuel cells (EFCs)**. The **use of renewable biocatalysts**, the **utilization of abundant green, safe, and high energy density fuels**, together with the capability of **working at modest and biocompatible conditions** make EFCs promising as next generation alternative power sources. However, the **main challenges (low energy density, relatively low power density, poor operational stability, and limited voltage output)** hinder future applications of EFCs. This review aims at exploring the underlying mechanism of EFCs and providing possible practical strategies, methodologies and insights to tackle these issues. First, this review summarizes approaches in achieving high energy densities in EFCs, particularly, employing enzyme cascades for the deep/complete oxidation of fuels. Second, strategies for increasing power densities in EFCs, including increasing enzyme activities, facilitating electron transfers, employing nanomaterials, and designing more efficient enzyme-electrode interfaces, are described. The potential of EFCs/(super)capacitor combination is discussed. Third, the review evaluates a range of strategies for improving the stability of EFCs, including the use of different enzyme immobilization approaches, tuning enzyme properties, designing protective matrixes, and using microbial surface displaying enzymes. Fourth, approaches for the improvement of the cell voltage of EFCs are highlighted. Finally, future developments and a prospective on EFCs are envisioned.

Comment: With around 600 references, this paper is certainly comprehensive enough for the layperson I am in this domain. This review provides a good understanding of this promising subject (i.e. enzymatic (bio)fuel cells). In my opinion, the authors manage to remain pragmatic and honest in the way they introduce this technology and the main drawbacks are well discussed as well as their potential solutions.

Synthetic Systems Powered by Biological Molecular Motors

Saper, G.; Hess, H.* *Chem. Rev.* **2019**, ASAP.

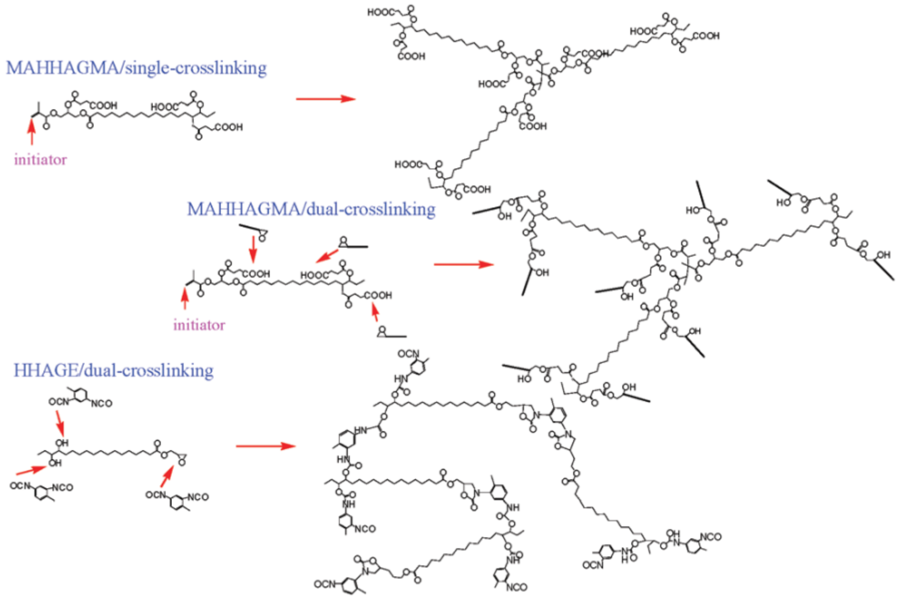


Biological molecular motors (or biomolecular motors for short) are nature's solution to the efficient conversion of chemical energy to mechanical movement. In biological systems, these fascinating molecules are responsible for movement of molecules, organelles, cells, and whole animals. In engineered systems, these motors can potentially be used to power actuators and engines, shuttle cargo to sensors, and enable new computing paradigms. Here, we **review the progress in the past decade in the integration of biomolecular motors into hybrid nanosystems**. After briefly introducing the motor proteins kinesin and myosin and their associated cytoskeletal filaments, we review recent work aiming for the integration of these biomolecular motors into actuators, sensors, and computing devices. In some systems, the creation of mechanical work and the processing of information become intertwined at the molecular scale, creating a fascinating type of "active matter". We discuss efforts to optimize biomolecular motor performance, construct new motors combining artificial and biological components, and contrast biomolecular motors with current artificial molecular motors. A recurrent theme in the work of the past decade was the induction and utilization of collective behavior between motile systems powered by biomolecular motors, and we discuss these advances. The exertion of external control over the motile structures powered by biomolecular motors has remained a topic of many studies describing exciting progress. Finally, we review the current limitations and challenges for the construction of hybrid systems powered by biomolecular motors and try to ascertain if there are theoretical performance limits. Engineering with biomolecular motors has the potential to yield commercially viable devices, but it also sharpens our understanding of the design problems solved by evolution in nature. This increased understanding is valuable for synthetic biology and potentially also for medicine.

Comment: This comprehensive review details the latest results in the field of biomolecular motors. I think that it could have been included in our own review if it was not already submitted. To sum up, it is worth it to at least take a look at the different figures and at the main examples of systems powered by these motors.

The design, preparation, and properties of dual-crosslinking copolymerized systems based on hemp oil

Yi, J.; Li, S.*; Xia, J.; Li, M.; Ding, H.; Xu L.; and Yang X. *New J. Chem.*, **2019**, *43*, 14928-14937

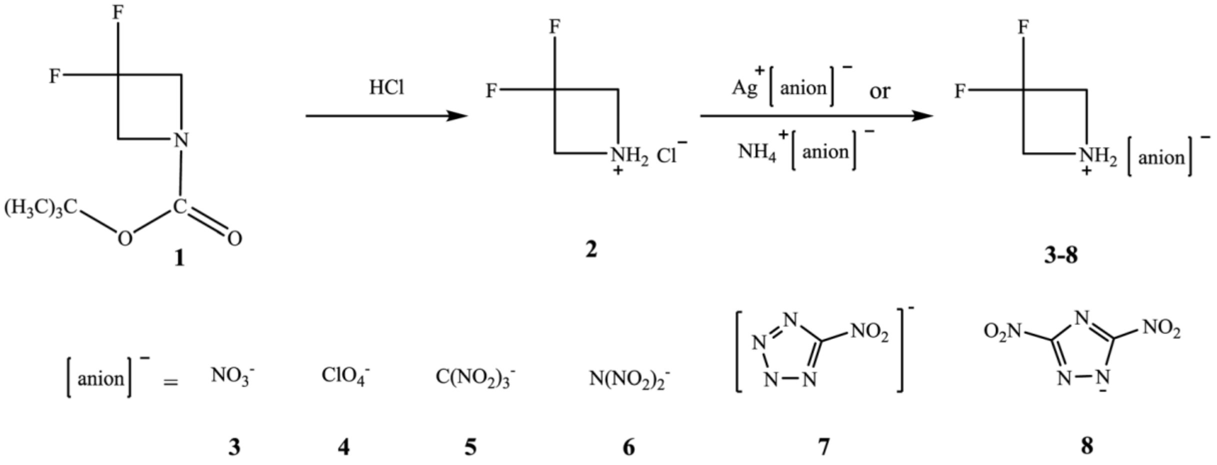


Novel, dual-crosslinking, reactive monomers of MAHHAGMA and HHAGE were synthesized using hemp oil (HO), and their successful syntheses were confirmed by FTIR and $_1$H-NMR analyses. Then, three copolymerized materials were obtained: MAHHAGMA/single-crosslinking, MAHHAGMA/dual-crosslinking, and HHAGE/dual-crosslinking systems. The properties of three as-prepared materials were tested. The two dual-crosslinking systems had better hardness, crosslinking density, and tensile properties than the single-crosslinking system. The HHAGE/dual-crosslinking copolymer, a combination of polyurethane and polyoxazolidinone systems, had superior tensile strength (30.17 MPa), the greatest elongation at break (31.42%), and the highest glass transition temperature (78.211C). The dual-crosslinking copolymer of MAHHAGMA, a combination of polymerized epoxy and polymerized vinyl ester systems, had the highest crosslinking density (381.24 mol m$_3$) and the highest initial decomposition temperature (365.51C). Thus, the present study offers a novel preparation method of dual-crosslinking copolymerized biomaterials based on a vegetable oil.

Comment: The authors describe here a rather new bio-based material based on hemp oil. The process is quite simple, the key point is the use of two different crosslinking (urethanes and mathacrylates) that enhance the mechanical properties of the final material. One could argue that despite the bio origin of the material, it remains a highly crosslinked thermoset and thus not recyclable and hardly degradable.

Energetic materials with fluorinated four-membered heterocyclic ring: 3,30-difluoroazetidine (DFAZ) salts

Chen, J.; Yu, Y.; Zhang, S.; Li, Y.*; and Siping Pang, S.* *New J. Chem.*, **2019**, *43*, 15115 15119

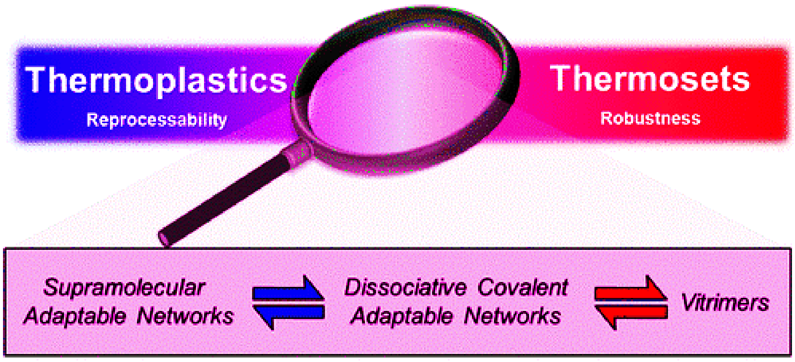


3,3’-Difluoroazetidinium (DFAZ) possesses a high-tensile four-membered ring and fluorine atoms, which contributes to the specific impulse, detonation pressure and detonation velocity. High-density energetic salts that contain oxygen-rich anions and cations were synthesized. All of the salts were fully characterized by IR spectroscopy, single-crystal X-ray diffraction, elemental analysis, differential scanning calorimetry (DSC) as well as impact and friction sensitivity. Their detonation properties were calculated according to the densities and heats of formation. The results showed that compared to ADN, they all had a relatively high density and low impact sensitivity. The specific impulse of almost all of the salts were higher than that of the propellant component, ammonium dinitramide (ADN, Isp = 202 J). Moreover, the 3,3’-difluoroazetidinium nitroformate salt had the highest specific impulse and was relatively more stable. It is possible to obtain energetic cations with good properties by combining four-membered high-tension rings with fluorine atoms.

Comment: I hope no one is working in this field in our team but remains an interesting and important field. This article explains how to measure the different properties and stabilities of energetic materials and the authors compare them with classical energetic materials.

Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets

Scheutz, G. M.;* Lessard, J. J.; Sims, M. B.; Sumerlin, B. S.* *J. Am. Chem. Soc.* **2019**, ASAP

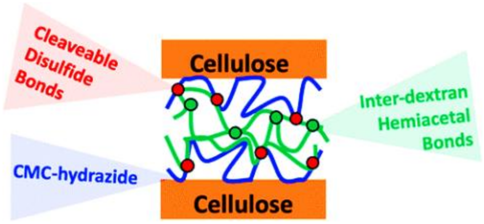


The classical division of polymeric materials into thermoplastics and thermosets based on covalent network structure often implies that these categories are distinct and irreconcilable. Yet, the past two decades have seen extensive development of materials that bridge this gap through incorporation of dynamic crosslinks, enabling them to behave as both robust networks and moldable plastics. Although their potential utility is significant, the growth of covalent adaptable networks (CANs) has obscured the line between "thermoplastic" and "thermoset" and erected a conceptual barrier to the growing number of new researchers entering this discipline. This Perspective aims to both outline the fundamental theory of CANs and provide a critical assessment of their current status. We emphasize throughout that the unique properties of CANs emerge from the network chemistry, and particularly highlight the role that the crosslink exchange mechanism (i.e., dissociative exchange or associative exchange) plays in the resultant material properties under processing conditions. Predominant focus will be on thermally induced dynamic behaviour, as the majority of presently employed exchange chemistries rely on thermal stimulus, and it is simple to apply to bulk materials. Lastly, this Perspective aims to identify current issues and address possible solutions for better fundamental understanding within this field.

Comment: A very interesting perspective about the introduction of dynamic crosslinks and the undergone dissociative and associative processes that influence the properties of the covalent and adaptable networks formed. Also, the production of these materials at industrial scale is envisioned.

Challenges to Achieving Strong but Fully Degradable Adhesive Joints between Wet Cellulose Surfaces

Yang, D.; Chen, Y.; Pelton, R.;* *Langmuir*, **2019**, ASAP

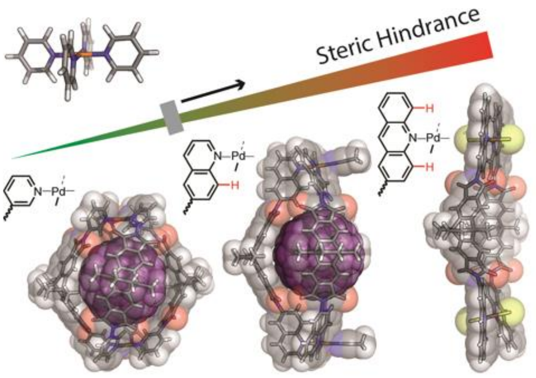


The dramatic loss of strength upon exposure to water is one of the challenges preventing the widespread substitution of plastic packaging with paper and paperboard. Although treatment with conventional wet strength resins and other adhesive polymers can strengthen wet paper, it is at the expense of green credentials, including easy recycling or rapid composting. The goal of this work was to demonstrate the adhesive requirements for strong, wet cellulose–cellulose joints that can be recycled easily because the joint strength can be destroyed by the presence of a weak reducing agent. Cellulose membrane surfaces were first treated with a bound layer of carboxymethyl cellulose, modified to have covalently tethered hydrazide groups. Joints were fabricated by laminating two hydrazide-modified membranes with a polymeric adhesive bearing aldehyde functionality. Aldehydes spontaneously condense with hydrazide to give hydrazone bonds. When the adhesive was oxidized dextran, the wet laminates had an intermediate strength. Upon exposure to a reducing agent, the joint strength was reduced to nearly zero because every hydrazone moiety connecting two cellulose surfaces included a cleavable disulfide linkage. By contrast, glyoxalated cationic polyacrylamide gave very strong wet joints. However, the wet adhesion was dominated by polyelectrolyte complexation, and the presence of hydrazone linkages had little influence on the wet adhesion. We conclude that robust joint degradability will require cleavable linkages in the adhesive backbone while minimizing polyelectrolyte complexation.

Comment: Very interesting article about the modification of cellulose in order to obtain wet cellulose-cellulose strong joints through the formation of hydrazone bonds that allow us to obtain waterproof materials that can be easily recyclable. What an environmentally friendly paper!

Tunable Fullerene Affinity of Cages, Bowls and Rings Assembled by Pd(II) Coordination Sphere Engineering

Chen, B.; Horiuchi, S.; Holstein, J. J.; Tessarolo, J.; Clever, G. H.* *Chem. Eur. J.* **2019**, *ASAP.*

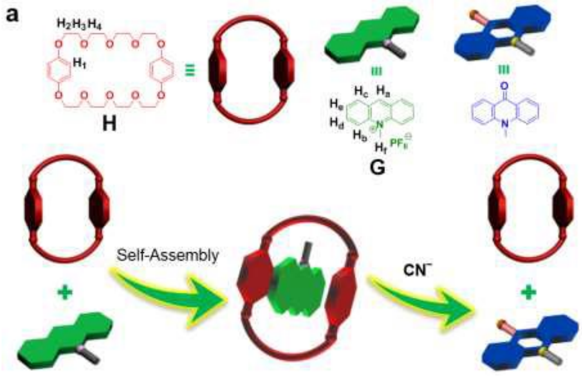


For metal-mediated host compounds, the development of strategies to reduce symmetry and introduce multiple functionalities in a non-statistical way is a challenging task. We show that the introduction of steric stress around the coordination environment of square-planar Pd(II) cations and bis-monodentate nitrogen donor ligands allows to control the size and shape of the assembly product, from $[Pd_2L_4]$ cages over $[Pd_2L_3]$ bowl-shaped structures to $[Pd_2L_2]$ rings. Therefore, banana-shaped ligand backbones were equipped with pyridines, two different quinoline isomers and acridine, the latter three introducing steric congestion through hydrogen substituents on annelated benzene rings. Differing behavior of the four resulting hosts towards the binding of C_{60} and C_{70} fullerenes was studied and related to structural differences by NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. The three cages based on pyridine, 6-quinoline or 3-quinoline donors were found to either bind C_{60}, C_{70} or no fullerene at all.

Comment: The affinity of self-assembled cages by metal-coordination towards fullerene guests was tuned by changing the size and shape of the cage by chemical modification of the ligands.

[2]Pseudorotaxane-Based Supramolecular Optical Indicator for the Visual Detection of Cellular Cyanide Excretion

Zhou, J.;* Yu, G.; Li, Y.; Shen, J.; Wang, M.; Li, Z.; Wei, P.; Tang, J.;* Huang, F.* Chem. Eur. J. **2019**, ASAP.

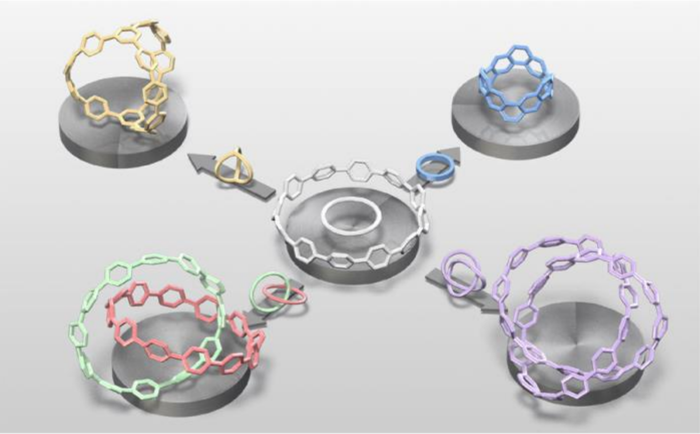


Cyanide is one of the most concerned anions and is extremely hazardous to living organism and environment. Due to its wide range of applications and high toxicity, the development of functional materials for cyanide detection and sensing is highly desirable. Host–guest complexation between bis(*p*-phenylene)-34-crown-10 **H** and *N*-methylacridinium salt **G** remarkably decreases the detection limit for cyanide anion as compared with that of the guest itself. The [2]pseudorotaxane selectively recognizes the cyanide anion with high optical sensitivity as a result of the nucleophilic addition of cyanide anion at the 9-position of **G**. The host–guest complexation is further incorporated into supramolecular materials for the visual detection of cyanide anion, especially the detection of cellular cyanide excretion with a detection limit of 0.6 μM. This supramolecular method provides an extremely distinct strategy for the visual detection of cyanide.

Comment: This is a nice idea for the detection of cyanide anions. When present with the pseudorotaxane, the in-situ modification of the thread by the cyanide anions decreases its affinity toward the macrocycle and enables its detection by fluorescence spectroscopy.

Topologically Unique Molecular Nanocarbons

Segawa, Y.; Levine, D. R.; Itami, K.* Acc. Chem. Res. **2019**, ASAP.

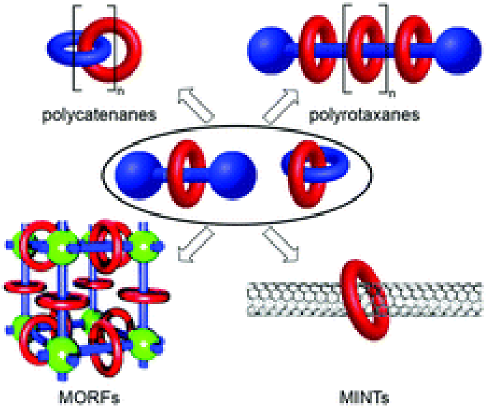


As new forms of carbon are unearthed, they invariably transform the scientific landscape. Numerous researchers have been inspired to discover the unique characteristics of these fascinating materials, consistently leading to the development of important technological innovations in materials science. Recently, studies on the preparation of molecular nanocarbons (small molecule analogues of larger carbon nanostructures) by precision organic synthesis have attracted much attention. Cycloparaphenylene (CPP), the substructure of carbon nanotubes (CNTs), is the oldest of such organic molecules, and since 2008 the successful synthesis of CPP dramatically advanced the synthetic chemistry of molecular nanocarbons. In fact, as pioneering research, we succeeded in producing carbon nanotubes using seed CPP molecules in 2013. This method represented an important landmark in the quest for controlling the diameter of CNTs via utilization of a well-defined small molecule as a template. Other avenues of research on graphene nanoribbons and partial structures of fullerenes such as corannulene and sumanene are also highly active at the current time. On the other hand, carbon forms with nontrivial topologies, i.e., topological nanocarbons, are virtually unexplored. In addition to the 3D network structures represented by the Mackay crystal, many topologically complex structures have been envisioned. To date, there is no rational approach toward the bottom-up synthesis of these carbon structures. As with the case of fullerenes and CNTs, access to these unique carbon structures should undoubtedly revolutionize a wide range of sciences. This Account highlights our efforts toward the synthesis of topologically unique molecular nanocarbons. Starting from CPP as the topologically simple subunit, we have successfully created novel molecular nanocarbons that have more complexed topologies. The first topic is carbon nanobelts, fully fused cylinder-shaped molecular nanocarbons representing the segment structure of armchair-type CNTs. The second topic is carbon nanocages, molecular nanocarbons having a “three-holed” topology representing the joint unit of branched CNTs. The third and fourth topics are all-benzene catenanes consisting of two CPP rings and an all-benzene trefoil knot topologically related to a carbon nanotorus. The world of nanocarbon molecules is only limited by our imagination and creativity. As history has proved, the synthesis of new forms of carbon and topologically complex molecules has always subsequently led to new fields and applications associated with their unforeseen properties and functions.

Comment: This account shows us how vast the world of carbon nanostructure is and yet a lot of things to discover. I encourage you to read it.

Mechanically interlocked materials. Rotaxanes and catenanes beyond the small molecule

Mena-Hernando, S.; Pérez, E. M.* *Chem. Soc. Rev.* **2019**, *Advance Article*



A mechanical bond presents a combination of the best features of covalent and supramolecular chemistries (stability and structural integrity), plus a unique dynamic nature, that makes it a very interesting tool for materials chemistry. Here, we overview the chemistry of the mechanical bond applied to polymers, metal-organic frameworks (MOFs) and carbon nanotubes. We first describe synthetic strategies towards polycatenanes and polyrotaxanes, and highlight their potential impact in polymer chemistry, exemplified by their use to make stimuli-responsive gels and as binders in battery electrodes. We continue by showing how to include mechanically interlocked components in MOFs, and analyse the distinctive dynamic properties of the final constructs. Finally, we describe the strategies towards mechanically interlocked derivatives of single-walled carbon nanotubes (SWNTs), and discuss the potential of the mechanical bond to tackle some of the classic problems of SWNT chemistry.

Comment: A new review that covers mechanically interlocked materials in the field of polymers, MOFs and carbon nanotubes and some applications.