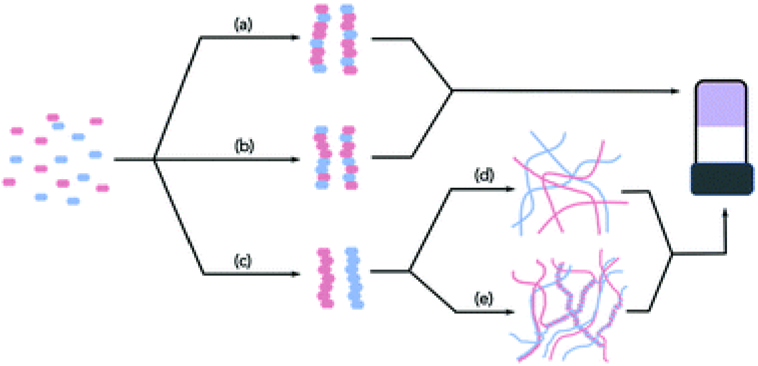
How Should Multicomponent Supramolecular Gels Be Characterized?

Draper, A. R.*; Adams, D. J.* *Chem. Soc. Rev.*10.1039/C7CS00804J .

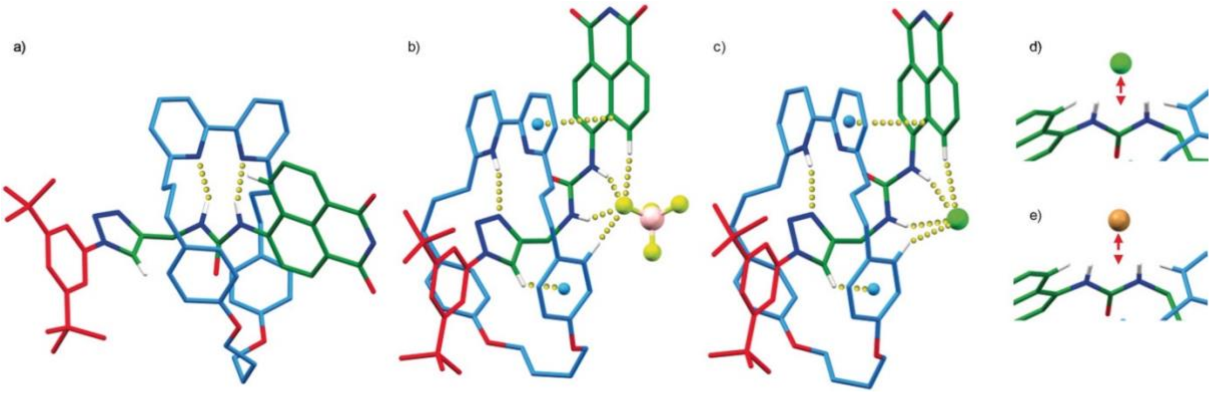


Well-defined Low molecular weight gels, or supramolecular gels, are formed when small molecules self-assemble into fibrous structures. Above a critical concentration, the entanglement and cross-linking of these structures leads to the formation of a self-supporting gel. There are many examples where a single component is used to form such gels. There is however an ever-increasing interest in using multiple components. Here, if each component is able to form a gel by itself, a range of fibre types are possible, formed by either random or specific associations between the low molecular weight gelators (LMWG). The properties of the networks will depend on how the LMWG assemble into the primary fibrous structures and then how these primary structures entangle. As such, to understand these gels, it is necessary to understand the networks across multiple length scales. Here, we discuss the current state of the art, the effectiveness of the different techniques that have been used, and hopefully provide the impetus for the field to move away from the cartoon-level discussion of assembly.

Comment: Many of us are working, or will have to work, on the elaboration and characterization of quite complicated systems. This short (and easy to read) review or some of the references cited within may give some ideas about **how to manage the characterization of supramolecular materials**.

A Fluorescent Ditopic Rotaxane Ion-pair Host

Denis, M.; Qin, L.; Turner, P.; Jolliffe, K. A.*; Goldup, S. M.* *Angew. Chem. Int. Ed.* **2018,** *ASAP*

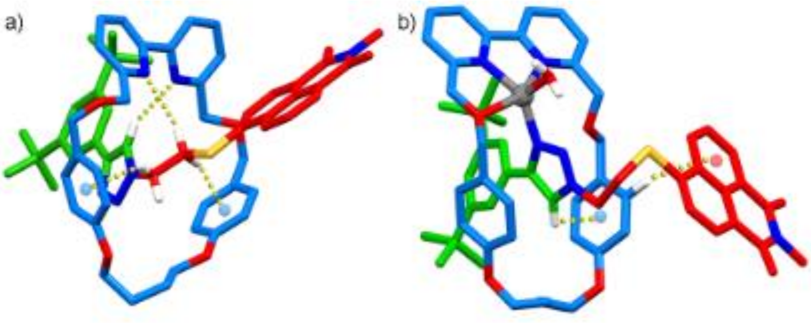


We report a rotaxane based on a simple urea motif that binds Cl^- selectively as a separated ion pair with H^+ and reports the anion binding event through a fluorescence switch-on response. The host selectively binds Cl^- over more basic anions, which deprotonate the framework, and less basic anions, which bind more weakly. The mechanical bond also imparts size selectivity to the ditopic host.

Comment: Personal point of view: I think Goldup's group is an *interesting group to follow* as they publish a lot in quite good journals recently (example here and below).

Chelating Rotaxane Ligands as Fluorescent Metal Ion Sensors

Denis, M.; Pancholi, J.; Jobe, K.; Watkinson, M.*; Goldup, S. M.* *Angew. Chem. Int.* **2018**, *ASAP*

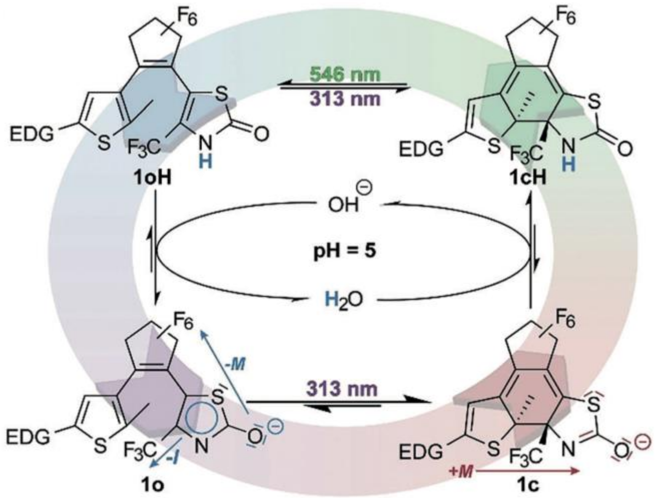


Although metal ion-binding interlocked molecules have been under intense investigation for over three decades, their application as scaffolds for the development of sensors for metal ions remains under-explored. Here we demonstrate the potential of simple rotaxane scaffolds as metal ion-responsive ligand scaffolds through the development of a proof-of-concept selective sensor for Zn^{2+}.

Comment: Paired with the previous paper, we have a nice example of "how to make different papers from very similar systems". The previous system could have been integrated in the screening presented in this paper, but the authors subtly play by separating anion-recognition and cation-recognition as two different topics (which is true but still).

Efficient Light-Induced pK_a-Modulation Coupled to Base-Catalyzed Photochromism

Gurke, J.; Budzák, S.; Schmidt, B. M.; Jacquemin, D.; Hecht, S.* *Angew. Chem. Int. Ed.* **2018**, *ASAP.*

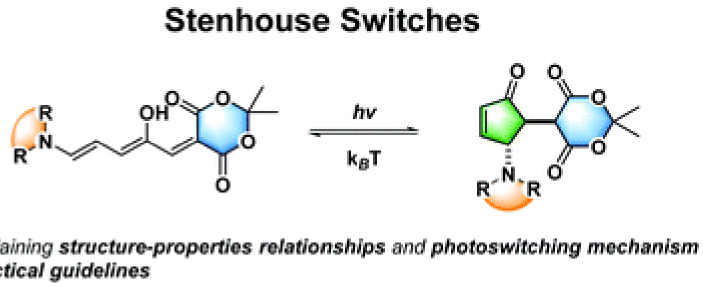


Photoswitchable acid–base pairs, whose pK_a values can be reversibly altered, are attractive molecular tools to control chemical and biological processes with light. A significant, light-induced pK_a change of three units in aqueous medium has been realized for two thermally stable states, which can be interconverted using UV and green light. The light-induced pK_a modulation is based on incorporating a 3-H-thiazol-2-one moiety into the framework of a diarylethene photoswitch, which loses the heteroaromatic stabilization of the negatively charged conjugate base upon photochemical ring closure, and hence becomes significantly less acidic. In addition, the efficiency of the photoreactions is drastically increased in the deprotonated state, giving rise to catalytically enhanced photochromism. It appears that protonation has a significant influence on the shape of the ground- and excited-state potential energy surfaces, as indicated by quantum-chemical calculations.

Comment: Nice example of a clean characterization of a (special) photoswitch coupled with efficient modelization.

The (Photo)Chemistry of Stenhouse Photoswitches: Guiding Principles and System Design

Lerch, M. M.; Szymanski, W.*; Feringa, B. L.* *Chem. Soc. Rev.*, **2018**, *47*, 1910-1937



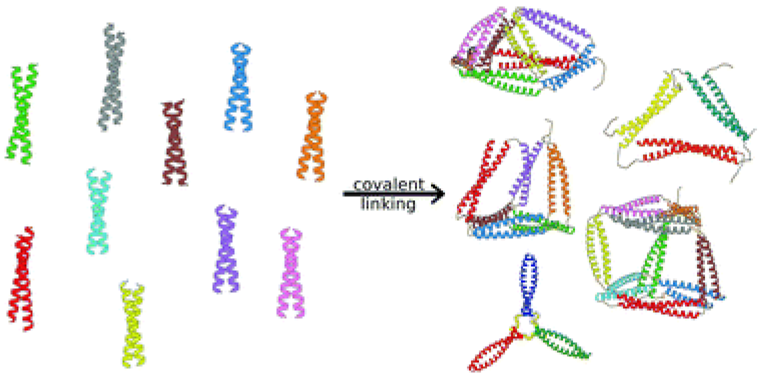
- Explaining *structure-properties relationships* and *photoswitching mechanism*
- *Practical guidelines*

Molecular photoswitches comprise chromophores that can be interconverted reversibly with light between two states with different photochemical and physicochemical properties. This feature renders them useful for diverse applications, ranging from materials science, biology (specifically photopharmacology) to supramolecular chemistry. With new and more challenging systems to control, especially extending towards biomedical applications, using visible or near-infrared light for photoswitch activation becomes vital. Donor–acceptor Stenhouse adducts are a novel class of visible light-responsive negative photochromes that provide a possible answer to current limitations of other photoswitch classes in the visible and NIR window. Their rapid development since their discovery in 2014, together with first successful examples of applications, demonstrate both their potential and areas where improvements are needed. A better understanding of DASA characteristics and its photoswitching mechanism has revealed that they are in fact a subset of a more general structural class of photochromes, namely Stenhouse photoswitches. This tutorial review aims at providing an introduction and practical guide on DASAs: it focuses on their structure and synthesis, provides fundamental insights for understanding their photoswitching behavior and demonstrates guiding principles for tailoring these switches for given applications.

Comment: Just because Feringa does not only speak about molecular motors.

Coiled Coil Protein Origami: From Modular Design Principles towards Biotechnological Applications

Lapenta, F.; Aupic, J.; Strmsek, Z.; Jerala, R.* *Chem. Soc. Rev.*10.1039/C7CS00822H

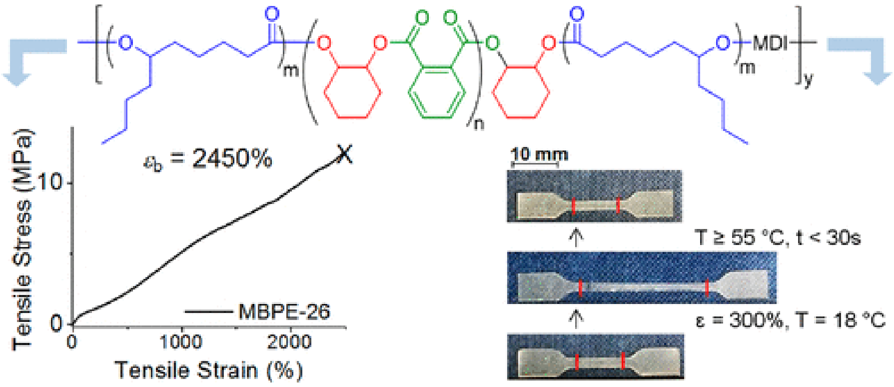


The design of new protein folds represents a grand challenge for synthetic, chemical and structural biology. Due to the good understanding of the principles governing its pairing specificity, coiled coil (CC) peptide secondary structure elements can be exploited for the construction of modular protein assemblies acting as a proxy for the straightforward complementarity of DNA modules. The prerequisite for the successful translation of the modular assembly strategy pioneered by DNA nanotechnology to protein design is the availability of orthogonal building modules: a collection of peptides that assemble into CCs only with their predetermined partners. Modular CC-based protein structures can self-assemble from multiple polypeptide chains whose pairing is determined by the interaction pattern of the constituent building blocks. Orthogonal CC sets can however also be used for the design of more complex coiled coil protein origami (CCPO) structures. CCPOs are based on multiple CC modules concatenated into a single polypeptide chain that folds into a polyhedral protein cage as the peptide segments assemble into CC dimers. The CCPO strategy has hitherto led to successful *de novo* design of protein cages in the shape of a tetrahedron, square pyramid and triangular prism. Recent advances in the design of CC modules and design principles have enabled the construction of CCPOs that self-assemble *in vivo* without any apparent toxicity to human cells or animals, opening the path towards therapeutic applications. The CCPO platform therefore has potential for diverse applications in biomedicine and biotechnology, from drug delivery to molecular cages.

Comment: Not really long to read, this review is a cool discussion about protein assembly, with a particular aim of specific topologies.

Multiblock Polyesters Demonstrating High Elasticity and Shape Memory Effects

Zhu, Y.; Radlauer, M.; Schneiderman, D.; Shaffer, M.; Hillmyer, M. and Williams, C.*
Macromolecules **2018**, ASAP.

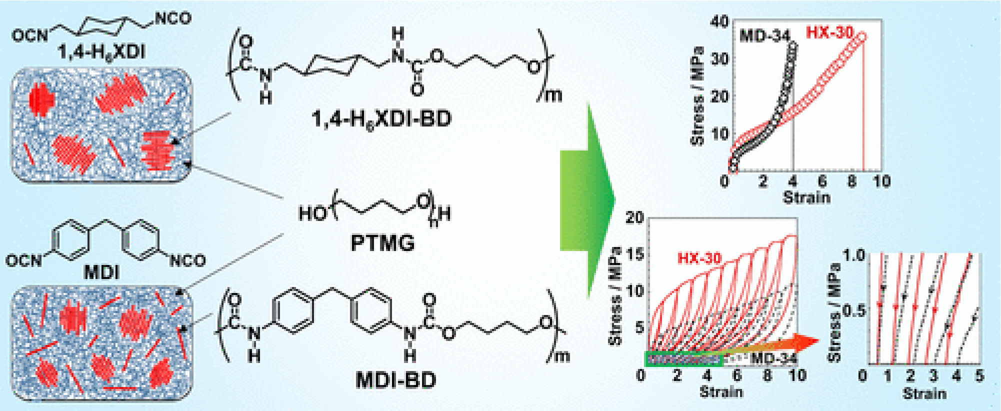


Polyester block polymers containing **polylactide** have garnered significant attention as **renewable, degradable alternatives to traditional elastomers**. However, the low glass transition of the PLA blocks limits the upper-use temperatures of the resulting elastomers. To improve the thermal performance, we explore a series of multiblock polyesters composed of poly(ε-decalactone) (PDL) and poly(cyclohexene phthalate) (PCHPE). These materials are prepared using **switchable polymerization catalysis followed by chain extension**. The strategy involves (i) alternating ring-opening copolymerization (ROCOP) of cyclohexene oxide and phthalic anhydride, (ii) ε-decalactone ring-opening polymerization (ROP), and (iii) diisocyanate coupling of the telechelic triblocks to increase molar mass. The resulting multiblock polyesters are amorphous, and the blocks are phase separated; glass transition temperatures are ∼−45 and 100 °C. They show thermal resistance to mass loss with $T_{d5\%}$ ∼ 285 °C and higher upper use temperatures compared to alternative aliphatic polyesters. The nanoscale phase behavior and correlated mechanical properties are highly sensitive to the block composition. The sample containing PCHPE = 26 wt % behaves as a thermoplastic elastomer with **high elongation at break** ($\varepsilon_b > 2450\%$), **moderate tensile strength** (σ_b = 12 MPa), and **low residual strain** (ε_r ∼ 4%). It shows elastomeric behavior from −20 to 100 °C and has a processing temperature range of ∼170 °C. At higher PCHPE content (59 wt %), the material has shape memory character with **high strain fixation** (250%) and recovery (96%) over multiple (25) recovery cycles. The multiblock polyesters are straightforward to prepare, and the methods presented here can be extended to produce a wide range of new materials using a other epoxides, anhydrides, and lactones. This first report on the thermal and mechanical properties highlights the significant potential for this class of polyesters as elastomers, rigid plastics, and shape memory materials.

Comment: They designed a thermoplastic material with high T_g and with highly recyclable shape memory properties up to 300% strain.

Superior Properties of Polyurethane Elastomers Synthesized with Aliphatic Diisocyanate Bearing a Symmetric Structure

Nozaki, S.; Masuda, S.; Kamitani, K.; Kojio, K.*; Takahara, A.; Kuwamura, G.; Hasegawa, D.; Moorthi, K.; Mita, K.; Yamasaki, S. *Macromolecules* **2017**, *50*, 1008.

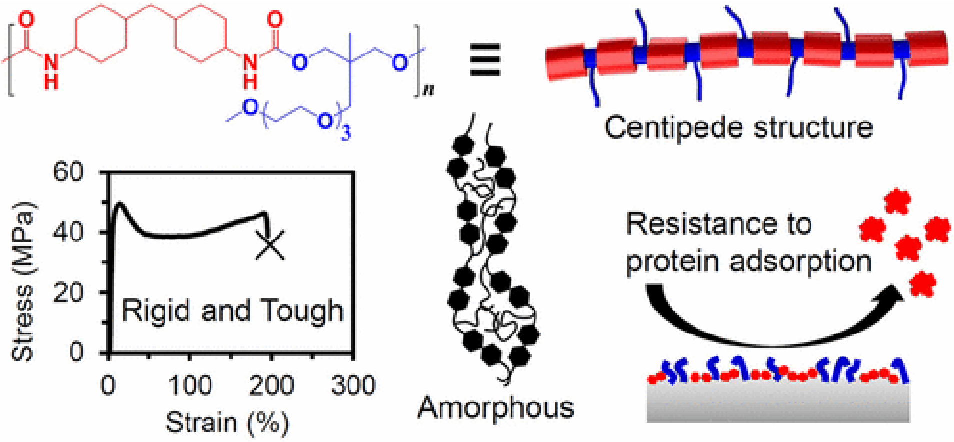


Abstract of the paper. Polyurethane elastomers (PUEs) containing **trans-1,4-bis(isocyanatomethyl)cyclohexane** (1,4-H_6XDI) have been synthesized by polymerizing 1,4-H_6XDI with poly(oxytetramethylene) glycol and 1,4-butanediol. The molecular aggregation state and mechanical properties of these PUEs have been compared with those exhibited by PUE analogues made of MDI and diols. The hard segment chains in the 1,4-H_6XDI-based PUEs are found to readily crystallize and form **strong hydrogen bonds due to a high symmetry** of 1,4-H_6XDI molecule. Consequently, the 1,4-H_6XDI-based PUEs exhibit well-organized hard segment domains. This leads to their generally superior mechanical properties as compared to those of the well-known MDI-based PUEs. 1,4-H_6XDI's lack of aromatic moieties is expected to greatly enhance color stability of resulting PUEs. All the above features suggest 1,4-H_6XDI could replace MDI in a range of applications.

Comment: Strong hydrogen bonds within the PU with a huge hard block content lead to highly crystalline material with nice mechanical properties.

Design of Polyurethane Composed of Only Hard Main Chain with Oligo(ethylene glycol) Units as Side Chain Simultaneosly Achieved High Biocompatible and Mechanical Properties

Aoki, D.; Ajiro, H.* *Macromolecules* **2017**, *50*, 6529.

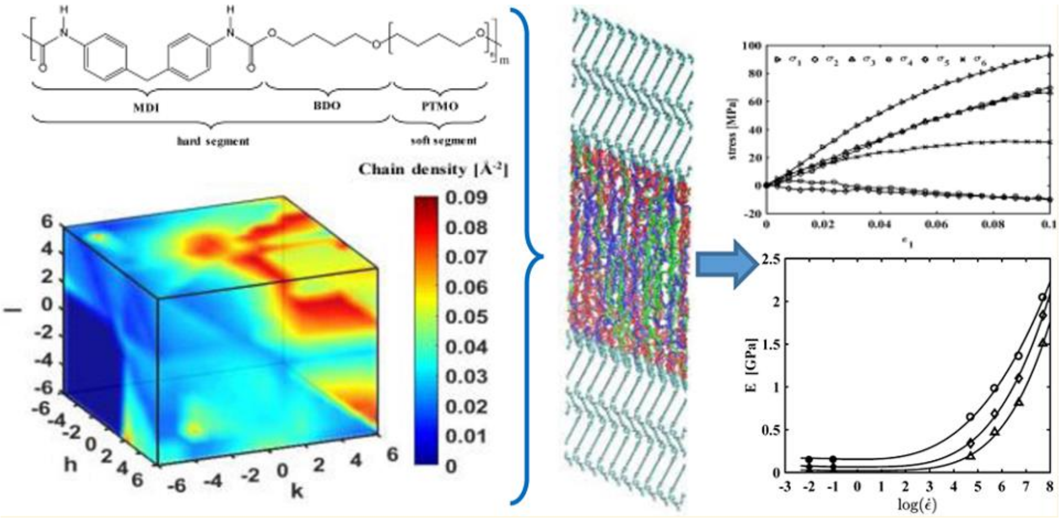


Abstract of the paper. In order to create a novel rigid polymer material for biomedical application, we designed the polymer structure of polyurethane, bearing **oligo(ethylene glycol)** (OEG) as the side chain, which was synthesized by only hard main chain using diisocyanate and short diol monomers. We investigated the effect of the graft structure of OEG units on polymer properties using pentaethylene glycol (OEG_5) or propanediol (PDO) in the main chain as the other diol monomers. Furthermore, the rigid 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) and symmetric **hexamethylene diisocyanate (HDI)** were selected for the isocyanate monomers. As a result, there is a significant difference in various properties, depending on both the existence and the position of OEG units in the polymer structure. For example, differential scanning calorimetry (DSC) showed that the graft structure of OEG caused a decrease in the glass transition temperature from 73 to 35 °C in the case of using HMDI as well as a disappearance of the melting point in the case of using HDI. The Fourier transform infrared (FT-IR) spectra showed that the ordered hydrogen bonding of C═O stretching vibration at 1682 cm^{-1} was not observed in the polyurethane grafted with OEG. In the mechanical test of polyurethane composed of HMDI, the sample grafted with OEG exhibited excellent values of elastic modulus of 1.7 GPa and elongation at break of 184%, while that with OEG_5 and PDO in the main chain showed 115 MPa with 370% and 739 MPa with 19%, respectively. The polyurethane grafted with OEG showed around 0.6 $\mu g/cm^2$ of protein adsorption, almost the same as that with OEG_5 in the main chain, while that using PDO in the main chain showed more than 3.0 $\mu g/cm^2$. Therefore, the polyurethane design bearing OEG as the side chain provides excellent rigidity, toughness, and biocompatibility simultaneously.

Comment: A unique biocompatible TPU with graft structure has been designed. The material has excellent mechanic properties taking into account for this TPU to be amorphous. However, industrial scaling is an issue.

Atomistic Simulation of a Thermoplastic Polyurethane and Micromechanical Modeling

Lempesis, N.; in ‘t Veld, P. J.; Rutledge, G. C.* *Macromolecules* **2017**, *50*, 7399.



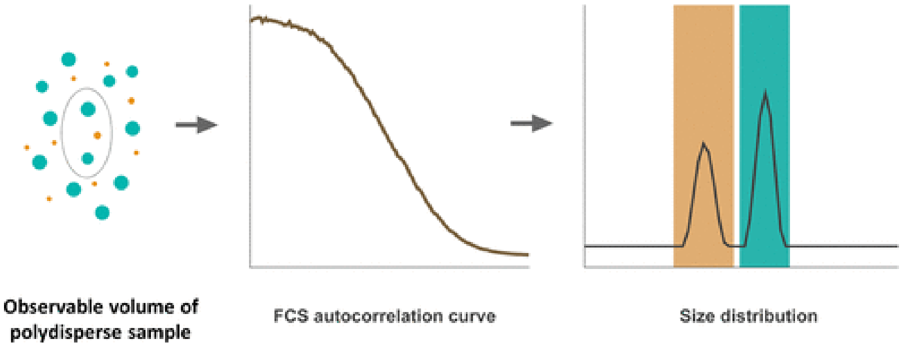
Thermoplastic polyurethanes constitute a versatile family of materials with a broad variety of engineering applications. However, **connection between their chemical structure and mechanical properties remains elusive**, in large part due to their heterogeneous nature, arising from segregation of chemically distinct segments into separate domains, with resulting complex morphologies. Using atomistic simulations, we examine the structure and mechanical properties of a common family of thermoplastic polyurethanes (TPU) **comprising 4,4'-diphenylmethane diisocyanate and *n*-butanediol (hard segment) and poly(tetramethylene oxide) (soft**

segment). A lamellar stack model previously developed for the study of semicrystalline polymers is applied here for the first time to a phase-segregated copolymer. Equilibrium structure and properties were evaluated for TPUs with different ratios of hard and soft components, using a combination of Monte Carlo and molecular dynamics simulations. Stress–strain behaviors were then evaluated using nonequilibrium molecular dynamics (NEMD) simulations. The compositional dependence of the Young's moduli thus obtained is shown to be well-approximated by a **micromechanical homogenization model of the hard and soft components**. Voigt (upper) and Reuss (lower) bounds of modulus were obtained for orientationally averaged aggregates and shown to be greater than those measured experimentally. The discrepancy is explained in terms of the strain rate dependence of elastic moduli, characterized by an Eyring-like function.

Comment: A molecular model for a heterogeneous block copolymer was simulated at atomic resolution using a united atom force field. According to the authors, the chemical potentials of loops, bridges and tales have been estimated for the first time using an atomistic simulation.

Distribution of Diffusion Times Determined by Fluorescence (Lifetime) Correlation Spectroscopy

Pánek, J.; Loukotová, L.; Hrubý, M.; Štěpánek, P.* *Macromolecules* **2018**, ASAP.

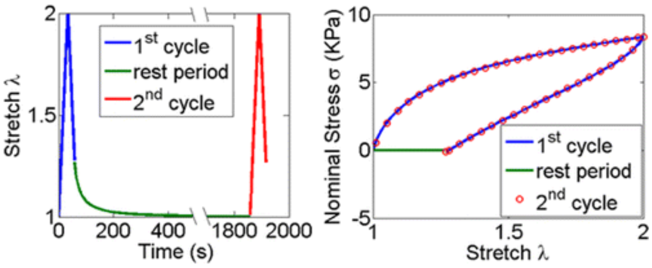


Fluorescence correlation spectroscopy (FCS) provides most commonly values of diffusion coefficients of fluorescently labeled species in a solution, especially biopolymers. A newly developed procedure for the determination of diffusion coefficient distributions applicable to polydisperse polymers or nanoparticles, based on the well-known CONTIN algorithm, is described and tested on both simulated FCS correlation functions and real experimental data. Good resolution of bimodal distributions is observed, and it is quantitatively established how the resolution depends on the level of experimental noise. Effects of incorrect calibration of the focal volume on the obtained diffusion coefficient and its distribution are described for single-focus FCS. With rapid expansion of the FCS method from biology and biochemistry into the polymer field, and recently into many other disciplines including, e.g., environmental sciences, such a technique was very much needed.

Comment: Regularized inverse Laplace transform (a.k.a. CONTIN) has been finally used for FCS data to estimate size-distribution functions of fluorescence species in solution. It is surprising that it had not been done a few decades ago. Anyway, this method might be useful in some limited cases.

Mechanics of a Dual Cross-Link Gel with Dynamic Bonds: Steady State Kinetics and Large Deformation Effects

Guo, J.; Long, R.; Mayumi, K.; Hui, C.-Y.* *Macromolecules* **2016**, *49*, 3497.

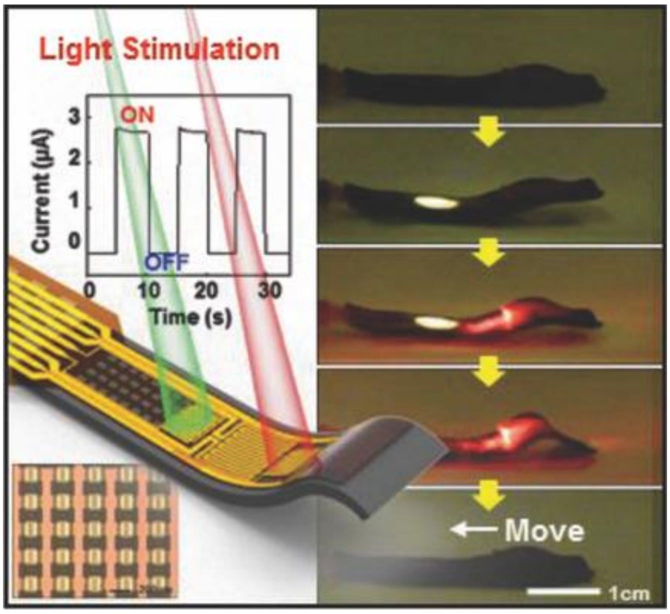


We develop a **three-dimensional continuum theory for a dual cross-link gel** with permanent and transient bonds. This theory connects the breaking and re-forming kinetics of the transient bonds to the large deformation behavior of the gel. Although based on similar principles as our previous theory for the same gel, the new theory addresses a limitation of the previous theory and agrees equally well with experimental data. Specifically, in the new theory we assume that breaking and re-forming kinetics of transient bonds reaches a steady state. This assumption leads to fewer material parameters and enables **the new theory to capture the healing process** of the dual cross-link gel. In addition, the steady state assumption also allows the new theory to reduce to classical linear viscoelastic theory in the limit of infinitesimal strains, where the kinetics of bond breaking and re-formation can be linked directly to the relaxation function. We also extend the theory to account for strain stiffening under very large deformation. The extended theory with strain stiffening agrees well with experimental data for nominal **strain up to 400%**. Finally, we extend our theory to gels with multiple types of dynamic bonds which has been recently exploited as a strategy to engineer viscoelastic behavior of gels.

Comment: The possibility to predict the mechanical properties of self-healed double crosslinked (permanent + dynamic bonds) gels might be quite useful.

Soft Ultrathin Electronics Innervated Adaptive Fully Soft Robots

Wang, .; Sim, K.; Chen, J.; Kim, H.; Rao, Z.; Li, Y.; Chen, W.; Song, J.; Verduzco, R. and Yu, C.* *Adv. Mat.* **2018**, *30*, 1706695.

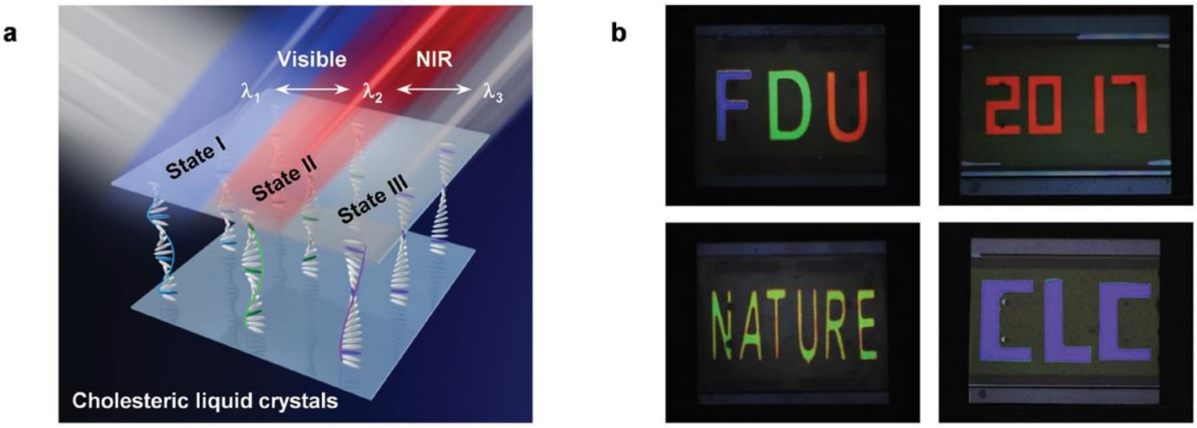


Soft robots outperform the conventional hard robots on significantly enhanced safety, adaptability, and complex motions. The development of fully soft robots, especially fully from smart soft materials to mimic soft animals, is still nascent. In addition, to date, existing soft robots cannot adapt themselves to the surrounding environment, i.e., sensing and adaptive motion or response, like animals. Here, compliant ultrathin sensing and actuating electronics innervated fully soft robots that can sense the environment and perform soft bodied crawling adaptively, mimicking an inchworm, are reported. The soft robots are constructed with actuators of open-mesh shaped ultrathin deformable heaters, sensors of single-crystal Si optoelectronic photodetectors, and thermally responsive artificial muscle of carbon-black-doped liquid-crystal elastomer (LCE-CB) nanocomposite. The results demonstrate that adaptive crawling locomotion can be realized through the conjugation of sensing and actuation, where the sensors sense the environment and actuators respond correspondingly to control the locomotion autonomously through regulating the deformation of LCE-CB bimorphs and the locomotion of the robots. The strategy of innervating soft sensing and actuating electronics with artificial muscles paves the way for the development of smart autonomous soft robots.

Comment: I think this is really quite impressive. There is *a lot* of information, but because of this, sometimes important details (experimental challenges) are only explained in the SI or are missing.

Precise Phototuning of Self-organized Helical Superstructures

Qin, L.; Gu, W.; Wei, J. and Yu, Y.* *Adv. Mat.* **2017**, *30*, 1704941.

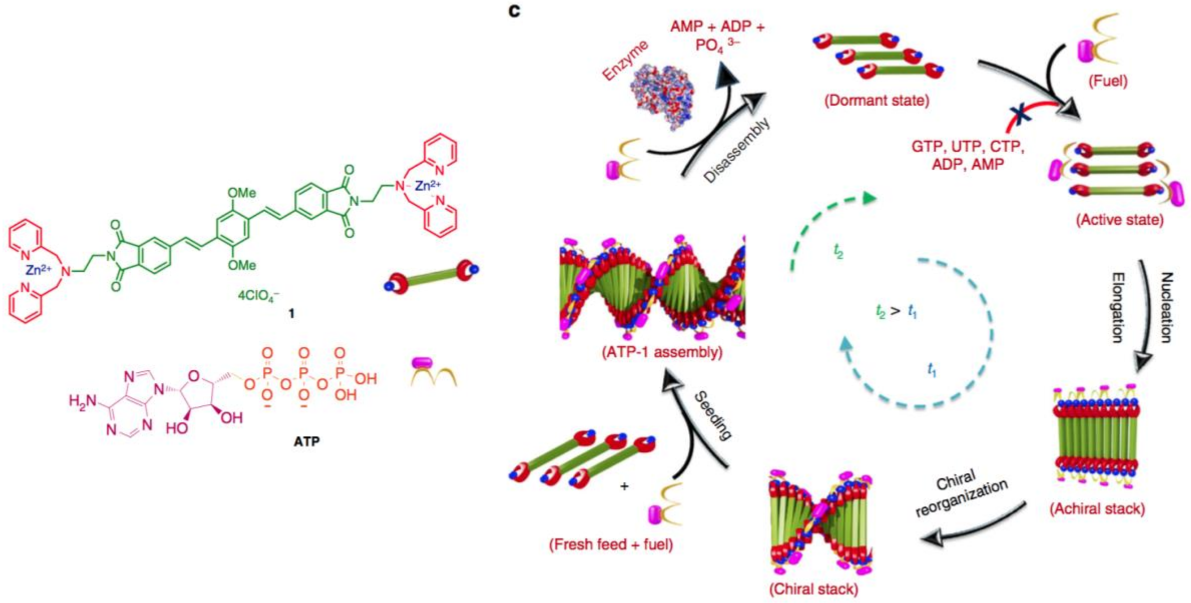


Cholesteric liquid crystals (CLCs) exhibit selective reflection that can be tuned owing to the dynamic control of inherent self-organized helical superstructures. Although phototunable reflection is reported, these systems hitherto suffer from a limitation in that the tuning range is restricted to one narrow period and the optically addressed images have to sacrifice one color in the visible spectrum to serve as the background, resulting from the insufficient variation in helical twisting power of existing photoresponsive chiral switches that are all bistable. Here, delicate patterns of three primary red, green, and blue (RGB) colors with a black background are presented, which is realized based on piecewise reflection tuning of the CLC induced by a newly designed photoresponsive tristable chiral switch. Three stable configurations of the chiral switch endow the CLC with two continuous and adjacent tuning periods of the reflection, covering not only entire visible spectrum, but also one wider period within near-infrared region. Therefore, the concept of piecewise tuning in CLC system demonstrates a new strategy for phototunable RGB and black reflective display.

Comment: Very promising results. The article is well written and complete. They discuss their novel and exciting break-through results, as well as the drawback of their system. They also directly compare it to other systems found in literature.

Biomimetic Temporal Self-assembly via Fuel-driven Controlled Supramolecular Polymerization

Mishra, A.; Korlepara, D. B.; Kumar, M.; Jain, A.; Jonnalagadda, N.; Bejagam, K. K.; Balasubramanian, S.*; George, S. J.* *Nat. Commun.* **2018**, *ASAP*.

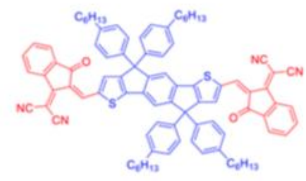


Temporal control of supramolecular assemblies to modulate the structural and transient characteristics of synthetic nanostructures is an active field of research within supramolecular chemistry. Molecular designs to attain temporal control have often taken inspiration from biological assemblies. One such assembly in Nature which has been studied extensively, for its well-defined structure and programmable self-assembly, is the ATP-driven seeded self-assembly of actin. Here we show, in a synthetic manifestation of actin self-assembly, an ATP-selective and ATP-fuelled, controlled supramolecular polymerization of a phosphate receptor functionalised monomer. It undergoes fuel-driven nucleation and seeded growth that provide length control and narrow dispersity of the resultant assemblies. Furthermore, coupling via ATP-hydrolysing enzymes yielded its transient characteristics. These results will usher investigations into synthetic analogues of important biological self-assembly motifs and will prove to be a significant advancement toward biomimetic temporally programmed materials.

Comment: Again on the topic of out-of-equilibrium supramolecular systems, this paper is a delightful paper to read in detail if you want a nice headache, but a headache that is totally worth it! They studied a relatively simple system in which self-assembly, chirality, and bio-like control are combined. The detail in which they studied the system is, mainly, the reason it ended published in Nat. Commun., and it is also the reason why I recommend it here. In addition, I further take the occasion to mention that **Nat. Commun. has an awesome feature**: it publishes also the reviewers' comments and the provided answers, which in this particular case is worth a visit! They are also the one journal that has manage to have not working DOI numbers…

Nonfullerene Acceptor Molecules for Bulk Heterojunction Organic Solar Cells

Zhang, G.; Zhao, J.; Chow, P. C. Y.; Jiang, K.; Zhang, J.; Zhu, Z.; Zhang, J.; Huang, F.; Yan, H.* *Chem. Rev.* **2018**, *ASAP.*



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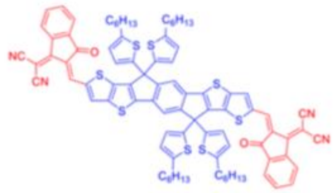

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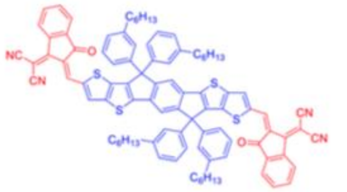

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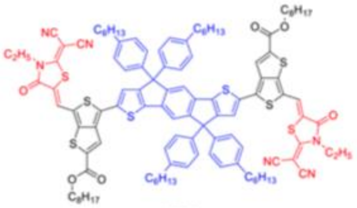

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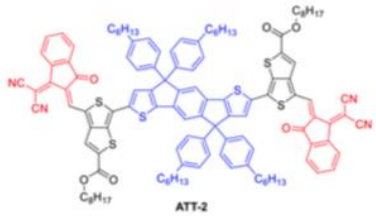

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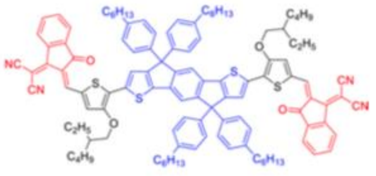

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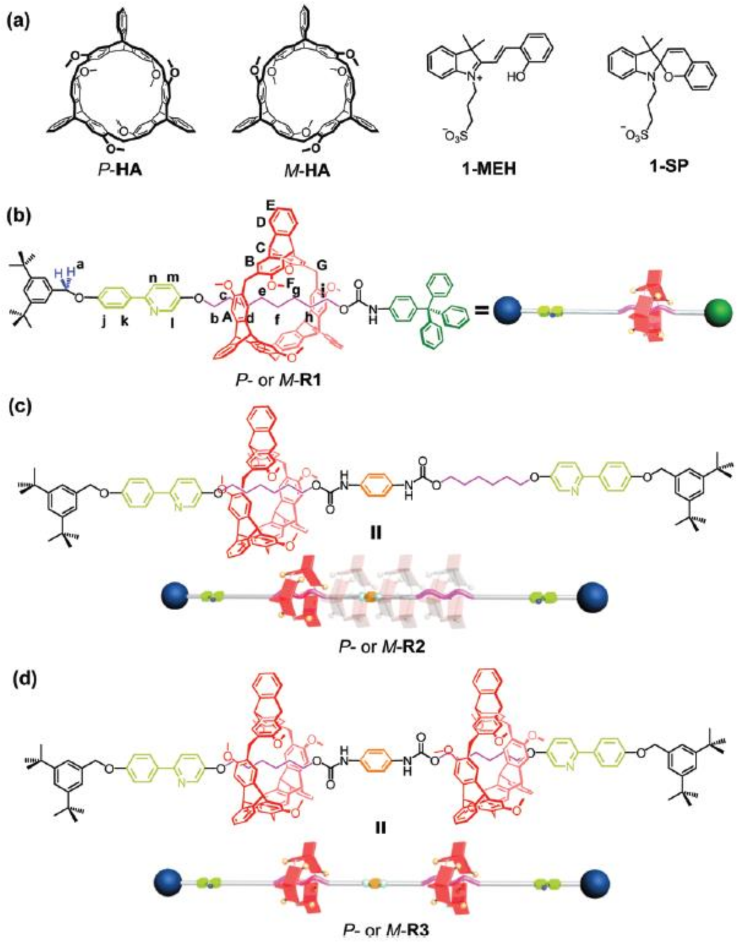
5.20

The bulk-heterojunction blend of an electron donor and an electron acceptor material is the key component in a solution-processed organic photovoltaic device. In the past decades, a p-type conjugated polymer and an n-type fullerene derivative have been the most commonly used electron donor and electron acceptor, respectively. While most advances of the device performance come from the design of new polymer donors, fullerene derivatives have almost been exclusively used as electron acceptors in organic photovoltaics. Recently, nonfullerene acceptor materials, particularly small molecules and oligomers, have emerged as a promising alternative to replace fullerene derivatives. Compared to fullerenes, these new acceptors are generally synthesized from diversified, low-cost routes based on building block materials with extraordinary chemical, thermal, and photostability. The facile functionalization of these molecules affords excellent tunability to their optoelectronic and electrochemical properties. Within the past five years, there have been over 100 nonfullerene acceptor molecules synthesized, and the power conversion efficiency of nonfullerene organic solar cells has increased dramatically, from ∼2% in 2012 to >13% in 2017. This review summarizes this progress, aiming to describe the molecular design strategy, to provide insight into the structure–property relationship, and to highlight the challenges the field is facing, with emphasis placed on most recent nonfullerene acceptors that demonstrated top-of-the-line photovoltaic performances. We also provide perspectives from a device point of view, wherein topics including ternary blend device, multijunction device, device stability, active layer morphology, and device physics are discussed.

Comment: This might be a bit, or completely, off-topic. The reason I suggest this review is not to read it but rather to be a reference if at any time in the future we need to modulate the electronic properties of our materials. The collection of molecules presented is just impressive and the compilation of the data is remarkable. Additional bonus: the possibility of a drinking game: any time you find a typo in the structures… But I have not managed to find any penta-valent carbon as of yet.

Efficient Control of Movement in Non-photoresponsive Molecular Machines by a Photo-induced Proton-transfer Strategy

Shi, Q.; Meng, Z.; Xiang, J.; Chen, C.* *Chem. Commun.* **2018**. Doi: 10.1039/c8cc01570h.

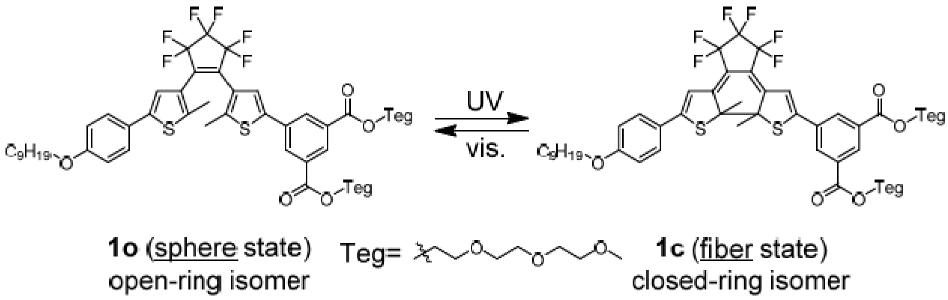


The movement of three pairs of different non-photoresponsive rotaxanes can be efficiently controlled by visible light through a photo-induced proton-transfer (PIPT) strategy in the presence of the photoacid 1-MEH. Moreover, the PIPT strategy also provides systems with a good fatigue resistance after more than 50 cycles.

Comment: Although this work is not the first example triggering motion within the rotaxanes by a PIPT strategy, it achieves the reversible movement only using photoacid 1-MEH. PIPT is a novel strategy to control molecular machines. We could consider to apply this strategy to smart materials and avoid the inevitable chemical pollution.

Bundle Formation of Supramolecular Fibers of Amphiphilic Diarylethene by Depletion Force

Sakaguchi, A.; Higashiguchi, K.*; Matsuda, K.* *Chem. Commun.* **2018**, ASAP.

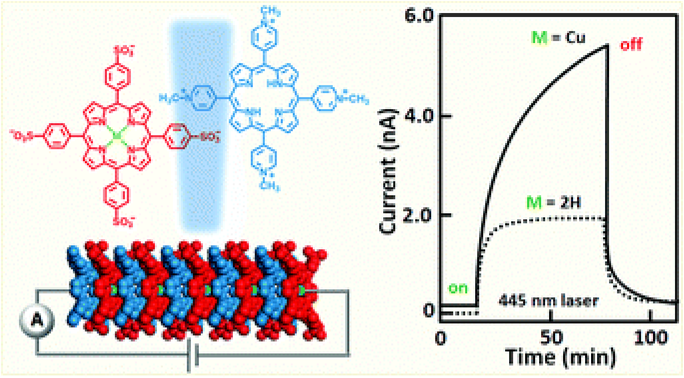


Supramolecular nanofibers composed of the closed-ring isomer of a diarylethene formed bundles in methylcellulose aqueous solution by depletion force while the spheres composed of the open-ring isomer were not coagulated. Upon irradiation with UV light to the suspension of the open-ring isomer, the fibers were found to be generated and the formed submillimeter-sized bundles showed photoinduced shrinking over than 100 μm by the visible light irradiation.

Comment: Two supramolecular architectures are constructed using an amphiphilic diarylethene. The nanofibers formed by assembly of **1c**, forming H-aggregates, could further form bundles due to depletion force in the presence of methylcellulose. We should keep in mind that depletion force could be used to reach large-scale assemblies.

Tuning the Optoelectronic Characteristics of Ionic Organic Crystalline Assemblies

Borders, B.; Adinehnia, M.; Chilukuri, B.; Ruf, M.; Hipps, K. W.; Mazur, U.* *J. Mater. Chem. C.* **2018**, Advance Article.



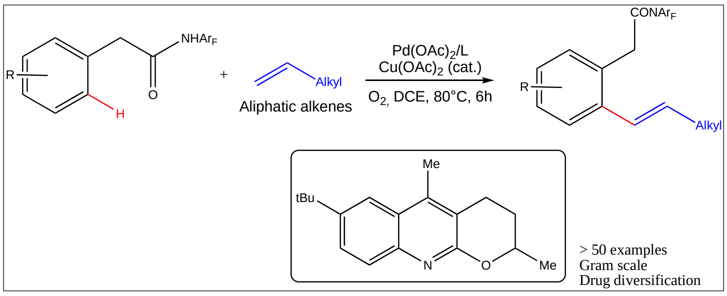
The **effect** of **selective metallation** of **free-base ionic porphyrin tectons** on the structural, electronic, and optical properties of their crystalline self-assemblies is presented. Rod-like crystals were prepared under neutral pH conditions by combining *meso*-tetra(*N*-methyl-pyridyl)porphyrin, H_2TMPyP, and *meso*-tetra(4-sulfonatophenyl)porphyrin, H_2TSPP, with either a nickel or a copper ion contained in one of the synthons. These materials were **characterized by optical microscopy, X-ray diffraction methods, thermogravimetric analysis, diffuse reflectance UV-visible and**

luminescence spectroscopies, and conductivity and photoconductivity measurements. All the porphyrin assemblies formed monoclinic $P2_1/c$ crystals with pseudo-hexagonal cross-sections. Thermogravimetric experiments indicate that water molecules associated with crystals desorb at two different rates. In addition, temperature dependent XRD showed that the dehydration of the porphyrin solids causes modification in the crystals which is completely reversible up to 100 °C annealing (*i.e.*, crystals return to their original structural geometry upon rehydration). All the metallated porphyrin crystals exhibit dark conductivity at moderately high temperatures and become more conductive upon photoexcitation. The photoresponse of the H_2TMPyP:CuTSPP-substituted crystals is significantly higher than that of the CuTMPyP:H_2TSPP and the Ni-substituted crystals. The Cu-substituted systems, like the parent free-base, exhibit persistent photoconductivity resulting from excitations into the Q and Soret bands. The primary charge carriers in these solids upon photoexcitation are electrons and the charge recombination mechanism follows monomolecular kinetics. Quantum mechanical calculations provide the electronic band structure and the density of states and explain the experimental prompt photoconductivity measurements of the porphyrin self-assemblies. This work provides evidence that optoelectronic properties of organic semiconductors can be effectively tuned by introducing transition metals into their crystal structures.

Comment: This paper may interest those who are working on the triarylamines project. Indeed, the authors studied the self-assembling of porphyrin tectons and the effect of the nature of a chelating metal to the properties of the obtained crystals. A large variety of characterization techniques have been used to determine these properties (optical microscopy, X-ray diffraction methods, thermogravimetric analysis, diffuse reflectance, luminescence spectroscopies and conductivity/photoconductivity measurements). In my opinion, the way these methods are applied and interpreted is well explained and may, therefore, be relatively easy to replicate and adapt to your own work.

Ligand-Enabled ortho-C−H Olefination of Phenylacetic Amides with Unactivated Alkenes

Lu, M. Z.; Chen, X. R.; Xu, H.; Dai, H. X.*; Yu, J. Q.* *Chem. Sci.* **2018**, *9*, 1311-1316.

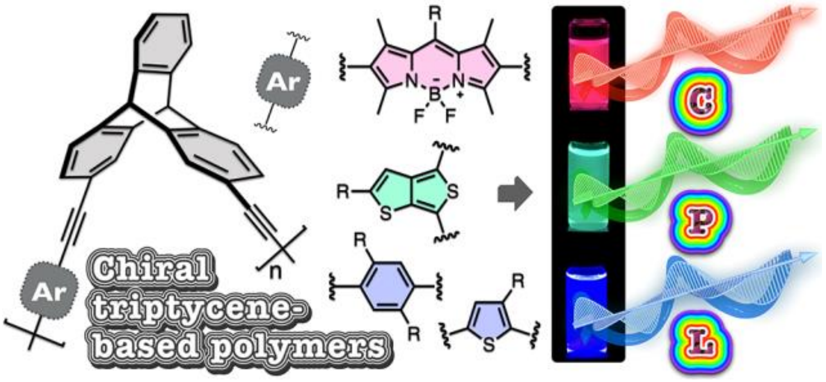


Although chelation-assisted C–H olefination has been intensely investigated, Pd(II)-catalyzed C–H olefination reactions are largely restricted to acrylates and styrenes. Here we report a **quinoline-derived ligand** that **enables the Pd(II)-catalyzed olefination of the C(sp^2)–H bond with** simple **aliphatic alkenes** using a weakly coordinating monodentate amide auxiliary. Oxygen is used as the terminal oxidant with catalytic copper as the co-oxidant. A variety of functional groups in the aliphatic alkenes are tolerated. Upon hydrogenation, the *ortho*-alkylated product can be accessed. The utility of this reaction is also demonstrated by the late-stage diversification of drug molecules.

Comment: The activation of a C(sp^2)-H bond is often challenging. In this paper, a new approach is presented through more than 50 examples. The syntheses seem to be quite easy to perform and, more importantly, scalable (up to 1g). Therefore, it could be good to keep this work in mind for future multi-steps syntheses.

Circularly Polarized Luminescent Triptycene-Based Polymers

Ikai, T.*; Yoshida, T.; Awata, S.; Wada, Y.; Maeda, K.; Mizuno, M.; Swager, T. M.* *ACS Macro Lett.* **2018**, *7*, 364–369.

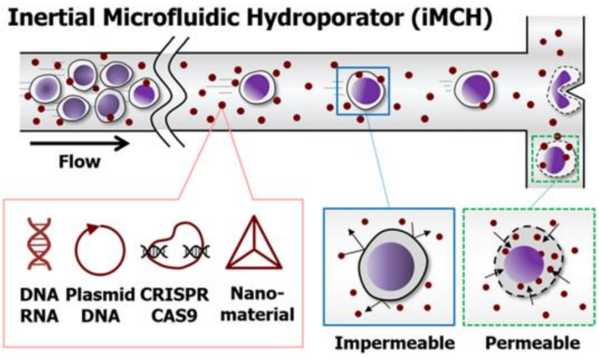


A series of chiral fluorescent polymers containing optically active triptycene units in the main chain were synthesized via Sonogashira−Hagihara coupling copolymerizations of (*R*,*R*)- or (*S*,*S*)-2,6-diethynyltriptycene with a range of diiodoaryls. Their optical and chiroptical properties were investigated under various solution conditions. We observe that **these polymers emitted circularly polarized light** owing to the chiral triptycene framework with a handed twisted rigid structure, and **the fluorescence colors could be tuned** in the whole visible range from blue to red by replacing the achiral comonomer units. They possessed luminescence dissymmetry factors of approximately 1.0 × 10^{-3}, regardless of the incorporated comonomer units.

Comment: In a previous work, the authors showed that supramolecular aggregates of triptycene derivatives could emit circularly polarized light, but potential applications were difficult because of the **high sensitivity to external parameters** (temperature, solvent…). In this work, copolymers incorporating chiral triptycene units were prepared instead, and the emission wavelength was tuned with the achiral comonomer unit.

Intracellular Delivery of Nanomaterials via an Inertial Microfluidic Cell Hydroporator

Deng, Y.; Kizer, M.; Rada, M.; Sage, J.; Wang, X.; Cheon, D.-J.; Chung, A. J.* *Nano Lett.* **2018**, ASAP.

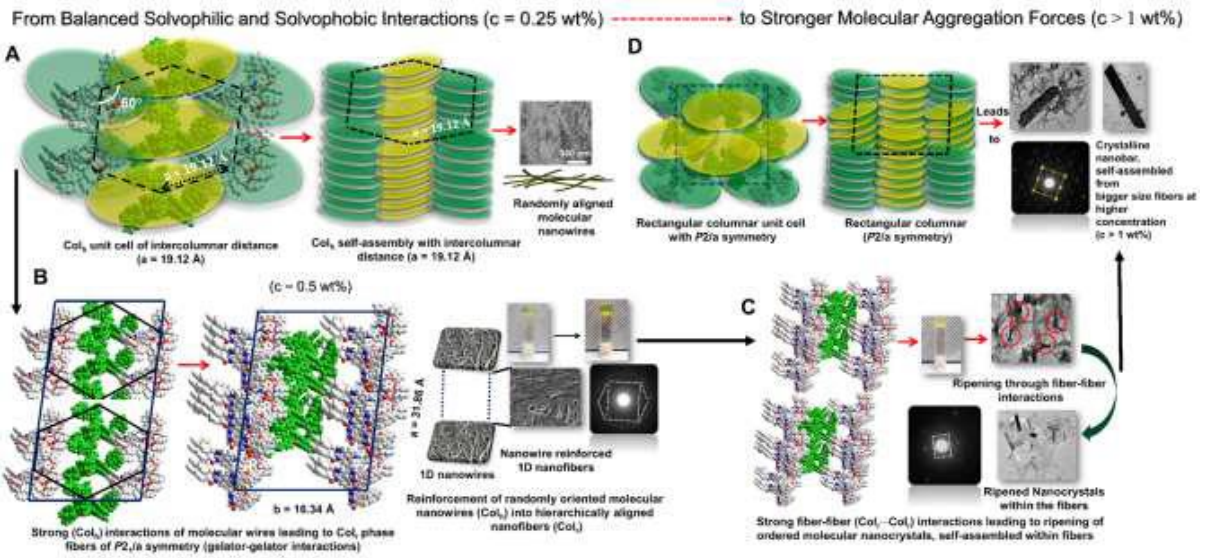


The introduction of nanomaterials into cells is an indispensable process for studies ranging from basic biology to clinical applications. To deliver foreign nanomaterials into living cells, traditionally endocytosis, viral and lipid nanocarriers or electroporation are mainly employed; however, they critically suffer from toxicity, inconsistent delivery, and low throughput and are time-consuming and labor-intensive processes. Here, we present a novel inertial microfluidic cell hydroporator **capable of delivering a wide range of nanomaterials to various cell types** in a single-step without the aid of carriers or external apparatus. The platform inertially focuses cells into the channel center and guides cells to collide at a T-junction. Controlled compression and shear forces generate transient membrane discontinuities that facilitate passive diffusion of external nanomaterials into the cell cytoplasm while maintaining high cell viability. This hydroporation method shows superior delivery efficiency, is high-throughput, and has high controllability; moreover, its extremely simple and low-cost operation provides a powerful and practical strategy in the applications of cellular imaging, biomanufacturing, cell-based therapies, regenerative medicine, and disease diagnosis.

Comment: The authors did a considerable work to characterize their new system and to compare its performance to what currently exists. It is surprising to see that a cell survives to such a collision and the fact that this technique is **potentially independent of the nanomaterial** to be delivered inside the cell. It might open a wide range of possibilities.

Augmenting Photoinduced Charge Transport in a Single Component Gel System through Room Temperature Controlled In Situ Gel-Crystal Transformation

Satapathy, S.*; Prabakaran, P.*; Prasad, E.* *Chem. Eur. J.* 10.1002/chem.201800218

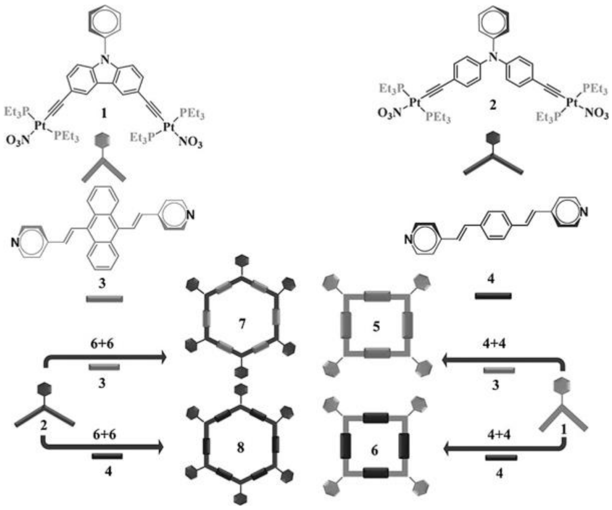


Smart single component materials with versatile functions requires pre-programming of a higher order molecular assembly. The contribution here introduces an electroactive supergelator (c = 0.07 wt%), i.e., triphenyl amine core appended poly(aryl ether) dendron (TPAPAE), where the substantial dendritic effect improves the order and crystallinity by switching the local minimum from self-assembled molecular wires to thermodynamically favourable global minimum of ordered crystals, ripened within the fibers. Controlled in situ phase change at room temperature ultimately stabilized the mixed valence states in the single component supramolecular assembly with an amplified photoluminescence and photoinduced charge transport by two orders of magnitude.

Comment: The switching from gel state to crystals and the related change in the properties of the system is very unusual.

Aggregation-Induced Emission of Platinum(II) Metallacycles and their Ability to Detect Nitroaromatics

Chowdhury, A.; Howlader, P.; Mukherjee, P. S.* *Chem. Eur. J.* **2018**, ASAP.

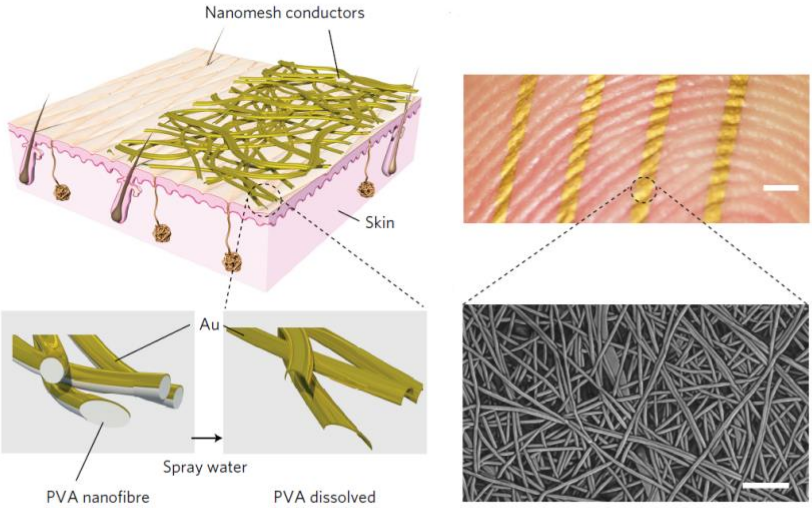


Two new acceptors containing platinum–carbazole (**1**) and platinum–triphenylamine (**2**) backbones with bite angles of 90° and 120°, respectively, have been synthesized and characterised. Reactions of the rigid acceptor 1 with linear dipyridyl-based donors (**3** and **4**) generated [4+4] self-assembled molecular squares (**5** and **6**), and similar treatments with acceptor **2** instead of **1** yielded [6+6] self-assembled molecular hexagons (**7** and **8**). The metallacycles were characterised by multinuclear NMR spectroscopy (1H and 31P) and ESI-MS. The geometries of the metallacycles were optimized by using the PM6 method. When aggregates of the metallacycles were formed by adding hexane solutions in dichloromethane, aggregation-induced emission was observed for metallacycles **5** and **7**, and aggregation-caused quenching was observed for metallacycles **6** and **8**. The formation of aggregates was verified by dynamic light scattering and TEM analyses. Macrocycles **5** and **7** are white-light emitters in THF. Moreover, their high luminescence in both solution and the solid state was utilised for the recognition of nitroaromatic explosives.

Comment: An interesting application for the AIE phenomenon.

Inflammation-Free, Gas-permeable, Lightweight, Stretchable On-skin Electronic with Nanomeshes

Miyamoto, A.; Lee, S.; Cooray, N. F.; Lee, S.; Mori, M.; Matsuhisa, N.; Jin, H.; Yoda, L.; Yokota, T.; Itoh, A.; Sekino, M.; Kawasaki, H.; Ebihara, T.; Amagai, M.; Someya, T.* *Nat. Nanotechnol.* **2017**, *12*, 907.

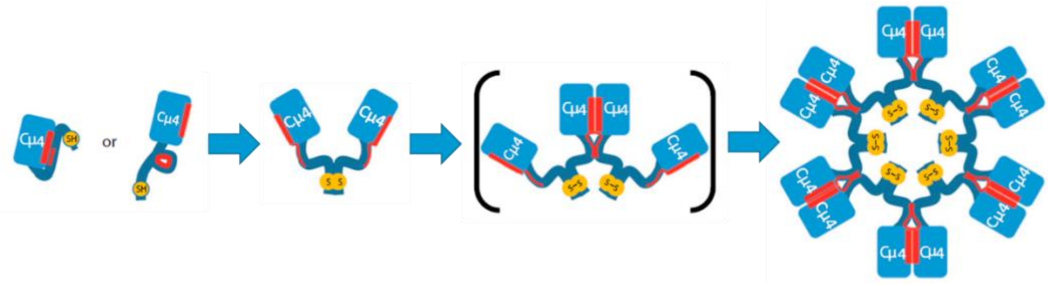


Thin-film electronic devices can be integrated with skin for health monitoring and/or for interfacing with machines. Minimal invasiveness is highly desirable when applying wearable electronics directly onto human skin. However, manufacturing such on-skin electronics on planar substrates results in limited gas permeability. Therefore, it is necessary to systematically investigate their long-term physiological and psychological effects. As a demonstration of substrate-free electronics, here we show the successful fabrication of inflammation-free, highly gas-permeable, **ultrathin, lightweight and stretchable sensors** that can be directly **laminated onto human skin** for long periods of time, realized with a conductive nanomesh structure. A one-week skin patch test revealed that the risk of inflammation caused by on-skin sensors can be significantly suppressed by using the nanomesh sensors. Furthermore, a wireless system that can detect touch, temperature and pressure is successfully demonstrated using a nanomesh with excellent mechanical durability. In addition, electromyogram recordings were successfully taken with minimal discomfort to the user.

Comment: Someya *et al* have developed a hypoallergenic, breathable sensor that can be worn on the skin continuously for a week without discomfort. The biocompatible sensor is a Au nanofiber-mesh which was laminated directly onto skin (nanofiber diameter: 300–500 nm prepared by electrospinning a polyvinyl alcohol solution). It can be used reliably as an electrode for electromyogram recordings. Spoiler: There was only one case in which contact dermatitis (possible Au allergy) occurred among the test participants.

A Peptide Extension Dictates IgM Assembly

Pasalic, D.; Weber, B.; Giannone, C.; Anelli, T.; Müller, R.; Fagioli, C.; Felkl, M.; John, C.; Mossuto, M. F.; Becker, C. F. W.; Sitia, R.*; Bucher, J.* *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 8575.

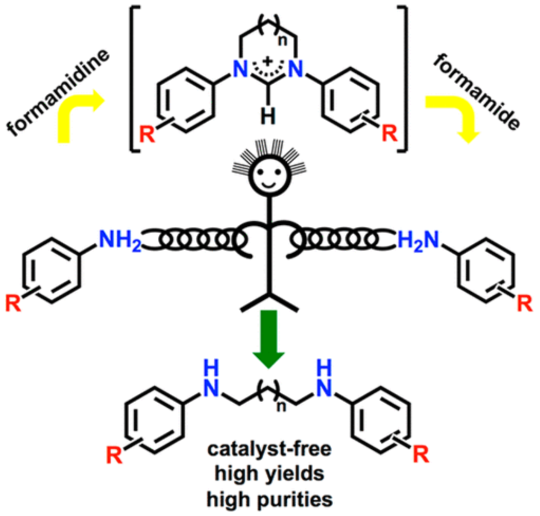


Professional secretory cells can produce large amounts of **high-quality complex molecules**, including IgM antibodies. Owing to their multivalency, polymeric IgM antibodies provide an efficient first-line of defense against pathogens. To decipher the **mechanisms of IgM assembly**, we investigated its biosynthesis in living cells and faithfully reconstituted the underlying processes in vitro. We find that **a conserved peptide extension** at the C-terminal end of the IgM heavy (Ig-μ) chains, termed the tailpiece, is **necessary and sufficient to establish the correct geometry**. Alanine scanning revealed that hydrophobic amino acids in the first half of the tailpiece contain essential information for generating the correct topology. Assembly is triggered by the formation of a disulfide bond linking two tailpieces. This induces conformational changes in the tailpiece and the adjacent domain, which drive further **polymerization**. Thus, the biogenesis of large and topologically challenging IgM complexes is dictated by a local conformational switch in a peptide extension.

Comment: A structural biology problem solved for IgM protein assemblies. The intriguing antibody IgM forms a complex of over 1200 kDa (i.e. 1 200 000 Da) consisting of six antibody subunits. These subunits are arranged in a ring-like structure kept together by disulfide bonds. This paper points out that the assembly trigger is a short peptide extension of the IgM heavy chain. This sequence is sufficient to steer the formation of the hexameric complex.

Catalyst-free Synthesis of Aryl Diamines via a Three-step Reaction Process

Bulut, S.; Queen, W. L.* *J. Org. Chem.* **2018**, just accepted.

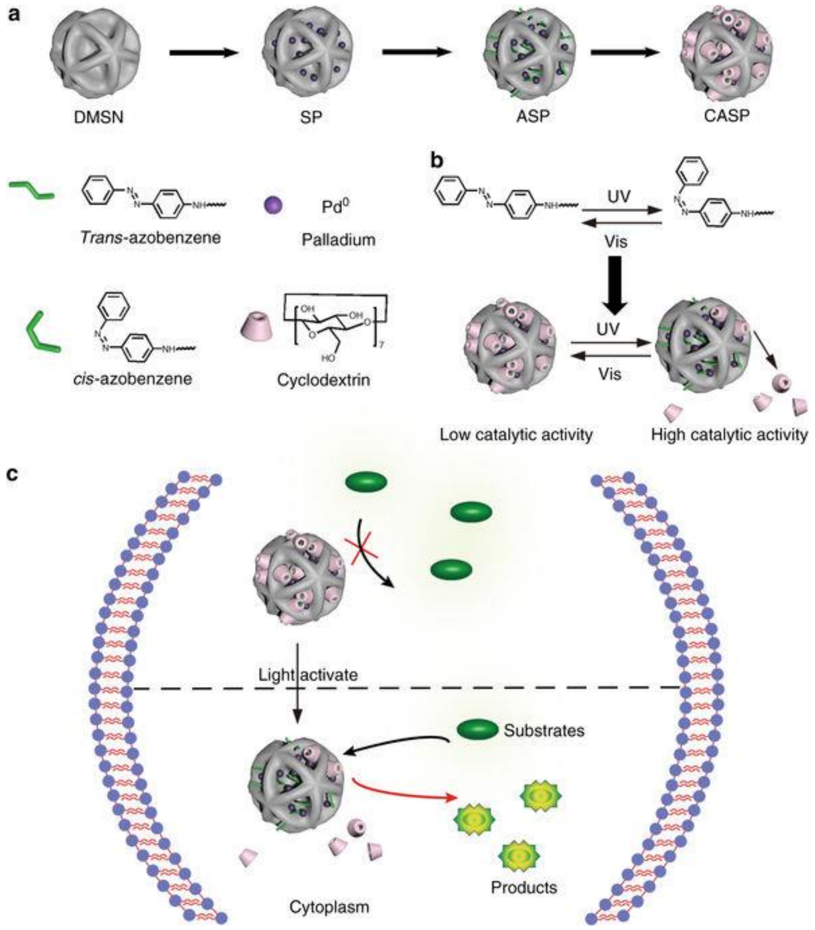


The formation of C–N bonds with aryl amines is one of the most widely studied reactions in organic chemistry. Despite this, it is still highly challenging, often requiring expensive, precious metal-based catalysts. Here we report an easy catalyst-free methodology for constructing C–N bonds. The method, which proceeds via the in situ formation of closed ring amidinium ions, allows the preparation of a series of symmetrical and/or unsymmetrical aryl diamines in notably high yields (82–98%) and purity and with a variety of different substituents. The methodology is shown successful for the preparation of aryl diamines having *para*- and/or *meta*-substituted carboxyl, nitro, bromo, methoxy, or methyl groups. This green synthetic pathway, which is catalyst free, requires only three steps, and proceeds without the need for purification. Further, it is a new sustainable, economically viable method to achieve an otherwise challenging bond formation.

Comment: I truly appreciate that new C-N bonds can be formed straight from aryl amines by a less challenging catalyst-free method. However, this paper with its TOC was worth sharing as a potential candidate for TOC ROFL (funny table-of-contents images from scientific journal articles). For more info, visit this amazing blog tocrofl.tumblr.com

Designed Heterogeneous Palladium Catalysts for Reversible Light-controlled Bioorthogonal Catalysis in Living Cells

Wang, F.; Zhang, Y.; Du, Z.; Ren, J.; Qu, X.* *Nat. Commun.* **2018**, 9, 1209.

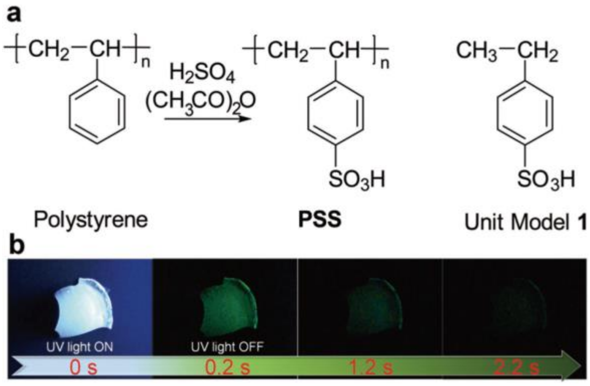


As a powerful tool for chemical biology, bioorthogonal chemistry broadens the ways to explore the mystery of life. In this field, transition metal catalysts (TMCs) have received much attention because TMCs can rapidly catalyze chemical transformations that cannot be accomplished by bio-enzymes. However, fine controlling chemical reactions in living systems like bio-enzymes is still a great challenge. Herein, we construct a versatile light-controlled bioorthogonal catalyst by modifying macroporous silica-Pd^0 with supramolecular complex of azobenzene (Azo) and β-cyclodextrin (CD). Its catalytic activity can be regulated by light-induced structural changes, mimicking allosteric regulation mechanism of bio-enzymes. The light-gated heterogeneous TMCs are important for in situ controlling bioorthogonal reactions and have been successfully used to synthesize a fluorescent probe for cell imaging and mitochondria-specific targeting agent by Suzuki–Miyaura cross-coupling reaction. Endowing the bioorthogonal catalyst with new functions is highly valuable for realizing more complex researches in biochemistry.

Comment: Although the authors mentioned that the reversible interaction between Azo and CD would endow the bioorthogonal catalyst with reversibility, in their study the reversibility was not achieved because the host-guest system is based on pseudorotaxanes. Changing the host-guest system to a rotaxane-based one or fixing the CDs on the DMSN with some flexibility might make the reversibility possible.

Ultralong Room-temperature Phosphorescence from Amorphous Polymer Poly(Styrene Sulfonic Acid) in Air in the Dry Solid State

Ogoshi, T.*; Tsuchida, H.; Kakuta, T.; Yamagishi, T.-a.; Taema, A.; Ono, T.; Sugimoto, M.; Mizuno, M., *Adv. Funct. Mater.* **2018**, 1707369.

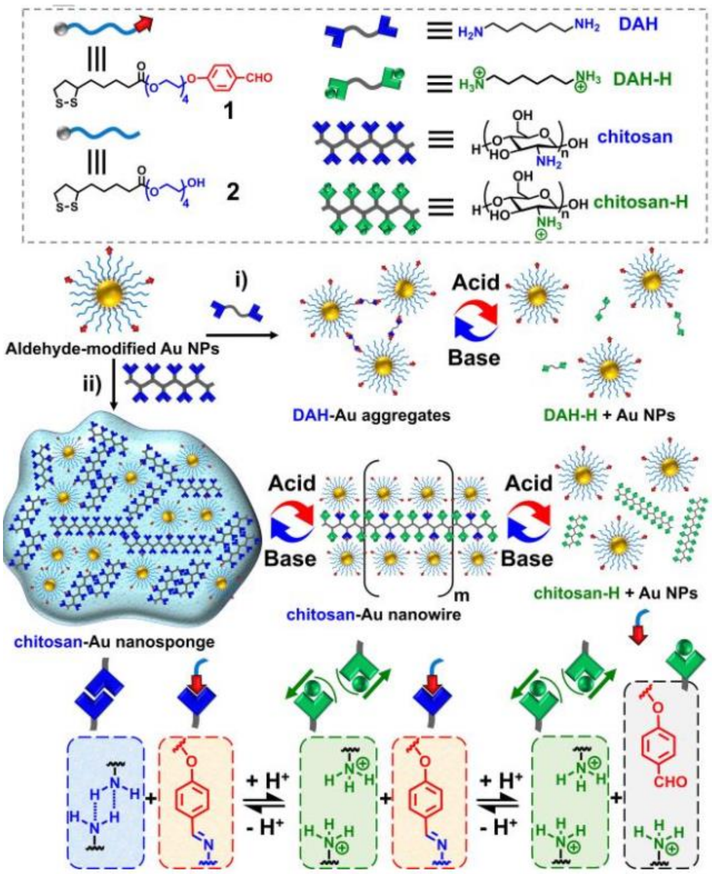


Polymer-based room-temperature-phosphorescent (RTP) materials are attractive alternatives to low-molecular-weight organic RTP compounds because they can form self-standing transparent films with high thermal stability. However, their RTP lifetimes in air are usually short (<≈0.4 s). Here, the simple organic amorphous polymer, poly(styrene sulfonic acid) (PSS), exhibits an ultralong RTP lifetime in air when desiccated. The maximum lifetime is 1.22 s, which is three times that of previously reported RTP amorphous organic polymers. The lifetime can be controlled by the PSS molecular weight and by the ratio of sulfonic acid groups introduced into the polymer. The dry polymers should enable unprecedented molecular engineering in organic molecule-based optoelectronic devices because of the self-standing and thermal stability attributes.

Comment: A quite specialized study on polymer-based room-temperature-phosphorescent (RTP) based on poly(styrene sulfonic acid). The point I want to highlight is that they use solid-state cross-polarized magic angle spinning ^{13}C NMR to prove the breaking of the hydrogen bonds around the sulfonic acid groups. This methodology was not applied in previous studies.

Dynamic Self-assembly of Gold/Polymer Nanocomposites: pH-Encoded Switching between 1D Nanowires and 3D Nanosponges

Zhang, Q.; Xu, T. Y.; Zhao, C. X.; Jin, W. H.; Wang, Q.; Qu, D. H.* *Chem. Asian J.* **2018,** *12,* 2549.

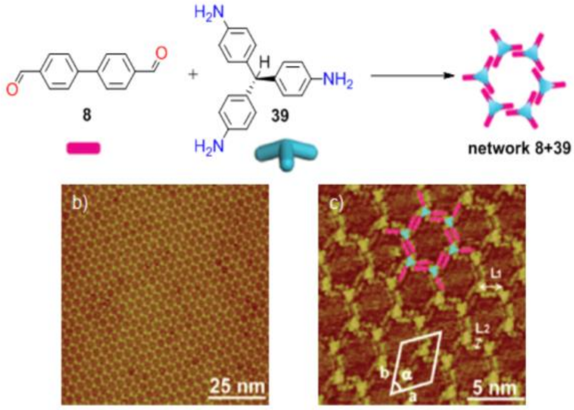


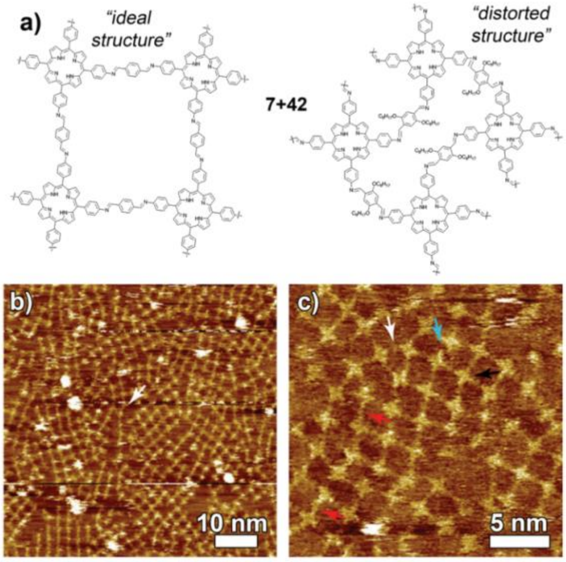
The design of tunable dynamic self-assembly of nanoparticles with switchable assembled dimensions and morphologies is a challenging goal whose realization is vital for the evolution of smart nanomaterials. Herein, we report on chitosan polymer as an effective supramolecular “glue” for aldehyde-modified Au nanoparticles to reversibly modulate the states of self-assembled nanocomposites. By simultaneous integration of dynamic covalent Schiff base interactions and noncovalent hydrogen bonds, the chitosan/Au nanocomposites could reversibly transform their assembled morphologies from one-dimensional nanowires to three-dimensional nanosponges in response to the variation of pH value. Moreover, the obtained nanosponges could be used as an efficient pH-controlled cargo release system.

Comment: This paper shows an advanced NP-based self-assembly system which can change between one-dimensional nanowires and three-dimensional nanosponges.

Imine-based Architectures at Surfaces and Interfaces: From Self-assembly to Dynamic Covalent Chemistry in 2D

Janica, I.; Patroniak, V.; Samorì, P.*; Ciesielski, A.* *Chem. Asian J.* **2018**, *13*, 465.



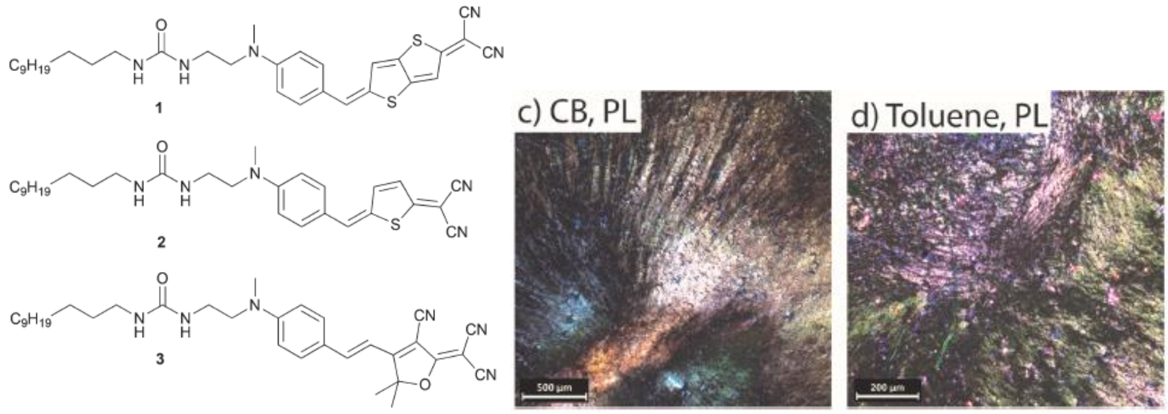


Within the last two decades, dynamic covalent chemistry (DCC) has emerged as an efficient and versatile strategy for the design and synthesis of complex molecular systems in solution. While early examples of supramolecularly assisted covalent synthesis at surfaces relied strongly on kinetically controlled reactions for post-assembly covalent modification, the DCC method takes advantage of the reversible nature of bond formation and allows the generation of the new covalently bonded structures under thermodynamic control. These structurally complex architectures obtained by means of DCC protocols offer a wealth of solutions and opportunities in the generation of new complex materials that possess sophisticated properties. In this Focus Review we examine the formation of covalently bonded imine-based discrete nanostructures as well as one-dimensional (1D) polymers and two-dimensional (2D) covalent organic frameworks (COFs) physisorbed on solid substrates under various experimental conditions, for example, under ultra-high vacuum (UHV) or at the solid–liquid interface. Scanning tunneling microscopy (STM) was used to gain insight, with a sub-nanometer resolution, into the structure and properties of those complex nanopatterns.

Comment: A review about the engineering of one-dimensional (1D) and two-dimensional (2D) imine-based supramolecular structures through the self-association of aldehydes and amines by using scanning tunneling microscopy (STM).

(Super)Gelators Derived from Push-pull Chromophores: Synthesis, Gelling Properties and Second Harmonic Generation

Belen Marco, A.; Gindre, D.; Iliopoulos, K.; Franco, S.; Andreu, R.*; Canevet, D.*; Salle, M.* *Org. Biomol. Chem.* **2018**, *ASAP.*

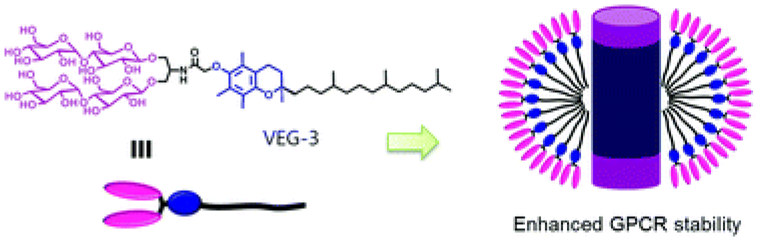


The present work takes advantage of the self-assembly process occurring along organogelation, to organize Second Harmonic Generation (SHG) active chromophores. To do so, three push-pull chromophores endowed with a dodecyl urea chain were synthesized and characterized. Their organogelating properties were studied in a wide range of solvents. Despite similar architectures, these derivatives exhibit very different gelling properties, from supergelation to the absence of gelling ability. The utilization of the Hansen solubility parameters allows for observing clear relationships between the gelled solvents and critical gelation concentrations. By evaporating the solvents from the organogels, xerogel materials were prepared and systematically studied by means of optical and electron microscopy as well as SHG microscopy. These studies demonstrate the critical role of the solvent over material structuring and allow generalizing the approach exploiting organogelation as a structuring tool to spontaneously organize push-pull chromophores into SHG-active materials.

Comment: This paper gives a comprehensive investigation on the effect of solvent on the gelation of gelators but without a clear explanation of the results. Here, a gelator with push-pull chromophores shows SHG. The concept of the combination of such molecules and the TPA system is intriguing.

Vitamin E-based Glycoside Amphiphiles for Membrane Protein Structural Studies

Ehsan, M.; Du, Y.; Molist, I.; Seven, A. B.; Hariharan, P.; Mortensen, J. S.; Ghani, L.; Loland, C. J.; Skiniotis, G.; Guan, L.; Byrne, B.; Kobilka, B. K.; Chae, P. S* *Org. Biomol. Chem.* **2018**, *ASAP.*

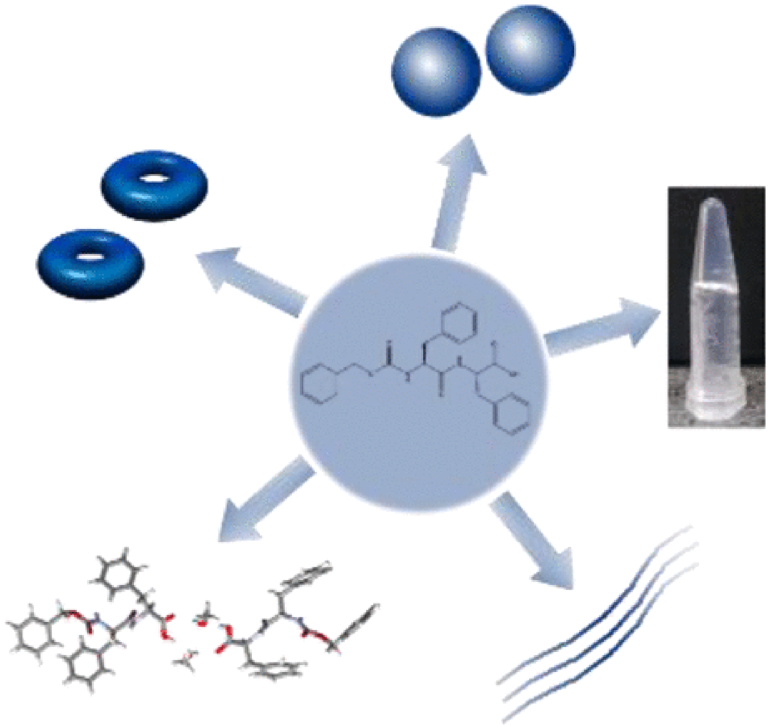


Membrane proteins play critical roles in a variety of cellular processes. For a detailed molecular level understanding of their biological functions and roles in disease, it is necessary to extract them from the native membranes. While the amphipathic nature of these bio-macromolecules presents technical challenges, amphiphilic assistants such as detergents serve as useful tools for membrane protein structural and functional studies. Conventional detergents are limited in their ability to maintain the structural integrity of membrane proteins and thus it is essential to develop novel agents with enhanced properties. Here, we designed and characterized a novel class of amphiphiles with vitamin E (i.e., α-tocopherol) as the hydrophobic tail group and saccharide units as the hydrophilic head group. Designated vitamin E-based glycosides (VEGs), these agents were evaluated for their ability to solubilize and stabilize a set of membrane proteins. VEG representatives not only conferred markedly enhanced stability to a diverse range of membrane proteins compared to conventional detergents, but VEG-3 also showed notable efficacy toward stabilization and visualization of a membrane protein complex. In addition to hydrophile-lipophile balance (HLB) of detergent molecules, the chain length and molecular geometry of the detergent hydrophobic group seem key factors in determining detergent efficacy for membrane protein (complex) stability.

Comment: The research presented combines scientific research and practical applications. The research results not only offer a theoretical reference for detergents but also produce a new detergent, which is cool.

Structural Polymorphism in a Self-Assembled Tri-Aromatic Peptide System

Brown, N.; Lei, J.; Zhan, C.; Shimon, L. J. W.; Adler-Abramovich, L.; Wei, G.*; Gazit, E.*
ACS Nano, **2018**, *ASAP.*



Self-assembly is a process of key importance in natural systems and in nanotechnology. Peptides are attractive building blocks due to their relative facile synthesis, biocompatibility, and other unique properties. Diphenylalanine (FF) and its derivatives are known to form nanostructures of various architectures and interesting and varied characteristics. The larger triphenylalanine peptide (FFF) was found to self-assemble as efficiently as FF, forming related but distinct architectures of plate-like and spherical nanostructures. Here, to understand the effect of triaromatic systems on the self-assembly process, we examined carboxybenzyl-protected diphenylalanine (z-FF) as a minimal model for such an arrangement. We explored different self-assembly conditions by changing solvent compositions and peptide concentrations, generating a phase diagram for the assemblies. We discovered that z-FF can form a variety of structures, including nanowires, fibers, nanospheres, and nanotoroids, the latter were previously observed only in considerably larger or co-assembly systems. Secondary structure analysis revealed that all assemblies possessed a β-sheet conformation. Additionally, in solvent combinations with high water ratios, z-FF formed rigid and self-healing hydrogels. X-ray crystallography revealed a “wishbone” structure, in which z-FF dimers are linked by hydrogen bonds mediated by methanol molecules, with a 2-fold screw symmetry along the *c*-axis. All-atom molecular dynamics (MD) simulations revealed conformations similar to the crystal structure. Coarse-grained MD simulated the assembly of the peptide into either fibers or spheres in different solvent systems, consistent with the experimental results. This work thus expands the building block library for the fabrication of nanostructures by peptide self-assembly.

Comment: How very simple molecules can lead to various architectures through self-assembly.

Polyphenol-Binding Amyloid Fibrils Self-Assemble into Reversible Hydrogels with Antibacterial Activity

Hu, B.*; Shen, Y.; Adamcik, J.; Fischer, P. ; Schneider, M.; Loessner, M. J.; Mezzenga, R.*
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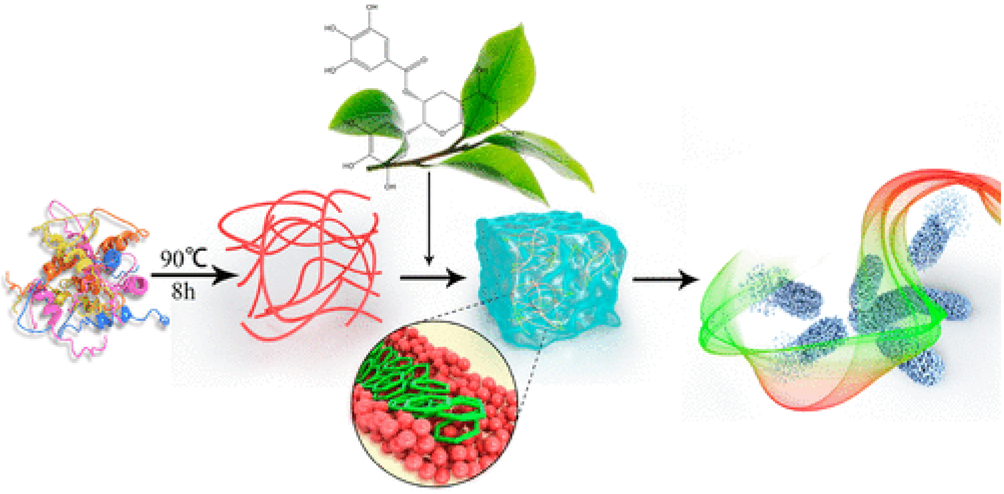

Adaptable hydrogel networks with reversible connectivity have emerged as a promising platform for biomedical applications. Synthetic copolymers and low-molecular-weight gelators (LMWG) have been shown to form reversible hydrogels through self-assembly of the molecules driven by self-complementary hydrophobic interaction and hydrogen bonding. Here, inspired by the adhesive proteins secreted by mussels, we found that simply adding natural polyphenols, such as epigallocatechin gallate (EGCG) to amyloid fibrils present in the nematic phase, successfully drives the formation of hydrogels through self-assembly of the hybrid supramolecules. The hydrogels show birefringence under polarized light, indicating that the nematic orientation is preserved in the gel phase. Gel stiffness enhances with incubation time and with an increase in molecular ratios between polyphenol and fibrils, fibril concentration, and pH. The hydrogels are shear thinning and thermostable from 25 to 90 °C without any phase transition. The integrity of the trihydroxyl groups, the gallate ester moiety in EGCG, and the hydrophobicity of the polyphenols govern the interactions with the amyloid fibrils and thus the properties of the ensuing hydrogels. The EGCG-binding amyloid fibrils, produced from lysozyme and peptidoglycans, retain the main binding functions of the enzyme, inducing bacterial agglomeration and immobilization on both Gram-positive and Gram-negative bacteria. Furthermore, the antibacterial mechanism of the lysozyme amyloid fibril hydrogels is initiated by membrane disintegration. In combination with the lack of cytotoxicity to human colonic epithelial cells demonstrated for these hybrid supramolecules, a potential role in combating multidrug-resistant bacteria in biomedical applications is suggested, such as in targeting diseases related to infection of the small intestine.

Comment: What I really enjoyed in this paper was the variety of techniques used to characterize the system.