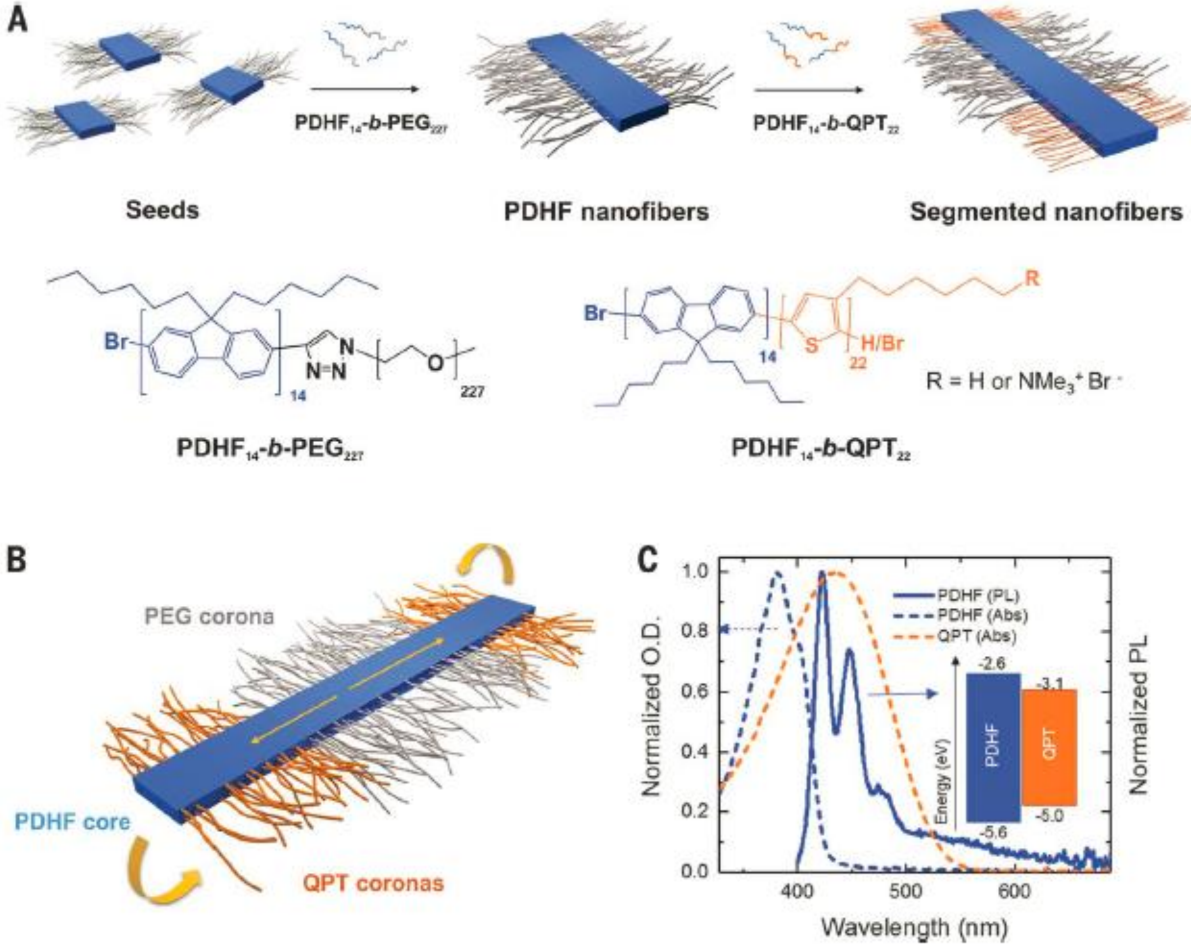
Long-range exciton transport in conjugated polymer nanofibers prepared by seeded growth

Jin, X.-H.; Price, M. B.; Finnegan, J. R.; Boott, C. E.; Richter, J. M.; Rao, A.; Menke, S. M.; Friend, R. H.; Whittell, G. R.*; Manners, I.* *Science* **2018**, *360*, 897-900.

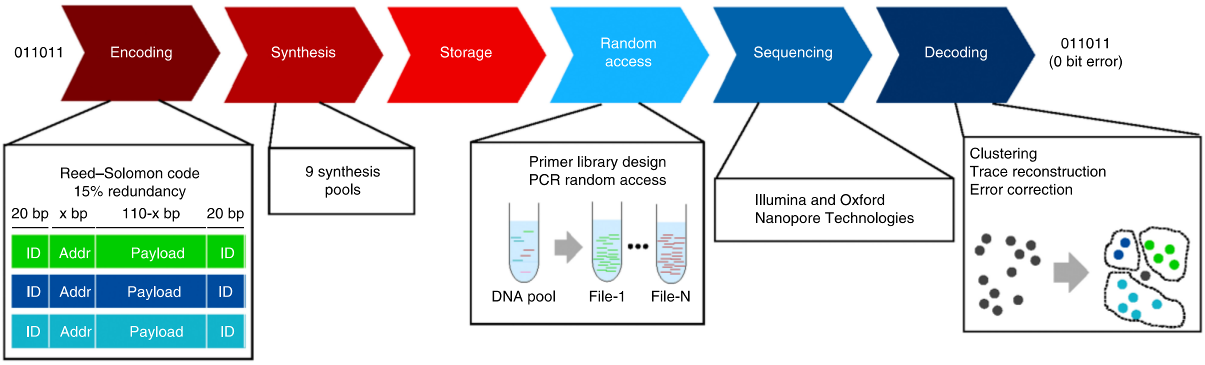


Easily processed materials with the ability to transport excitons over length scales of more than 100 nanometers are highly desirable for a range of light-harvesting and optoelectronic devices. We describe the preparation of organic semiconducting nanofibers comprising a crystalline poly(di-*n*-hexylfluorene) core and a solvated, segmented corona consisting of polyethylene glycol in the center and polythiophene at the ends. These nanofibers exhibit exciton transfer from the core to the lower-energy polythiophene coronas in the end blocks, which occurs in the direction of the interchain π-π stacking with very long diffusion lengths (>200 nanometers) and a large diffusion coefficient (0.5 square centimeters per second). This is made possible by the uniform exciton energetic landscape created by the well-ordered, crystalline nanofiber core.

Comment: It is a nice work. To investigate the exciton transfer from the core to the segmented coronas, it combines the diffusive Förster transport model and transient grating PL spectra.

Random Access in Large-Scale DNA Data Storage

Organick, L.; Ang, S. D.; Chen, Y.-J.; Lopez, R.; Yekhanin, S.; Makarychev, K.; Racz, M. Z.; Kamath, G.; Gopalan, P.; Nguyen, B.; Takahashi, C. N.; Newman, S.; Parker, H.-Y.; Rashtchian, C.; Stewart, K.; Gupta, G.; Carlson, R.; Mulligan, J.; Carmean, D.; Seelig, G.; Ceze, L.*; Strauss, K.* *Nature Biotech.* **2018**, *36*, 242–248

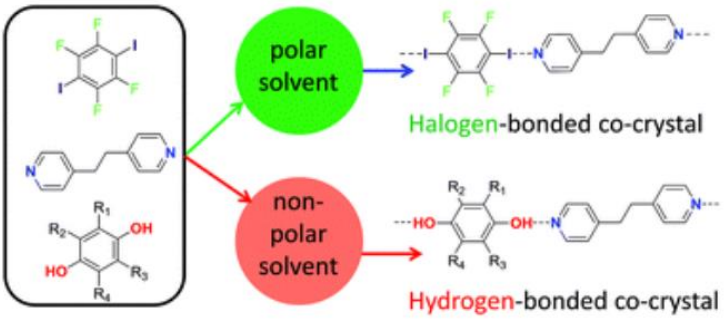


Synthetic DNA is **durable** and can **encode digital data with high density**, making it an attractive medium for data storage. However, recovering stored data on a large-scale currently requires all the DNA in a pool to be sequenced, even if only a subset of the information needs to be extracted. Here, we encode and store 35 distinct files (over 200 MB of data), in more than 13 million DNA oligonucleotides, and show that we can **recover each file individually** and **with no errors, using a random access approach**. We design and validate a large library of primers that enable individual recovery of all files stored within the DNA. We also develop an algorithm that greatly reduces the sequencing read coverage required for error-free decoding by maximizing information from all sequence reads. These advances demonstrate a viable, large-scale system for DNA data storage and retrieval.

Comment: This article is, in my opinion, closely related to the CMP team project. The main results are simply amazing. Even if this research thematic may be far away from our own, and some procedures difficult to understand (at least for me, as a modest chemist), this paper allows us to have an insight of what can be achieved in the field of DNA manipulation and data storage.

Hydrogen Bonding *vs.* Halogen Bonding: the Solvent Decides

Robertson, C., C.; Wright, J. S.; Carrington, Z., J.; Perutz, R. N.*; Hunter, C., A.*; Brammer, L.* *Chem. Sci.*, **2017**, *8*, 5392-5398.

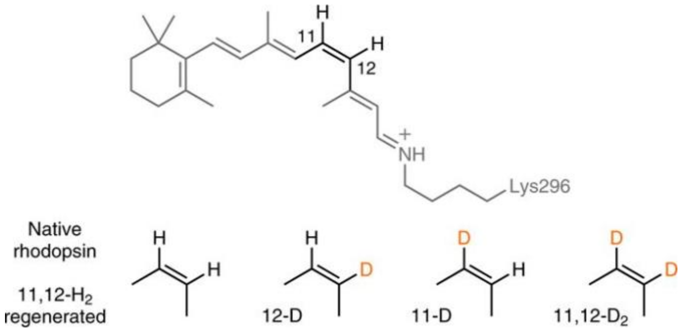


Control of intermolecular interactions is integral to harnessing self-assembly in nature. Here we demonstrate that **control of the competition between hydrogen bonds and halogen bonds**, the two most highly studied directional intermolecular interactions, **can be exerted by choice of solvent** (polarity) to **direct the self-assembly of co-crystals**. Competitive co-crystal formation has been investigated for three pairs of hydrogen bond and halogen bond donors, which can compete for a common acceptor group. These competitions have been examined in seven different solvents. Product formation has been determined and phase purity has been examined by analysis of powder X-ray diffraction patterns. Formation of hydrogen-bonded co-crystals is favoured from less polar solvents and halogen-bonded co-crystals from more polar solvents. The solvent polarity at which the crystal formation switches from hydrogen-bond to halogen-bond dominance depends on the relative strengths of the interactions, but is not a function of the solution-phase interactions alone. The results clearly establish that an appreciation of solvent effects is critical to obtain control of the intermolecular interactions.

Comment: Even if it may sound obvious, this article is a good reminder of something that should be taken into consideration when working on self-assembling systems. As you can see in this study, the solvent indeed possesses a major effect on the obtained structures.

Evidence for a Vibrational Phase-dependent Isotope Effect on the Photochemistry of Vision

Schnedermann, C.; Yang, X.; Liebel, M.; Spillane, K.; Lugtenburg, J.; Fernández, I.; Valentini, A.; Schapiro, I.; Olivucci, M.;* Kukura, P.;* Mathies, R.A.* *Nat. Chem.* **2018**, *10*, 449-455.

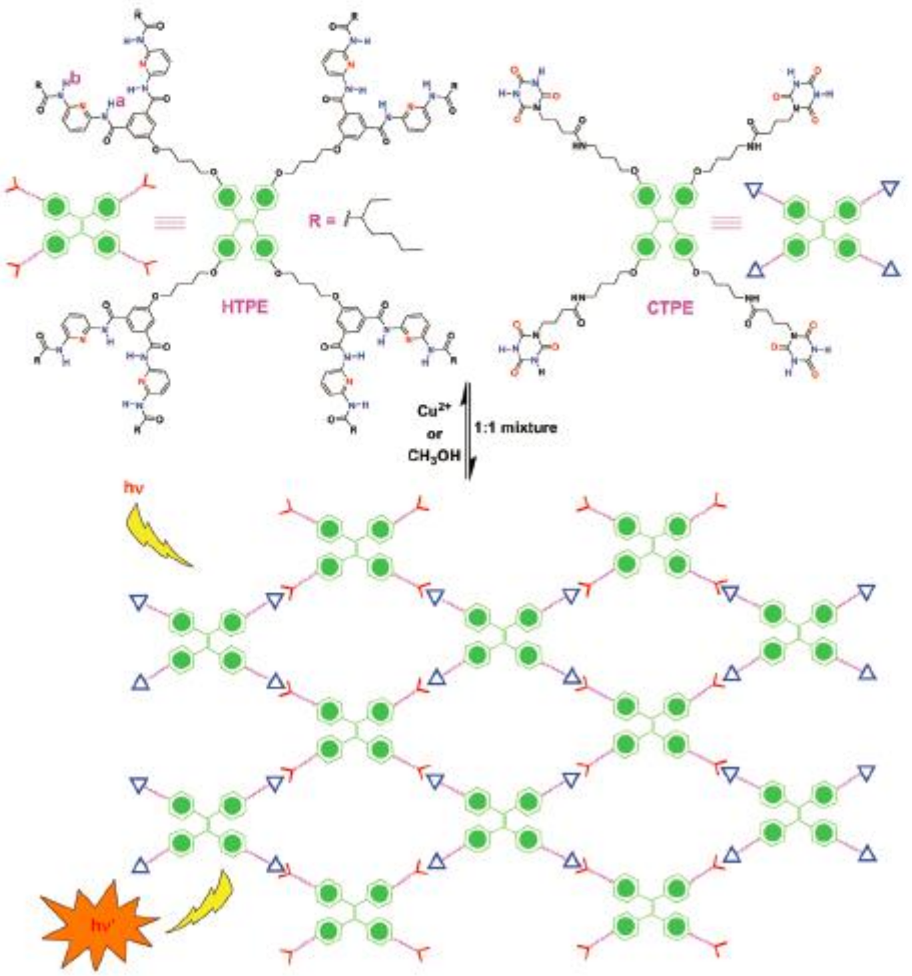


Vibronic coupling is key to efficient energy flow in molecular systems and a critical component of most mechanisms invoking quantum effects in biological processes. Despite increasing evidence for coherent coupling of electronic states being mediated by vibrational motion, it is not clear how and to what degree properties associated with vibrational coherence such as phase and coupling of atomic motion can impact the efficiency of light-induced processes under natural, incoherent illumination. Here, we show that deuteration of the $H_{11}\text{-}C_{11}=C_{12}\text{-}H_{12}$ double-bond of the 11-cis retinal chromophore in the visual pigment rhodopsin significantly and unexpectedly alters the photoisomerization yield while inducing smaller changes in the ultrafast isomerization dynamics assignable to known isotope effects. Combination of these results with non-adiabatic molecular dynamics simulations reveals a vibrational phase-dependent isotope effect that we suggest is an intrinsic attribute of vibronically coherent photochemical processes.

Comment: The change of quantum yields is unexpected because the normal isotope effects is basically about the kinetic changes. Further experimental results about other kinds of light-induced energy transfer systems using isotope labelling method are necessary to see if this “vibrational phase isotope effects” would be a general approach.

Tuning the fluorescence of tetraphenylethylene in dilute solutions via modulating multiple-hydrogen-bonding interactions between a Hamilton receptor and cyanuric acid

Wang, D.-H.; Zhu, D.-J.; Ding, W.; Xue, M.; Yang, Y.* *Org. Biomol. Chem.* **2018**, *Advance Article.*

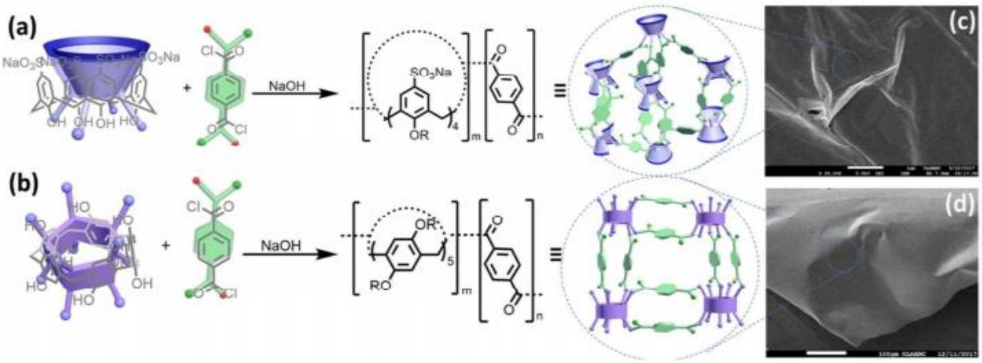


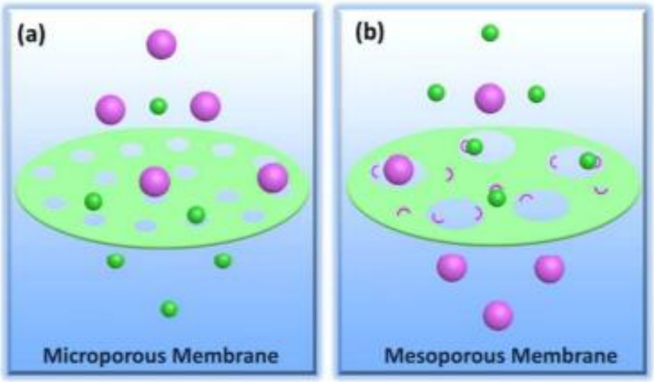
Four Hamilton receptors and four cyanuric acid modules were introduced into the tetraphenylethylene skeleton to form HTPE and CTPE, respectively. Upon 1:1 mixing of HTPE and CTPE in apolar dilute solution, a self-assembled supramolecular network was formed via multiple intermolecular hydrogen bonding interactions. The intramolecular rotation of phenyls in TPE skeletons was restricted, and thus the system became highly luminescent. Upon the addition of a hydrogen bonding competitive solvent to destroy the network, the fluorescence emission was substantially quenched. Besides, the fluorescence of the system could be further tuned by the addition of Cu^{2+} and other metal ions.

Comment: The H-bonding interaction between Hamilton receptors and cyanuric acid modules restricted the intramolecular rotation of phenyls in TPE skeletons and makes the self-assemblies luminescent even in dilute solution.

Macrocycles Crosslinked Mesoporous Polymers for Ultrafast Separation of Organic Dyes

Zhao, Q.; Liu, Y.* *Chem. Commun.* **2018**. ASAP.



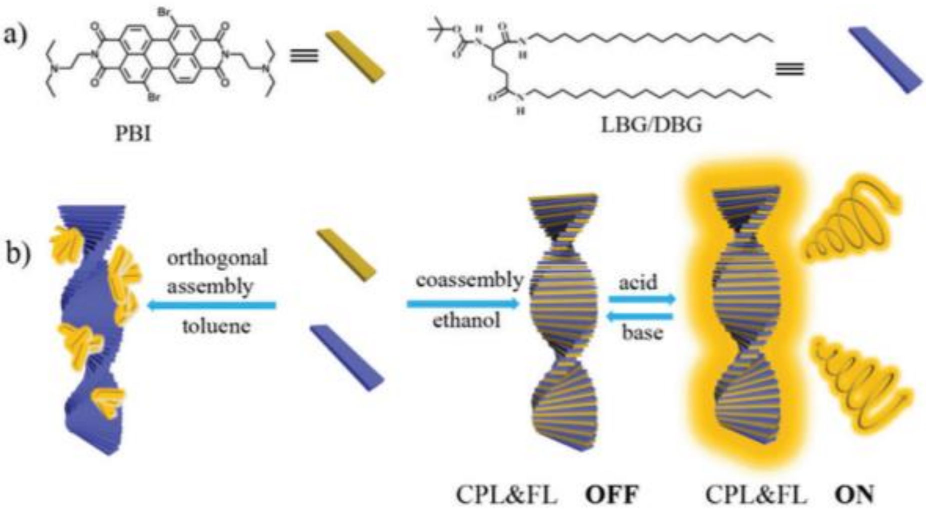


The mesoporous polymers were synthesized by interfacial polymerization of macrocycles (sulfonatocalix[4]arenes and pillar[5]arenes) and terephthaloyl chloride. Those polymer films showed ultrahigh permeabilities and excellent selectivities for molecular separations of organic dyes in water.

Comment: The authors used an interesting method (interfacial polymerization) to form two kinds mesoporous polymer. This strategy should be considered if we aim to construct a film containing more than two blocks. Both the films could encapsulate cationic dyes, which could act as filter to separate cations and anions.

Proton Triggered Circularly Polarized Luminescence in Orthogonal- and Co-assemblies of Chiral Gelators with Achiral Perylene Bisimide

Han, T.; Han, J.; Chao, S.; Huo, S.; Qu, Z.; Jiao, T.; Liu, M.; Duan, P. * *Chem. Commun.* **2018**, *54*, 5630.

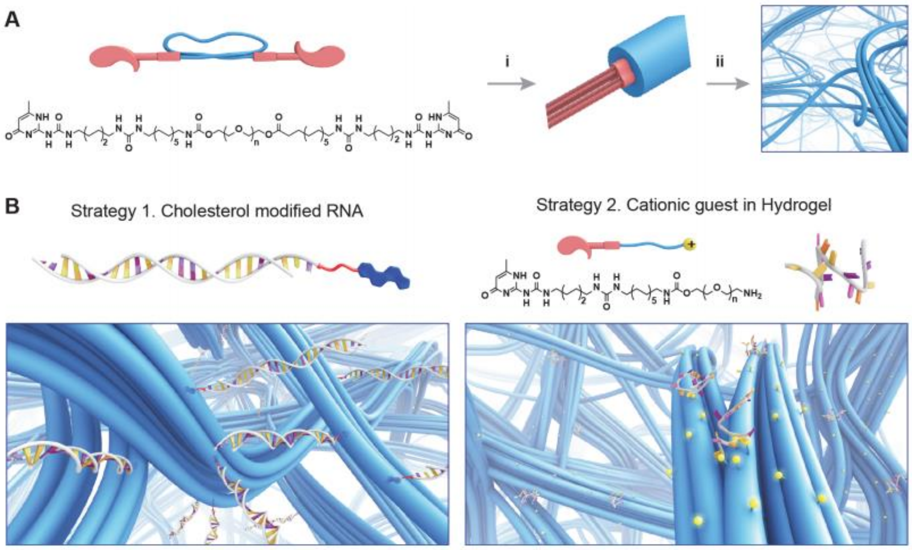


The orthogonal- or co-assembly of achiral perylene bisimide (PBI) with chiral gelators can be regulated by solvents. While the co-assembly leads to the formation of chiroptical nanofibers through chirality transfer, the orthogonal assemblies could not. Moreover, protonation on the co-assembled nanofibers could light up the circularly polarized luminescence (CPL).

Comment: The effect of solvents not only influences mono-molecular supramolecular polymers, but also the co-assembly. Another interesting point in this work is that the circularly polarized luminescence could be switched using acid and base chemistry.

Controlled Release of RNAi Molecules by Tunable Supramolecular Hydrogel Carriers

Bakker, M., van Rooij, E., Dankers, P.* *Chem. Asian J.* **2018**, ASAP.

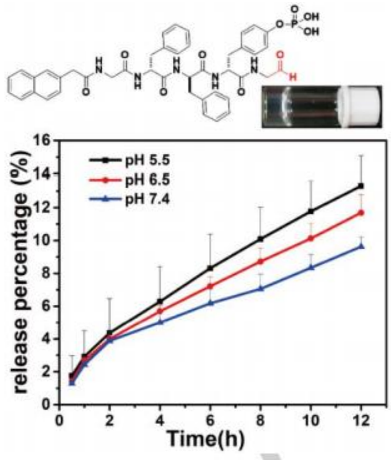


Local, sustained release and presentation of RNAi therapeutics can be achieved with hydrogel delivery systems. Here we show the development of a supramolecular hydrogel into a local RNAi delivery system. By careful material design, two simple but effective strategies are introduced to obtain controlled release of two classes of RNAi therapeutics, i.e. microRNA and antimiR. It was shown that the release of microRNA could be regulated using cholesterol-modification for interaction with the supramolecular hydrogel. Non-modified antimiR release could be controlled via supramolecular introduction of positively charged additive molecules into the supramolecular hydrogel. In this way, either the cholesterol-modification on the drug or the charge introduction into the hydrogel provides handles for controlled RNAi therapy.

Comment: The endogenous RNA interference (RNAi) pathway though supramolecular carrier is currently a very interesting topic. Conjugation of cholesterol to microRNA has been shown to be a successful approach to achieve transfection without additional agents.

An aldehyde-terminal peptide-based supramolecular hydrogel for controlled delivery of amine drugs

Wang, Y.; Zhang, Y.; Li, X.; Li, C.; Yang, Z.; Wang, L.* *Chem. Asian J.* **2018**, ASAP.

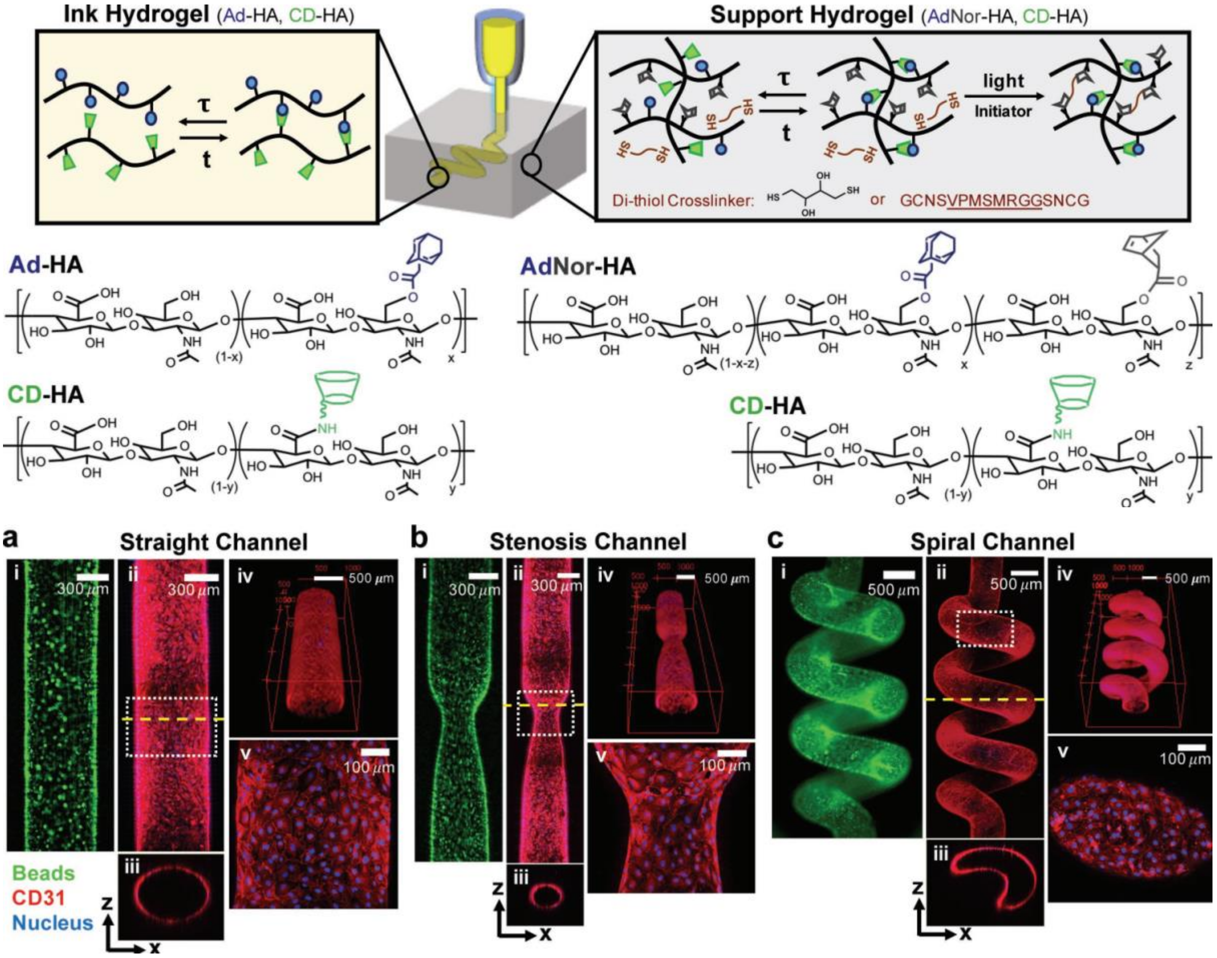


Supramolecular hydrogels hold great promise for controlled drug delivery. Herein we reported on a supramolecular hydrogel based on an aldehyde-terminal peptide. The hydrogel was prepared via the enzyme instructed self-assembly (EISA) process, and the resulting hydrogels showed an ultra-stable property in highly acidic or basic aqueous solutions. The hydrogelator could form Schiff base with amine drugs. Due to the pH-responsive property of Schiff base, the hydrogels could be applied for controlled release of encapsulated amine drugs. Our study provides a novel peptide-based hydrogel that may be applied for controlled delivery of amine containing therapeutics.

Comment: In general, very hydrophobic peptides that have poor water solubility are thought to be unable to form hydrogels. But this group developed hydrophobic short peptides that can could also form hydrogels *via* a hydrolysis processes and exploited for therapeutics.

Complex 3D-Printed Microchannels within Cell-Degradable Hydrogels

Song, K.; Highley, C.; Rouff, A.; Burdick, J.* *Adv. Funct. Mater.* **2018**, *1801331.*

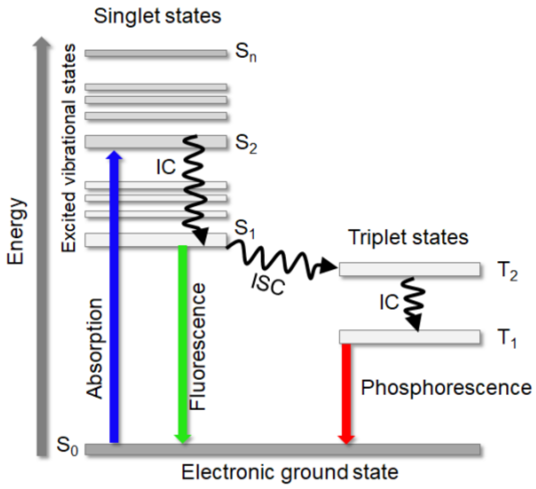


3D-printing is emerging as a technology to introduce microchannels into hydrogels, for the perfusion of engineered constructs. Although numerous techniques have been developed, new techniques are still needed to obtain the complex geometries of blood vessels and with materials that permit desired cellular responses. Here, a printing process where a shear-thinning and self-healing hydrogel "ink" is injected directly into a "support" hydrogel with similar properties is reported. The support hydrogel is further engineered to undergo stabilization through a thiol-ene reaction, permitting (i) the washing of the ink to produce microchannels and (ii) tunable properties depending on the crosslinker design. When adhesive peptides are included in the support hydrogel, endothelial cells form confluent monolayers within the channels, across a range of printed configurations (e.g., straight, stenosis, spiral). When protease-degradable crosslinkers are used for the support hydrogel and gradients of angiogenic factors are introduced, endothelial cells sprout into the support hydrogel in the direction of the gradient. This printing approach is used to investigate the influence of channel curvature on angiogenic sprouting and increased sprouting is observed at curved locations. Ultimately, this technique can be used for a range of biomedical applications, from engineering vascularized tissue constructs to modeling in vitro cultures.

Comment: It is very interesting that they fabricated the microchannel in this 3D print-washing method by taking advantage of host-guest interactions. But I guess there might be some interdisciplinary reasons (chemical, biological and mechanical) which explain why cells could sense the curvature in the blood vessels.

Phosphorescence Through Hindered Motion of Pure Organic Emitters

Hayduk, M; Riebe, N; Voskuhl, J;* *Chem. Eur. J.* **2018**, *ASAP.*

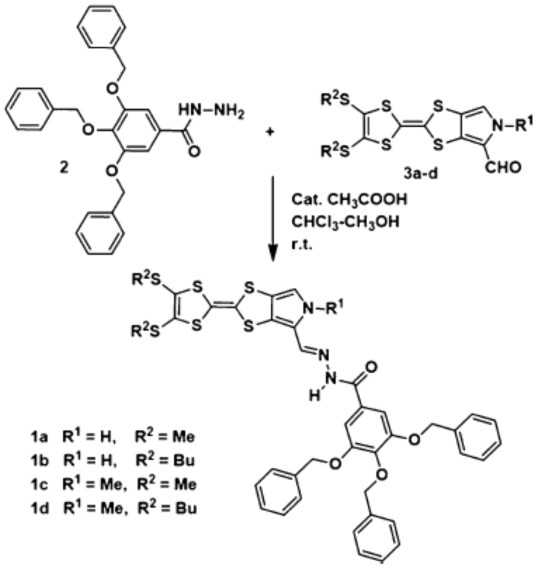


This review deals with the phenomenon of room temperature phosphorescence induced by aggregation or crystallisation. We focus on recent achievements as well as novel classes of these unique luminophores. In this fashion we describe different compounds which reveal delayed fluorescence or phosphorescence upon fixation in a crystal lattice or within aggregates. Furthermore we are describing the photophysical properties, the origin of the long-lived triplet states as well as possible applications of these fascinating classes of molecules. To conclude, we present here a short overview about the state of art in the field of pure organic phosphors at room temperature.

Comment: An interesting review about aggregation induced phosphorescence.

Poly(aryl ether) Dendrons with Monopyrrolotetrathiafulvalene Unit-Based Organogels exhibiting Gel-Induced Enhanced Emission (GIEE)

Liu, Y; Lei, W; Chen, T; Jin, Y; Sun, G; Yin, B ;* *Chem. Eur. J.* **2015**, *21*, 15235 – 15245

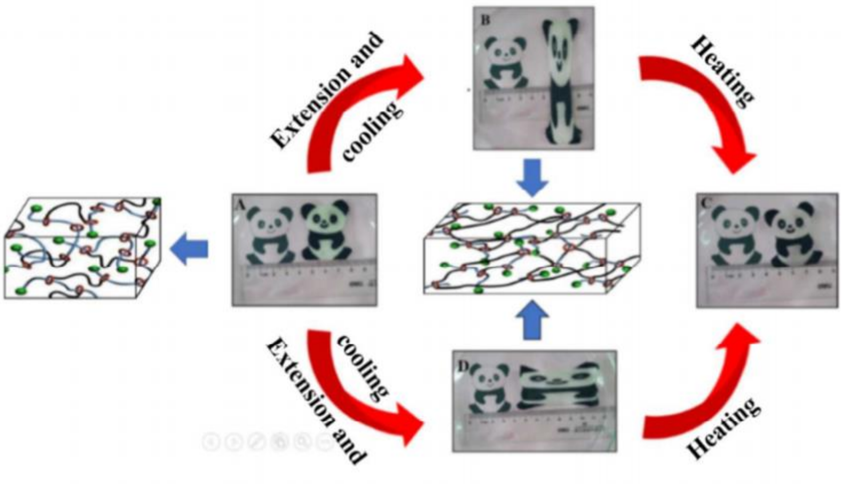


A series of poly(aryl ether) dendrons with a monopyrrolo-tetrathiafulvalene unit linked through an acyl hydrazone linkage were designed and synthesized as low molecular mass organogelators (LMOGs). Two of the dendrons could gelate the aromatic solvents and some solvent mixtures, but the others could not gel all solvents tested except for n-pentanol. A subtle change on the molecular structure produces a great influence on the gelation behavior. Note that the dendrons could form the stable gel in the DMSO/water mixture without thermal treatment and could also form the binary gel with fullerene (C60) in toluene. The formed gels undergo a reversible gel–sol phase transition upon exposure to external stimuli, such as temperature and chemical oxidation/reduction. A number of experiments (SEM, FTIR spectroscopy, 1H NMR spectroscopy, and UV/Vis absorption spectroscopy, and XRD) revealed that these dendritic molecules self-assembled into elastically interpenetrating one-dimensional fibrillar aggregates and maintain rectangular molecular-packing mode in organogels. The hydrogen bonding, p–p, and donor–acceptor interactions were found to be the main driving forces for formation of the gels. Moreover, the gel system exhibited gel-induced enhanced emission (GIEE) property in the visible region in spite of the absence of a conventional fluorophore unit and the fluorescence was effectively quenched by introduction of C60.

Comment: An interesting stimuli-responsive system.

High-strain Slide Ring Shape Memory Polycaprolactone-based Polyurethane

Wu, R.; Lai, J.; Pan, Y.; Zheng, Z.; Ding, X.* *Soft Matter* **2018**, *14*, 4558–4568.

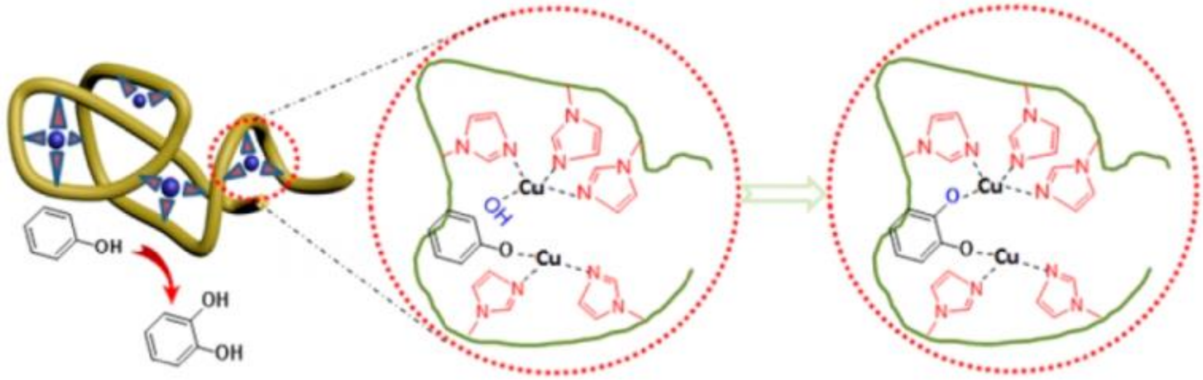


To enable the shape memory polymer networks to achieve recoverable high deformability with a simultaneous high shape fixity ratio and shape recovery ratio, a novel semi-crystalline slide ring shape memory polycaprolactone-based polyurethane (SR-SMPCLU) **with movable net-points** constructed by topologically interlocked slide ring structure is designed and fabricated. The SR-SMPCLU not only exhibits good shape fixity, almost complete shape recovery and fast shape recovery speed, but also shows outstanding recoverable high-strain capacity with 95.83% *R*r under the deformation strain 1410% due to the pulley effect of topological slide ring structure. Furthermore, The SRSMPCLUs system keep **excellent shape memory** performance with the increasing of the training cycle numbers at 45% and even 280% deformation strain. The effects of slide ring crosslinker content, deformation strain, and successive shape memory cycle on shape memory performance are investigated. A possible mechanism for the shape memory effect of the SR-SMPCLU system is proposed.

Comment: Last week, one of my contribution was about a computational study of networks with sliding crosslinks. Hence, this week, I submit an experimental work on this topic. They do not study absorption properties here –which was the most interesting result of the simulation experiments– but they show that the mechanical properties are greatly enhanced with sliding crosslinks, and that **they keep the shape memory effects**.

Single Chain Polymeric Nanoparticles to Promote Selective Hydroxylation Reactions of Phenol Catalyzed by Copper

Thanneeru, S.; Duay, S. S.; Jin, L.; Fu, Y.; Angeles-Boza, A. M.; He, J.* *ACS Macro Lett.* **2017**, *6*, 652–656.

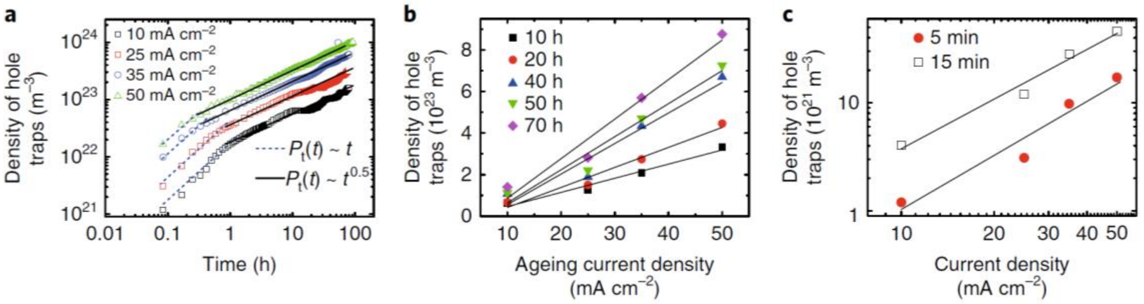


Metal-containing single chain polymeric nanoparticles (SCPNs) can be used as synthetic mimics of metalloenzymes. Currently, the role of the folded polymer backbones on the activity and selectivity of metal sites is not clear. Herein, we report our findings on how polymeric frameworks modulate the coordination of Cu sites and the catalytic activity/ selectivity of Cu-containing SCPNs mimicking monophenol hydroxylation reactions. Imidazole-functionalized copolymers of poly(methyl methacrylate-co-3-imidazolyl-2-hydroxy propyl methacrylate) were used for intramolecular Cu-imidazole binding that triggered the self-folding of polymers. Polymer chains imposed steric hindrance which yielded unsaturated Cu sites with an average coordination number of 3.3. Cu-containing SCPNs showed a high selectivity for the hydroxylation reaction of phenol to catechol, >80%, with a turnover frequency of >870 h−1 at 60 °C. **The selectivity was largely influenced by the flexibility of the folded polymer backbone** where a more flexible polymer backbone allows the cooperative catalysis of two Cu sites. The second coordination sphere provided by the folded polymer that has been less studied is therefore critical in the design of active mimics of metalloenzymes.

Comment: As the authors say in the introduction, SCPNs can act as mimics of metalloenzymes, among other properties. This paper is just about showing you one possible application, and I think there is a potential in adding an out-of-equilibrium behaviour…

Hole trap formation in polymer light-emitting diodes under current stress

Niu,Q.; Rohloff, R.; Wetzelaer, G.-J. A. H.; Blom, P. W. M.; Crăciun, N. I.* *Nat. Mater.* **2018**, *17*, 557-562

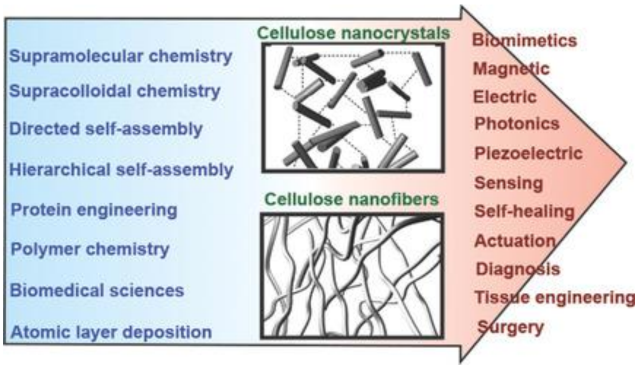


Polymer light-emitting diodes (PLEDs) are attractive for use in large-area displays and lighting panels, but their limited stability under current stress impedes commercialization. In spite of large efforts over the last two decades a fundamental understanding of the degradation mechanisms has not been accomplished. Here we demonstrate that the voltage drift of a PLED driven at constant current is caused by the formation of hole traps, which leads to additional non-radiative recombination between free electrons and trapped holes. The observed trap formation rate is consistent with exciton-free hole interactions as the main mechanism behind PLED degradation, enabling us to unify the degradation behaviour of various poly(p-phenylene) derivatives. The knowledge that hole trap formation is the cause of PLED degradation means that we can suppress the negative effect of hole traps on voltage and efficiency by blending the light-emitting polymer with a large-bandgap semiconductor. Owing to trap dilution these blended PLEDs show unprecedented stability.

Comment: This article shows that decreased hole transport in polymers (used in LED devices), upon electrical and optical stress, is most likely caused by hole trap formation. I think that the study of hole trap formation is of particular interest for our group if we want to enhance the triarylamine conductivity properties in devices (triarylamine nanofibers as hole transporting materials). Although they describe and explain the formation of traps versus ageing time well, they could have gone into more detail about the suppression of these effects.

Advanced Materials through Assembly of Nanocelluloses

Kontturi, E.; Laaksonen, P.; Linder, M. B.; Nonappa; Gröschel, A. H.; Rojas, O. J.; Ikkala, O.* Li, N.; Than, A.; Chen, L.; Xi, F.; Liu, J.; Chen, P. *Adv. Mater.* **2018**, *30*, 1703779

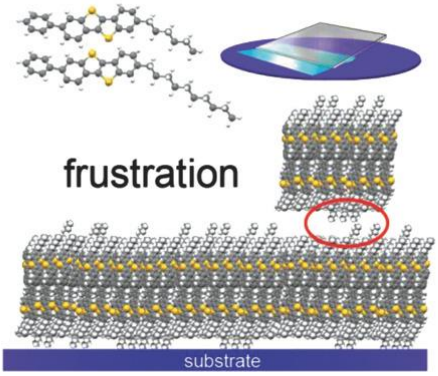


There is an emerging quest for lightweight materials with excellent mechanical properties and economic production, while still being sustainable and functionalizable. They could form the basis of the future bioeconomy for energy and material efficiency. Cellulose has long been recognized as an abundant polymer. Modified celluloses were, in fact, among the first polymers used in technical applications; however, they were later replaced by petroleum-based synthetic polymers. Currently, there is a resurgence of interest to utilize renewable resources, where cellulose is foreseen to make again a major impact, this time in the development of advanced materials. This is because of its availability and properties, as well as economic and sustainable production. Among cellulose-based structures, cellulose nanofibrils and nanocrystals display nanoscale lateral dimensions and lengths ranging from nanometers to micrometers. Their excellent mechanical properties are, in part, due to their crystalline assembly via hydrogen bonds. Owing to their abundant surface hydroxyl groups, they can be easily modified with nanoparticles, (bio)polymers, inorganics, or nanocarbons to form functional fibers, films, bulk matter, and porous aerogels and foams. Here, some of the recent progress in the development of advanced materials within this rapidly growing field is reviewed.

Comment: A nice review article showing possibilities for influencing self-assembly processes.

Semiconductive Single Molecular Bilayers Realized Using Geometrical Frustration

Arai, S.;* Inoue, S.; Hamai, T.; Kumai, R.; Hasegawa, T.* *Adv. Mater.* **2018**, *30*, 1707256

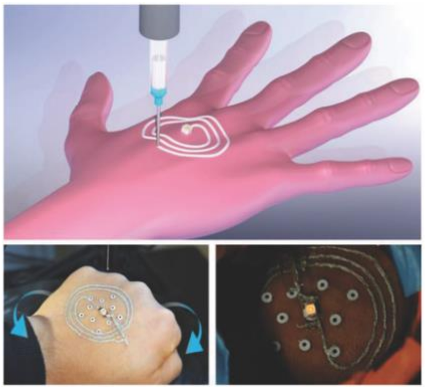


A unique solution-based technology to manufacture self-assembled ultrathin organic-semiconductor layers with ultra-uniform single-molecular-bilayer thickness over an area as large as wafer scale is developed. A novel concept is adopted in this technique, based upon the idea of geometrical frustration, which can effectively suppress the interlayer stacking (or multilayer crystallization) while maintaining the assembly of the intra-layer, which originates from the strong intermolecular interactions between π-conjugated molecules. For this purpose, a mixed solution of extended π-conjugated frameworks substituted asymmetrically by alkyl chains of variable lengths (i.e., (πCore)-Cn's) is utilized for the solution process. A simple blade-coating with a solution containing two (πCore)-Cn's with different alkyl chain lengths is effective to provide single molecular bilayers (SMBs) composed of a pair of polar monomolecular layers, which is analogical to the cell membranes of living organisms. It is demonstrated that the chain-length disorder does not perturb the in-plane crystalline order, but acts effectively as a geometrical frustration to inhibit multilayer crystallization. The uniformity, stability, and size scale are unprecedented, as produced by other conventional self-assembly processes. The obtained SMBs also exhibit efficient 2D carrier transport as organic thin-film transistors. This finding should open a new route to SMB-based ultrathin super flexible electronics.

Comment: A new technique is presented that allows the suppression of interlayer stacking by using 2 π-electron frameworks substituted by alkyl chains of different lengths (C6 and C10). If indeed this technique is applicable to a wide variety of molecules, this would have a great impact on device fabrications. However, for now this is just an assumption they make. They provide proof for only 2 different molecules.

3D Printed Functional and Biological Materials on Moving Freeform Surfaces

Zhu, Z.; Guo, S.-Z.; Hirdler, T.; Eide, C.; Fan, X.; Tolar, J.; McAlpine, M. C.**Adv. Mater.* **2018**, *30*, 1707495

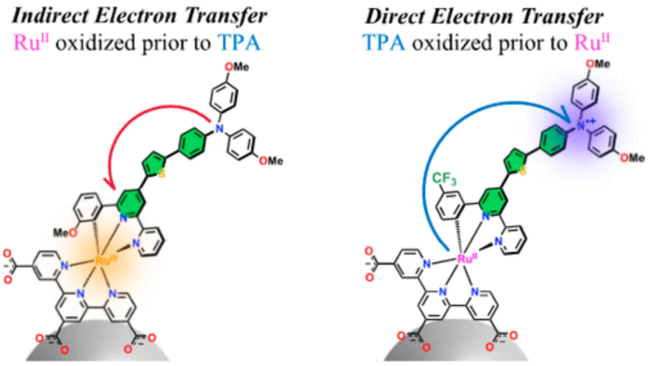


Conventional 3D printing technologies typically rely on open-loop, calibrate-then-print operation procedures. An alternative approach is adaptive 3D printing, which is a closed-loop method that combines real-time feedback control and direct ink writing of functional materials in order to fabricate devices on moving freeform surfaces. Here, it is demonstrated that the changes of states in the 3D printing workspace in terms of the geometries and motions of target surfaces can be perceived by an integrated robotic system aided by computer vision. A hybrid fabrication procedure combining 3D printing of electrical connects with automatic pick-and-placing of surface mounted electronic components yields functional electronic devices on a free moving human hand. Using this same approach, cell-laden hydrogels are also printed on live mice, creating a model for future studies of wound-healing diseases. This adaptive 3D printing method may lead to new forms of smart manufacturing technologies for directly printed wearable devices on the body and for advanced medical treatments.

Comment: This article has no direct relation with the projects we work on in our group. However, it shows the state-of-the-art in 3D printing and next-generation wearable multifunctional devices. Thus, it is very interesting from a general point of view (as it could / will have a direct impact on our (near) future lives).

Optical intramolecular electron transfer in opposite directions through the same bridge that follows different pathways

Piechota, E. J.; Troian-Gautier, L.; Sampaio, R. N.; Brennaman, M. K.; Hu, K.; Berlinguette, C. P.; Meyer, G. J.* *J. Am. Chem. Soc.*, **2018**, *ASAP* .

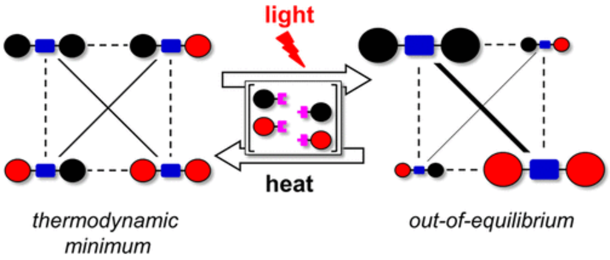


The electrochemical and spectroscopic properties of eight bis(tridentate) cyclometalated Ru^{II} compounds covalently linked by a phenyl- or xylyl-thiophene bridge to a pendant triphenylamine (TPA) were characterized in fluid solution and immobilized on metal oxide surfaces. Upon surface immobilization, the $TPA^{+/0}$ reduction potentials of the phenyl-bridged compounds exhibited large changes, ±100 mV, relative to solution-based values, yet those observed for the xylyl-bridged compounds were relatively unchanged. The highest occupied molecular orbital of the surface-immobilized compounds was associated with either TPA or Ru^{II}, enabling the study of the electron transfer in opposite directions. Electron transfer in the mixed-valent states of the compounds was found to proceed by different optical pathways for $Ru^{II} \rightarrow TPA^{+}$ relative to $TPA \rightarrow Ru^{III}$. Mulliken-Hush analysis of intervalence charge transfer bands for the phenyl-bridged compounds revealed that the electronic coupling matrix element, H_{DA}, was ~950 cm^{-1} for $Ru^{II} \rightarrow TPA^{+}$, while H_{DA} for $TPA \rightarrow Ru^{III}$ appeared to be 2500 cm^{-1}. In contrast, the xylyl-bridged compounds were weakly coupled. A superexchange analysis, where unoccupied bridge orbitals were taken directly into account, led to a very different conclusion: H_{DA} did not depend on the charge-transfer direction or path. The results imply that the electron-transfer direction can alter optical charge transfer pathways without influencing the electronic coupling.

Comment: Interesting article on intramolecular electron transfer in opposite direction between a ruthenium complex and a triarylamine. Depending the structure of the ligand, the triarylamine plays the role of the electron accepting group or electron donating group. This study is quite complete and might help us to understand more about the physical properties of electron transfer.

The Photodynamic Covalent Bond: Sensitized Alkoxyamines as a Tool to Shift Reaction Networks Out-of-Equilibrium Using Light Energy

Herder, M.; Lehn, J-M. * *J. Am. Chem. Soc.*, **2018**, *ASAP*.

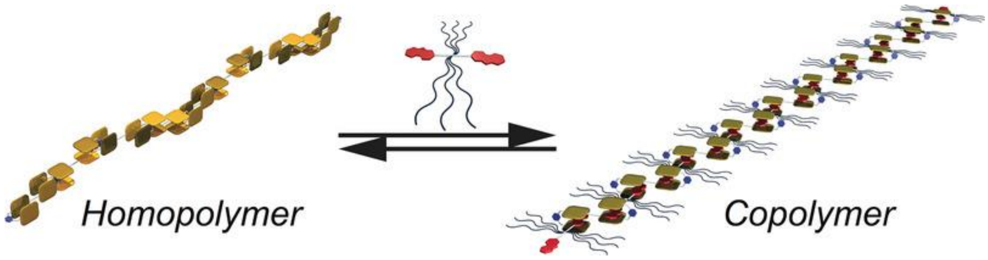


We implement sensitized alkoxyamines as “photodynamic covalent bonds”—bonds that, while being stable in the dark at ambient temperatures, upon photoexcitation efficiently dissociate and recombine to the bound state in a fast thermal reaction. This type of bond allows for the photochemically induced exchange of molecular building blocks and resulting constitutional variation within dynamic reaction networks. To this end, alkoxyamines are coupled to a xanthone unit as triplet sensitizer enabling their reversible photodissociation into two radical species. By studying the photochemical properties of three generations of sensitized alkoxyamines it became clear that the nature and efficiency of triplet energy transfer from the sensitizer to the alkoxyamine bond as well as the reversibility of photodissociation crucially depends on the structure of the nitroxide terminus. By employing the thus designed photodynamic covalent bonding motif, we demonstrate how to use light energy to shift a dynamic covalent reaction network away from its thermodynamic minimum into a photostationary state. The network could be repeatedly switched between its minimum and kinetically trapped out-of-equilibrium state by thermal scrambling and selective photoactivation of sensitized alkoxyamines, respectively.

Comment: Interesting paper about an adaptive system working as a reversible switch between a thermodynamic state and an out of equilibrium state through a dynamic covalent nitroxide bond. The general idea joins the peptide project and the motor project with an interesting concept.

Copolymerization by Sequence Reorganization of a Supramolecular Homopolymer

Nadamoto, K.; Maruyama, K.; Fujii, N.; Ikeda, T.; Kihara, S.-I.; Haino, T.* *Angew. Chem. Int. Ed.* **2018**, 57, 7028-7033

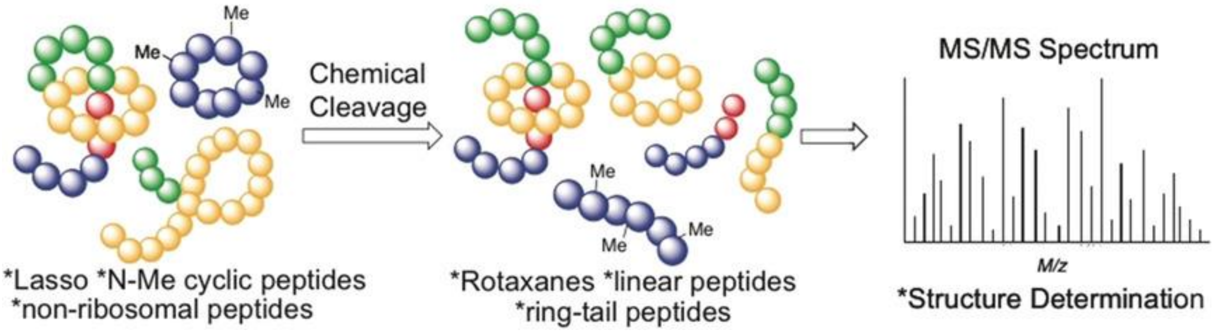


The homopolymeric sequence formed by the head-to-head association of tetrakisporphyrin **1** is completely dissociated by the competitive association of the ditopic guest **G2**, resulting in the supramolecular copolymer poly-**1**·**G2** with an alternatingly repeating host–guest sequence. The 1:1 stoichiometry of **1** and **G2** is confirmed by a Job plot using UV/Vis titration and diffusion-ordered NMR spectroscopy (DOSY). The solution viscometry for poly-**1** and poly-**1**·**G2** suggests that the supramolecular chain of poly-**1**behaves like a rod, whereas the supramolecular copolymer chain of poly-**1**·**G2** behaves like a swelled fat chain, which is entangled in the semi-dilute regime. Atomic force microscopy shows that the supramolecular polymer poly-**1**·**G2** is highly oriented through the interdigitation of the long alkyl chains.

Comment: The authors here report a nice characterization of supramolecular polymer systems. The reorganization of their homopolymer to a copolymer is well explained and highlighted by their experiments. From my point of view, the only thing lacking in their description would be the recyclability of their system. It is said early in the article that the formation of the homopolymer is completely reversible, but the reversibility of the system is not discussed for the copolymer at all.

Cyclic and Lasso Peptides: Sequence Determination, Topology Analysis, and Rotaxane Formation

Elashal, H. E.; Cohen, R. D.; Elashal, H. E.; Zong, C.; Link, A. J.; Raj, M.* *Angew. Chem. Int. Ed.* **2018**, 57, 6150-6154

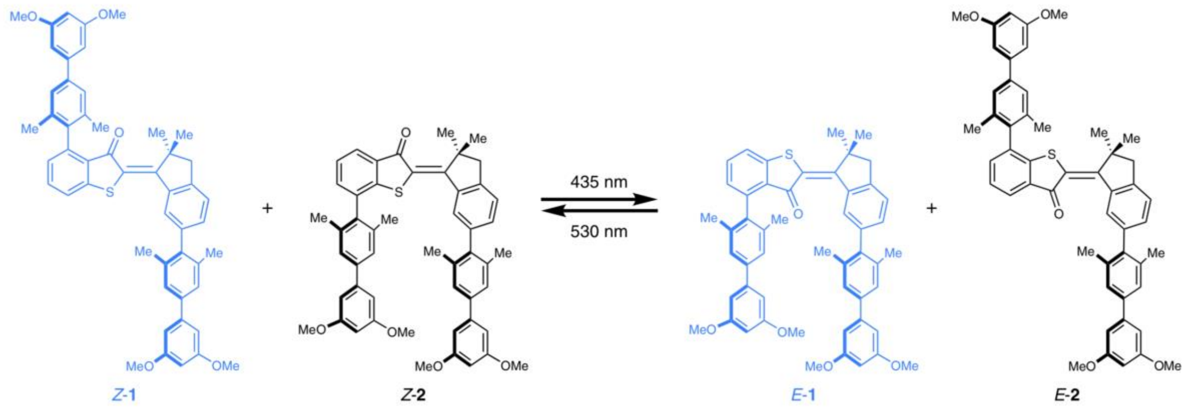


A broadly applicable chemical cleavage methodology to facilitate MS/MS sequencing was developed for macrocyclic and lasso peptides, which hold promise as exciting new therapeutics. Existing methods such as Edman degradation, CNBr cleavage, and enzymatic digestion are either limited in scope or completely fail in cleavage of constrained nonribosomal peptides. Importantly, the new method was utilized for synthesizing a unique peptide-based rotaxane (both cyclic and threaded) from the lasso peptide, benenodin-1 ΔC5.

Comment: When the study of the optimization of a characterization method leads to a new synthetic methodology of peptide-based rotaxanes… If the perspective seems of high interest, the rest of the article, focusing on the characterization, is a bit less attractive (probably not helped by the way the figures look).

Simultaneous complementary photoswitching of hemithioindigo tweezers for dynamic guest relocalization

Wiedbrauk, S.; Bartelmann, T.; Thumser, S.; Mayer, P.; Dube, H.* *Nat. Commun.* **2018**, *9*, 1456.

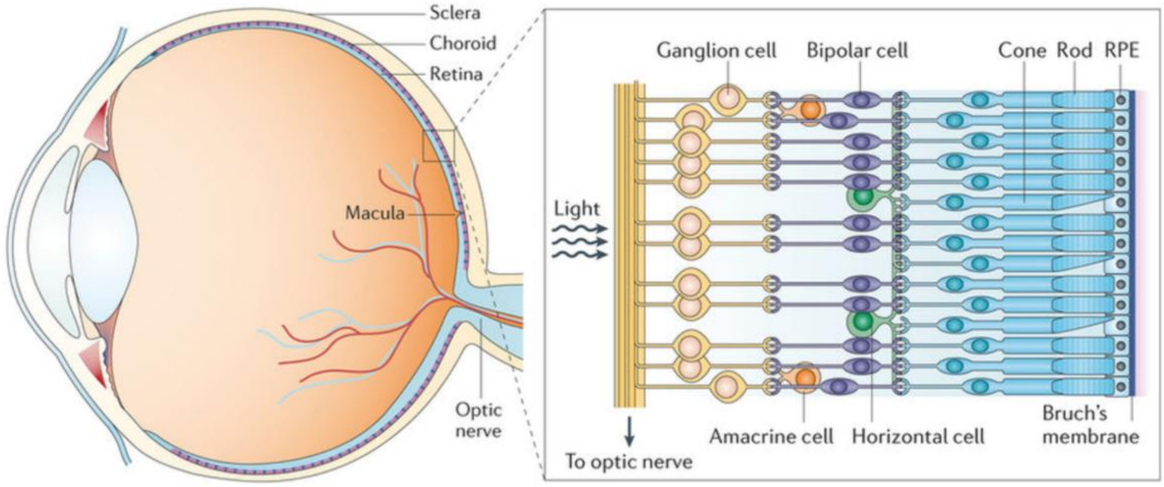


Remote control of complex molecular behavior and function is one key problem in modern chemistry. Using light signaling for this purpose has many advantages, however the integration of different photo processes into a wholesome yet complex system is highly challenging. Here we report an alternative approach to increase complexity of light control- simultaneous complementary photoswitching-in which spectral overlap is used as an advantage to drastically reduce the signaling needed for controlling multipart supramolecular assemblies. Two photoswitchable molecular tweezers respond to the same light signals with opposite changes in their binding affinities. In this way **the configuration of two host tweezers and ultimately the dynamic relocation of a guest molecule can be trigged by only one signal reversibly in the same solution**. This approach should provide a powerful tool for the construction of sophisticated, integrated, and multi-responsive smart molecular systems in any application driven field of chemistry.

Comment: It is fairly rare to see papers using **hemithioindigo**, which I find surprising because the properties of this kind of switches are rather impressive – with the notable exception of the color change. Yet, it is remarkably good in terms of fatigue resistance. In this case they use it to release a guess, which might be boring, but the fact of using a system that can undergo really numerous cycles makes it way more interesting. Also, in all honesty, it is a smart way to exploit the double bond rotation.

Restoring Vision to the Blind with Chemical Photoswitches

Tochitsky, I.; Kienzler, M. A.; Isacoff, E.*; Kramer, R. H.* *Chem. Rev.* **2018**, ASAP.

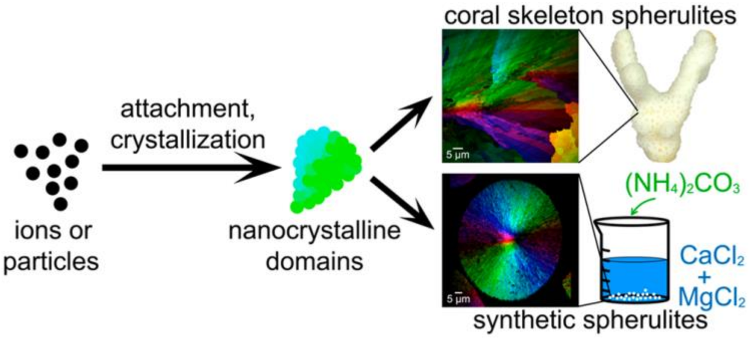


Degenerative retinal diseases such as retinitis pigmentosa (RP) and age- related macular degeneration (AMD) affect millions of people around the world and lead to irreversible vision loss if left untreated. **A number of therapeutic strategies have been developed over the years to treat these diseases or restore vision to already blind patients**. In this Review, we describe the development and translational **application of light-sensitive chemical photoswitches to restore visual function to the blind retina** and compare the translational potential of photoswitches with other vision-restoring therapies. This therapeutic strategy is enabled by an efficient fusion of chemical synthesis, chemical biology, and molecular biology and is broadly applicable to other biological systems. We hope this Review will be of interest to chemists as well as neuroscientists and clinicians.

Comment: I am completely fascinated by this review, mainly because of the subject. The idea of restoring vision to blind people is, of course, a great challenge and motivation. But the fact that this **is already happening** and **using artificial molecular switches** is altogether mind blowing to me. Sure, we are basically speaking here of “can the mouse know if there is light or not” but it still makes you wonder about how powerful chemistry really is.

Spherulitic Growth of Coral Skeletons and Synthetic Aragonite: Nature’s Three-Dimensional Printing

Sun, C. Y.; Marcus, M. A.; Frazier, M. J. ; Giuffre, A. J. ; Mass, T.; Gilbert, P. U. P. A.* *ACS Nano.* **2017**, *11*, 6612-6622.

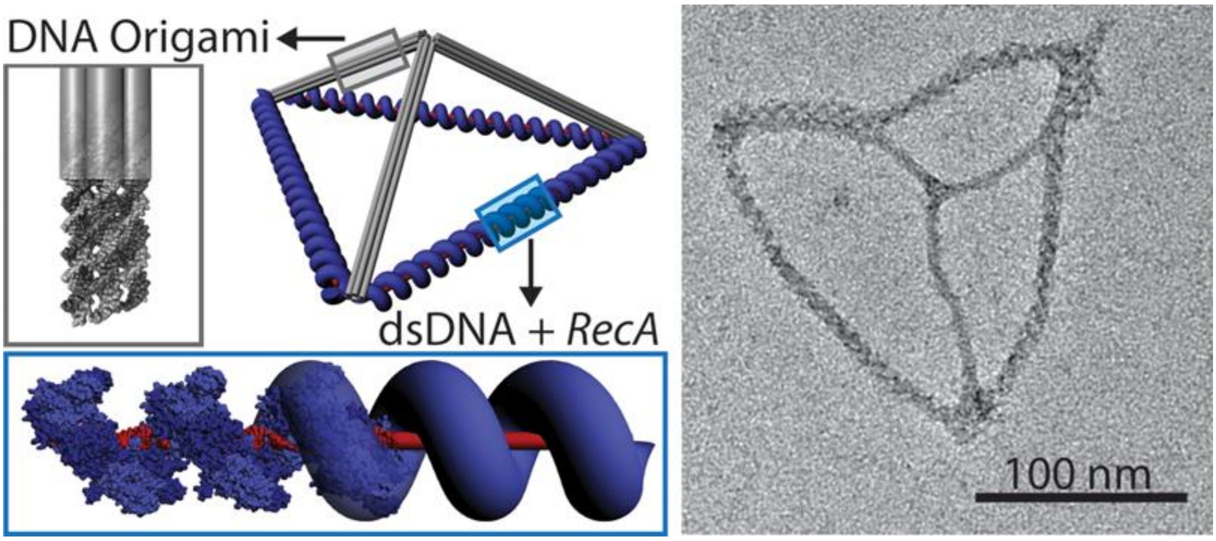


Coral skeletons were long assumed to have a spherulitic structure, that is, a radial distribution of acicular aragonite ($CaCO3$) crystals with their c-axes radiating from series of points, termed centers of calcification (CoCs). This assumption was based on morphology alone, not on crystallography. Here we measure the orientation of crystals and nanocrystals and confirm that corals grow their skeletons in bundles of aragonite crystals, with their caxes and long axes oriented radially and at an angle from the CoCs, thus precisely as expected for feather-like or “plumose” spherulites. Furthermore, we find that in both synthetic and coral aragonite spherulites at the nanoscale adjacent crystals have similar but not identical orientations, thus demonstrating by direct observation that even at nanoscale the mechanism of spherulite formation is non-crystallographic branching (NCB), as predicted by theory. Finally, synthetic aragonite spherulites and coral skeletons have similar angle spreads, and angular distances of adjacent crystals, further confirming that coral skeletons are spherulites. This is important because aragonite grows anisotropically, 10 times faster along the c-axis than along the a-axis direction, and spherulites fill space with crystals growing almost exclusively along the c-axis, thus they can fill space faster than any other aragonite growth geometry, and create isotropic materials from anisotropic crystals. Greater space filling rate and isotropic mechanical behavior are key to the skeleton’s supporting function and therefore to its evolutionary success. In this sense, spherulitic growth is Nature’s 3D printing.

Comment: The paper is quite boring to read (unless you enjoy crystallographic discussions) but it provides hints to understand one of the most intriguing achievements of evolution.

Molecular Precision at Micrometer Length Scales: Hierarchical Assembly of DNA−Protein Nanostructures

Schiffels, D.; Szalai, V. A. ; Liddle A. J.* *ACS Nano.* **2017**, *11*, 6623-6629.

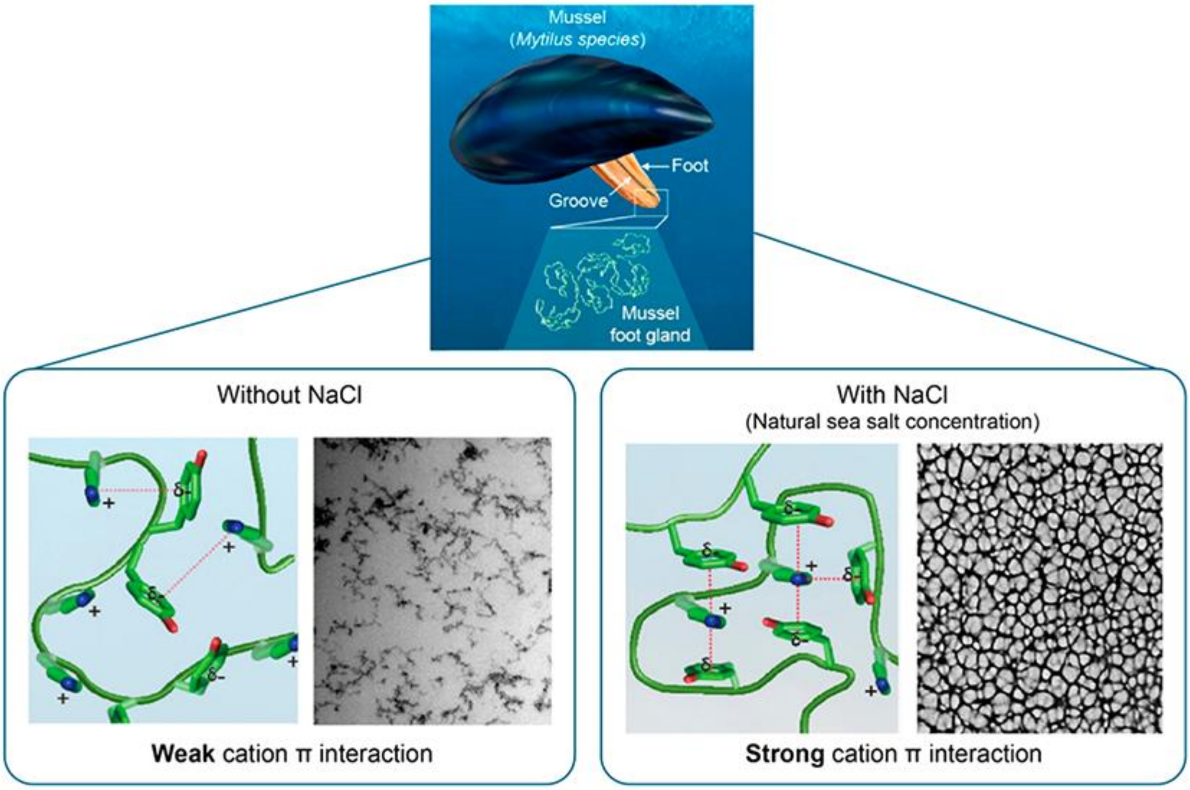


Robust self-assembly across length scales is a ubiquitous feature of biological systems but remains challenging for synthetic structures. Taking a cue from biology where disparate molecules work together to produce large, functional assemblies we demonstrate how to engineer microscale structures with nanoscale features: Our self-assembly approach begins by using DNA polymerase to controllably create double-stranded DNA (dsDNA) sections on a single-stranded template. The single-stranded DNA (ssDNA) sections are then folded into a mechanically flexible skeleton by the origami method. This process simultaneously shapes the structure at the nanoscale and directs the large-scale geometry. The DNA skeleton guides the assembly of RecA protein filaments, which provides rigidity at the micrometer scale. We use our modular design strategy to assemble tetrahedral, rectangular, and linear shapes of defined dimensions. This method enables the robust construction of complex assemblies, greatly extending the range of DNA-based self-assembly methods.

Comment: In this paper, the authors use both DNA origami techniques and protein filaments to yield self-assembled nanostructures. The images speak for themselves. Of course, I was sensitive to the quality of the imaging and the high resolution they obtain. The negative staining procedure they describe is quite original and obviously it's efficient.

Salt Triggers the Simple Coacervation of an Underwater Adhesive When Cations Meet Aromatic π Electrons in Seawater

Kim, S.; Yoo, H. Y.; Huang, J.; Lee, Y.; Park, S.; Park, Y.; Jin, S.; Jung, Y. M.; Zeng, H.*
Hwang, D. S.*; Jho, Y. S. *ACS Nano.* **2017**, *11*, 6764-6772.



Adhesive systems in many marine organisms are postulated to form complex coacervates (liquid−liquid phase separation) through a process involving oppositely charged polyelectrolytes. Despite this ubiquitous speculation, most well characterized mussel adhesive proteins are cationic and polyphenolic, and the pursuit of the negatively charged proteins required for bulk complex coacervation formation internally remains elusive. In this study, we provide a clue for unraveling this paradox by showing the bulky fluid/fluid separation of a single cationic recombinant mussel foot protein, rmfp-1, with no additional anionic proteins or artificial molecules, that is triggered by a strong cation−π interaction in natural seawater conditions. With the similar condition of salt concentration at seawater level (>0.7 M), the electrostatic repulsion between positively charged residues of mfp-1 is screened significantly, whereas the strong cation−π interaction remains unaffected, which leads to the macroscopic phase separation (i.e., bulky coacervate formation). The single polyelectrolyte coacervate shows interesting mechanical properties including low friction, which facilitates the secretion process of the mussel. Our findings reveal that the cation−π interaction modulated by salt is a key mechanism in the mussel adhesion process, providing new insights into the basic understanding of wet adhesion, self-assembly processes, and biological phenomena that are mediated by strong short-range attractive forces in water.

Comment: This paper provides some insights on the wet adhesion properties of mussels. It's inspiring to see how a simple molecule such as NaCl can mediate weak interactions, it is obvious that it can screen long range electrostatic interactions thus decreasing their strength but here the authors show how it can favor short range electrostatic interactions such as the cation-π.