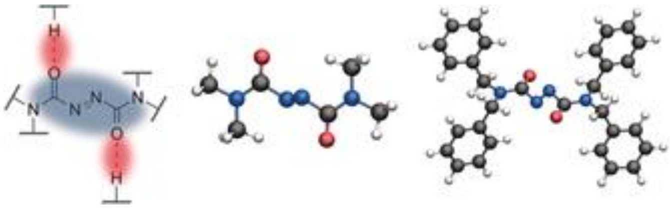
Photoinduced Pedalo-Type Motion in an Azodicarboxamide-Based Molecular Switch

Amirjalayer, S.*; Martinez-Cuezva, A.; Berna, J.; Woutersen, S.*; Buma, W. J.* *Angew. Chem., Int. Ed.* **2018**, *57*, 1792–1796.

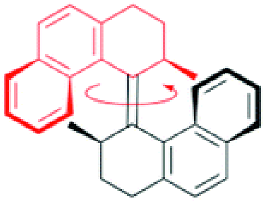


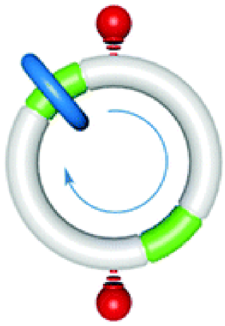
Well-defined structural changes of molecular units that can be triggered by light are crucial for the development of photoactive functional materials. Herein, we report on a novel switch that has azodicarboxamide as its photo-triggerable element. Time-resolved UV-pump/IR probe spectroscopy in combination with quantum-chemical calculations shows that the azodicarboxamide functionality, in contrast to other azo-based chromophores, does not undergo *trans–cis* photoisomerization. Instead, a photoinduced pedalo-type motion occurs, which because of its volume-conserving properties enables the design of functional molecular systems with controllable motion in a confined space.

Comment: Probably most of us may not be used to read descriptions on quantum-mechanical calculations for geometry determination. This article proposes a description of the theoretical work used to confirm experimental observation. The correlation between the experimental spectroscopy curves and the assimilation to energy levels may need to be read a few times, but it might be a **nice exercise** with an example of a molecular switch with unusual conformation.

Artificial Molecular Motors

Kassem, S.; van Leeuwen, T.; Lubbe, A. S.; Wilson, M. R.; Feringa, B. L.*; Leigh, D. A.* *Chem. Soc. Rev.* **2017**, *46*, 2592–2621.



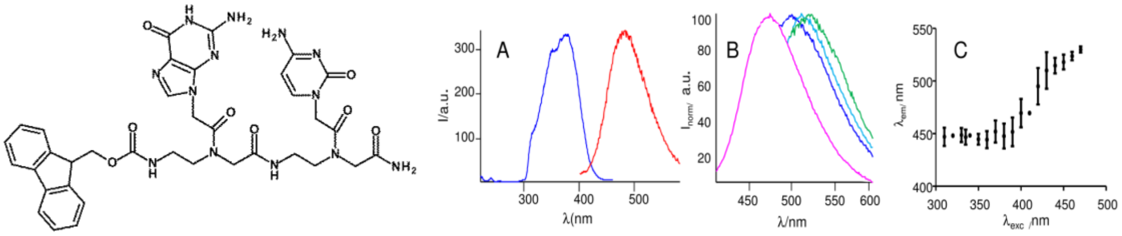


Motor proteins are nature's solution for directing movement at the molecular level. The field of artificial molecular motors takes inspiration from these tiny but powerful machines. Although directional motion on the nanoscale performed by synthetic molecular machines is a relatively new development, significant advances have been made. In this review an overview is given of the principal designs of artificial molecular motors and their modes of operation. Although synthetic molecular motors have also found widespread application as (multistate) switches, **we focus on the control of directional movement**, both at the molecular scale and at larger magnitudes. We identify some key challenges remaining in the field.

Comment: The first of this review might not be really a discovering as the explanation of the Brownian-ratchet mechanism is described deeper in other David Leigh reviews. But this one has the advantage to focus **only on molecular motors** (no switches or machines), and present a few new advances in the domain that didn't appear in the past reviews.

Self-assembling of Fmoc-GC Peptide Nucleic Acid Dimers into Highly Fluorescent Aggregates

Avitabile, C.; Diaferia, C.; Della Ventura, B.; Mercurio, F. A.; Leone, M.; Roviello, V.; Saviano, M.; Velotta, R.; Morelli, G.; Accardo, A.; Romanelli, A.* *Chem. Eur. J.* **2018,** ASAP.

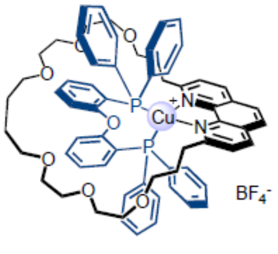


Self-assembling of molecules by non-covalent interactions is one of the most attracting topics in supramolecular chemistry. The use of short peptides or modified nucleotides as building blocks of the aggregates is particularly intriguing, as these are very easy to synthesize; moreover subtle changes in the chemical structure of such building blocks may drastically affect the properties of the aggregates. The ability of Peptide Nucleic Acids to aggregate is yet very little explored, despite its practical applications. In this work we investigated the self-assembling properties of a PNA dimer conjugated at the N-terminus to a fluorenylmethoxycarbonyl group. This PNA dimer forms nano-aggregates at low concentration in $CHCl_3/CH_3OH$ mixtures. The aggregates keep very interesting fluorescent properties (high quantum yield in the visible region with lifetime in the nanoseconds scale), which make them a promising material for applications in optoelectronic.

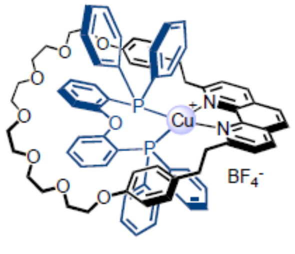
Comment: In this paper they describe an atypical aggregation induced emission system. The Fmoc-moiety is really well known to drive the self-assembly of short peptides but its properties as AIE group have never been described before.

Heteroleptic Copper(I) Pseudorotaxanes Incorporating Macrocyclic Phenanthroline Ligands of Different Sizes.

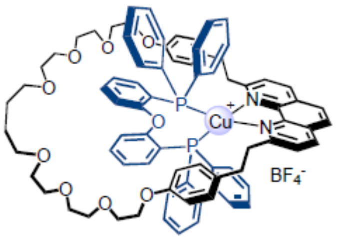
Mohankumar, M.; Holler, M.; Meichsner, E.; Nierengarten, J.-F.*; Niess, F.; Sauvage, J.-P.*; Delavaux-Nicot, B.*; Leoni, E.; Monti, F.; Malicka, J. M.; Cocchi, M.; Bandini, E.; Armaroli, N.* *J. Am. Chem. Soc.* **2018**, *140*, 2336.



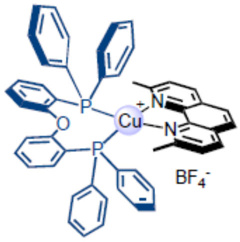
[Cu(m30)(POP)]BF_4



[Cu(m37)(POP)]BF_4



[Cu(m42)(POP)]BF_4



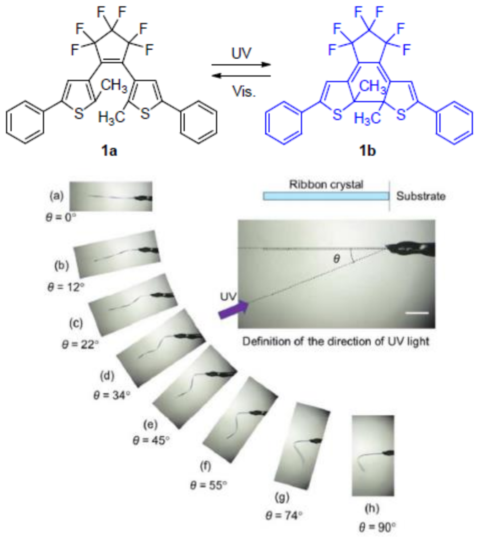
[Cu(dmp)(POP)]BF_4

A series of copper(I) pseudorotaxanes has been prepared from bis[2-(diphenylphosphino)phenyl] ether and macrocyclic phenanthroline ligands with different ring sizes (**m30**, **m37** and **m42**). Variable temperature studies carried out on the resulting [Cu(**mXX**)(POP)]$^+$ (**mXX** = **m30**, **m37** and **m42**) derivatives have revealed a dynamic conformational equilibrium due to the folding of the macrocyclic ligand. The absorption and luminescence properties of the pseudorotaxanes have been investigated in CH_2Cl_2. They exhibit metal-to-ligand-charge-transfer (MLCT) emission with photoluminescence quantum yields (PLQYs) in the range 20-30%. The smallest system [Cu(**m30**)(POP)]$^+$ shows minimal differences in spectral shape and position compared to its analogues, suggesting a slightly distorted coordination environment. PLQY is substantially enhanced in PMMA films (≈ 50-60%). The study of emission spectra and excited state lifetimes in powder samples as a function of temperature (78-338 K) reveals thermally activated delayed fluorescence (TADF), with sizeable differences in the singlet-triplet energy gap compared to the reference compound [Cu(dmp)(POP)]$^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) and within the pseudorotaxane series. The system with the largest ring ([Cu(**m42**)(POP)]$^+$) has been tested as emissive material in OLEDs and affords bright green devices with higher luminance and greater stability compared to [Cu(dmp)(POP)]$^+$, which lacks the macrocyclic ring. This highlights the importance of structural factors in the stability of electroluminescent devices based on Cu(I) materials.

Comment: This paper presents a well-known way to synthesis an interlocked molecular architecture. However, they proved that the enhanced of the ring size increase significantly the physicochemical properties (reduction of the concomitant distortion on the coordination sphere around the copper). As they decreased the steric hindrance, is it possible to introduce on the pseudo catenane structure some molecules with electronics properties (for example triarylamine) in the idea to get a longer time-scale exited state? And also get a self-assembly of the emissive structure?

Control of Photomechanical Crystal Twisting by Illumination Direction

Kitagawa, D.; Tsujioka, H.; Tong, F.; Dong, X.; Bardeen, C.J.; Kobatake, J.* *J. Am. Chem. Soc.* **2018**, just accepted

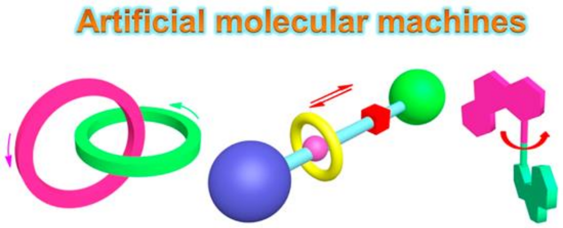


Photomechanical molecular crystals have been investigated as mesoscopic photoactuators. Here, we report how the photomechanical twisting of 1,2-bis(2-methyl-5-phenyl-3- thienyl) perfluorocyclopentene (**1a**) crystals depends on illumination direction. The ribbon-like crystal of **1a** could be successfully by a sublimation method. The ribbon crystal exhibited reversible photomechanical crystal twisting upon alternating irradiation with ultraviolet (UV) and visible light. Moreover, changing the UV illumination direction with respect to the crystal resulted in different twisting modes, ranging from helicoid to cylindrical. Control of photomechanical crystal deformation by illumination direction provides a convenient and useful way to generate a variety of photomechanical motions from a single crystal.

Comment: It is an interesting paper about photomechanical crystals composed of diarylethene units. First, even if it is not the same properties, this paper could be compare with the Nature Nano on reversible gels because in both cases the motion of the material is controlled by the photostationary state of the diarylethene under UV/Visible light. Secondly, they describe a method to get ribbon-shaped crystals by sublimation which could be interesting to try on the molecular motors. Finally, it is fascinating to see how the influence of the incident light direction can control the mode (helicoidal or cylindrical) and the direction of the crystal motion.

Artificial Molecular Machines in Nanotheranostics

Yu, G.; Yung, B. C.; Zhou, Z.; Mao, Z.*; Chen, X.* *ACS Nano.*, **2018**, *12*, 7-12.

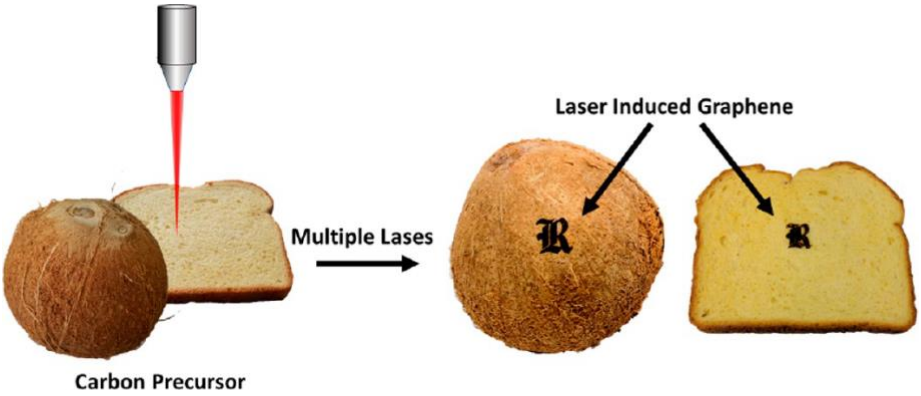


Due to their dynamic nature and excellent stimuli-responsiveness resulting from noncovalent driving forces, artificial molecular machines (AMMs) show great promise in cancer theranostics. In this Perspective, we introduce the potential applications of AMMs in controlled drug delivery, bioorthogonal catalysis, imaging, and cell membrane permeabilization, with the goal of enhancing cancer diagnosis and therapy. We expect this preliminary discussion will garner multidisciplinary interest from scientists to advance AMMs and to expand their future clinical applications.

Comment: Obviously, people working on molecular machines in the group should be aware of their potential applications as it is a question they will have to answer quite often (including at a PhD defense for instance). This paper shows the results published so far in the literature concerning theranostics applications of molecular machines.

Laser-Induced Graphene by Multiple Lasing: Toward Electronics on Cloth, Paper, and Food

Chyan, Y.; Ye, R.; Li, Y.; Singh, S. P.; Arnusch, C. J.*; Tour, J. M.* *ACS Nano.*, **2018**, *ASAP.*



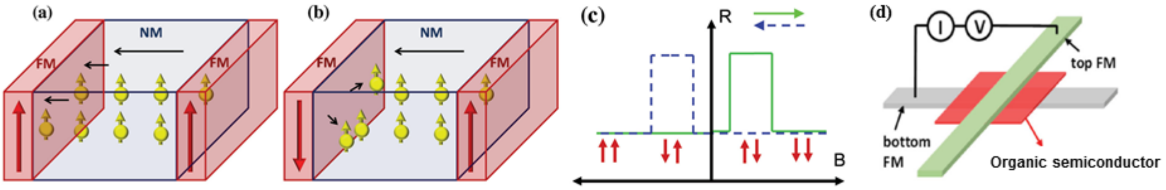
A simple and facile method for obtaining patterned graphene under ambient conditions on the surface of diverse materials ranging from renewable precursors such as food, cloth, paper, and cardboard to high-performance polymers like Kevlar or even on natural coal would be highly desirable. Here, we report a method of using multiple pulsed laser scribing to convert a wide range of substrates into laser-induced graphene (LIG). With the increased versatility of the multiple lase process, highly conductive patterns can be achieved on the surface of a diverse number of substrates in ambient atmosphere. The use of a defocus method results in multiple lases in a single pass of the laser, further simplifying the procedure. This method can be implemented without increasing processing times when compared with laser induction of graphene on polyimide

(Kapton) substrates as previously reported. In fact, any carbon precursor that can be converted into amorphous carbon can be converted into graphene using this multiple lase method. This may be a generally applicable technique for forming graphene on diverse substrates in applications such as flexible or even biodegradable and edible electronics.

Comment: This paper hit me because it was talking about edible electronics and I just found the concept interesting. It's fascinating to see how a simple physical process such as lasing allows to go from basic organic materials to electronics. It is interesting to check the genesis of this field by reading this paper first.

Organic Spin-Valves and Beyond: Spin Injection and Transport in Organic Semiconductors and the Effect of Interfacial Engineering

Jang, H-J.*; Richter C. A. *Adv. Mater*. **2016**, *29*, 1602739.



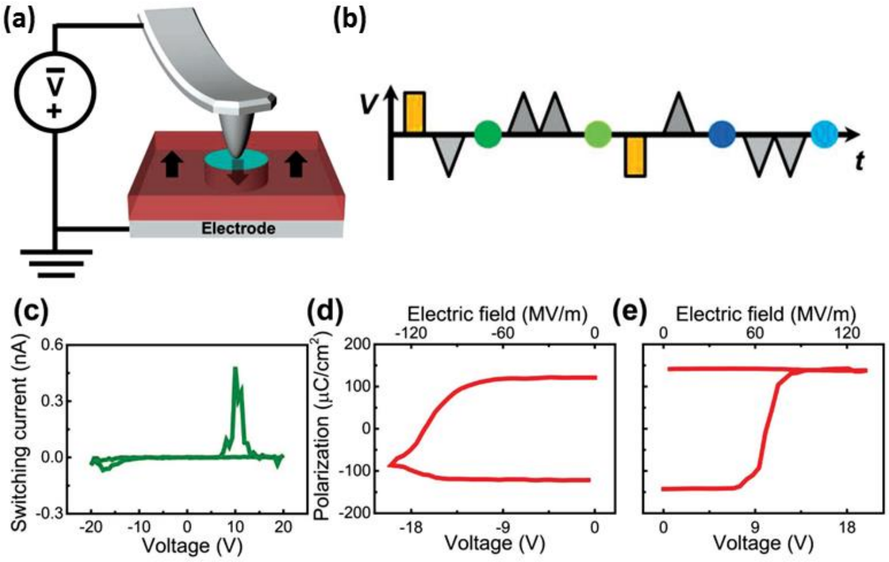
Schematic illustration of spin-valve effect: Depending on whether magnetizations (red arrows) of two ferromagnetic(FM) layers are parallel (a) or antiparallel (b), charge carriers (yellow circles) spin-polarized by the FM electrode in the right can transport (or tunnel) through the nonmangetic(NM) layer and be collected at the FM electrode in the left producing a low resistance (in parallel configuration), or they can be bounced off at the collector FM showing high resistance (in antiparallel configuration). The black arrows represent the flow and movement of carriers. c) Electrical resistance versus external magnetic field in spin-valve systems. Red arrows indicate the orientation of magnetizations of two FM layers and blue (solid) and green (dashed) arrows show the sweeping direction of the magnetic field. d) schematic diagram of a typical sandwich injector detector structure for transport perpendicular in direction to the surface.

Since the first observation of the **spin-valve effect** through **organic semiconductors**, efforts to realize novel spintronic technologies based on organic semiconductors have been rapidly growing. However, a complete understanding of spin-polarized carrier injection and transport in organic semiconductors is still lacking and under debate. For example, there is still no clear understanding of major spin-flip mechanisms in organic semiconductors and the role of hybrid metal–organic interfaces in spin injection. Recent findings suggest that **organic single crystals can provide spin-transport media with much less structural disorder relative to organic thin films**, thus reducing momentum scattering. Additionally, modification of the band energetics, morphology, and even spin magnetic moment at the metal–organic interface by **interface engineering** can greatly impact the efficiency of spin-polarized carrier injection. Here, progress on efficient spin-polarized carrier injection into organic semiconductors from ferromagnetic metals by using various interface engineering techniques is presented, such as inserting a metallic interlayer, a **molecular self-assembled monolayer (SAM)**, and a ballistic carrier emitter. In addition, efforts to realize long spin transport in single-crystalline organic semiconductors are discussed. The focus here is on *understanding and maximizing spin-polarized carrier injection and transport in organic semiconductors and insight is provided for the realization of emerging organic spintronics technologies.*

Comment: General review on spin-valve effect in organic semi-conductors. Especially interesting for us (for example in regards with the triarylamine fibers) is the discussion on single-crystalline semi-conductors and the measuring set-up for semi-conductors with 1D conduction perpendicular the surface.

Direct Probing of Polarization Charge at Nanoscale Level

Kwon, O.; Seol, D.; Lee, D.; Han, H.; Lindfors-Vrejoiu, I.; Lee, W.; Jesse, S.; Lee, H. N.; Kalinin, S. V.; Alexe, M.*; Kim, Y.* *Adv. Mater*. **2018**, *30*, 1703675.



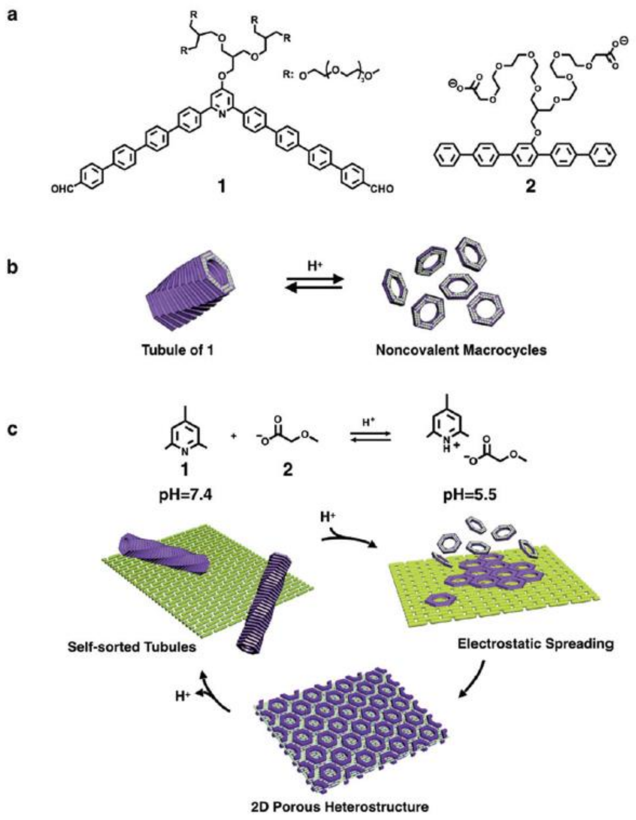
a) AFM-PUND measurement in a ferroelectric thin film. b) Schematics of the AFM-PUND waveform. The colored circles in (a) and (b) represent PFM imaging stages in the AFM-PUND sequence. c) switching current in the ferroelectric thin film. d,e) *P*–*E* hysteresis loop constructed from the switching current of d) negative and e) positive bias branches, respectively.

Ferroelectric materials possess spontaneous polarization that can be used for multiple applications. Owing to a long-term development of **reducing the sizes of devices**, the preparation of ferroelectric materials and devices is entering the **nanometer-scale regime**. Accordingly, to evaluate the ferroelectricity, there is a need to investigate the polarization charge at the nanoscale. Nonetheless, it is generally accepted that the **detection of polarization charges** using a conventional conductive atomic force microscopy (**CAFM**) without a top electrode is not feasible because the nanometer-scale radius of an atomic force microscopy (AFM) tip yields a very low signal-to-noise ratio. However, the detection is unrelated to the radius of an AFM tip and, in fact, a matter of the switched area. In this work, the **direct probing of the polarization charge** at the nanoscale is demonstrated using the **positive-up-negative down** method based on the conventional CAFM approach without additional corrections or circuits to reduce the parasitic capacitance. The polarization charge densities of 73.7 and 119.0 μC cm^{-2} are successfully probed in ferroelectric nano-capacitors and thin films, respectively. *The obtained results show the feasibility of the evaluation of polarization charge at the nanoscale and provide a new guideline for evaluating the ferroelectricity at the nanoscale.*

Comment: What captured my attention is that it is yet a novel AFM technique. Although AFM is a widely known and used technique, innovations are still being made, as is shown in this article. We have an AFM in our lab and I think it is good to know all we can do with it besides the standard topography imaging.

Assembly–disassembly Switching of Self-sorted Nanotubules Forming Dynamic 2-D Porous Heterostructure

Liu, X.; Li, H.; Kim, Y.; Lee, M.* *Chem. Commun.* **2018**. doi: 10.1039/c8cc01177j.

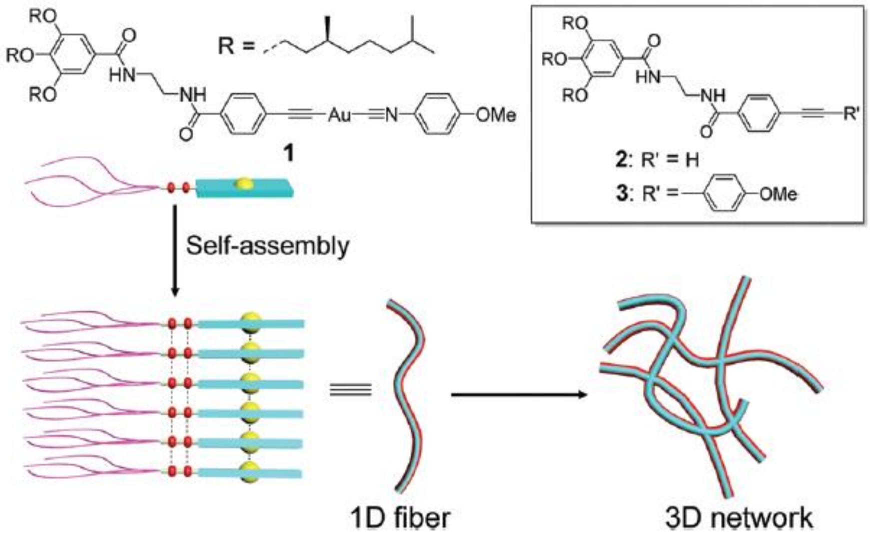


We report the pH-driven formation of a dynamic 2-D porous heterostructure through assembly–disassembly switching of the stacked macrocycles of nanotubules and their subsequent spreading on the surfaces of a self-sorted sheet assembly in a hierarchical co-assembly. The 2-D ordered porous heterostructure is able to discriminate spherical C_{60} from flat coronene through shape selective adsorption.

Comment: The amphiphilic molecules with bent-shaped aromatic segment are readily to form macrocycle even nanotube based on non-covalent interaction. This point provide a considerable method for the construction of nanostructure with cavity or porous. The interesting point in this paper is that the self-sorted supramolecular self-assemblies and the co-assembly are based on the electrostatic interaction between two nanostructures with different charge. Meanwhile, the authors corroborated the molar ratio of this complex using fluorescence measurements and found this complex structure could discriminate C_{60}.

Cooperative Self-assembly and Gelation of Organogold(I) Complexes via Hydrogen Bonding and Aurophilic Au···Au Interactions

Chen, J.; Zhang, Z.; Wang, C.; Gao, Z.; Gao, Z.; Wang, F.* *Chem. Commun.* **2017**, *53*, 11552.

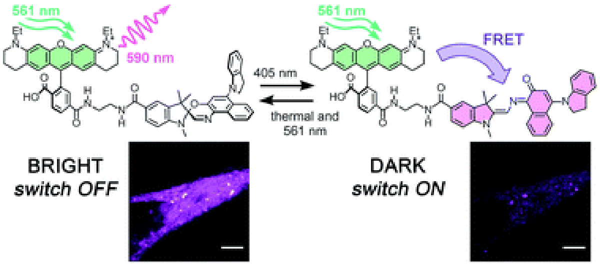


With the synergistic combination of intermolecular Au(I)–Au(I) and hydrogen bonding interactions, a rod–coil alkynyl–gold(I)–isocyanide monomer tends to form supramolecular fibers and gels via a cooperative nucleation–elongation self-assembly mechanism, which display Ag(I) ion-triggered responsiveness.

Comment: It should be noticed that the cooperative self-assembly prefers to form ordered and large-scale nanoarchitectures, maybe it's a good method for the construction of bottom-up self-assembly systems and longer fibers. The aurophilic interactions of Au(I)-Au(I) result in cyan emission, so the alteration of fluorescence can be observed in solution-gel transition processes due to the addition of Ag(I). So, we can properly consider the organogold(I) in the field of gel and/or other supramolecular self-assemblies.

Spironaphthoxazine Switchable Dyes for Biological Imaging

Xiong, Y.; Vargas Jentzsch, A.; Osterrieth, J. W. M.; Sezgin, E.; Sazanovich, I. V.; Reglinski, K.; Galiani, S.; Parker, A. W.; Eggeling, C.; Anderson, H. L.* *Chem. Sci.* **2018**, Advance Article

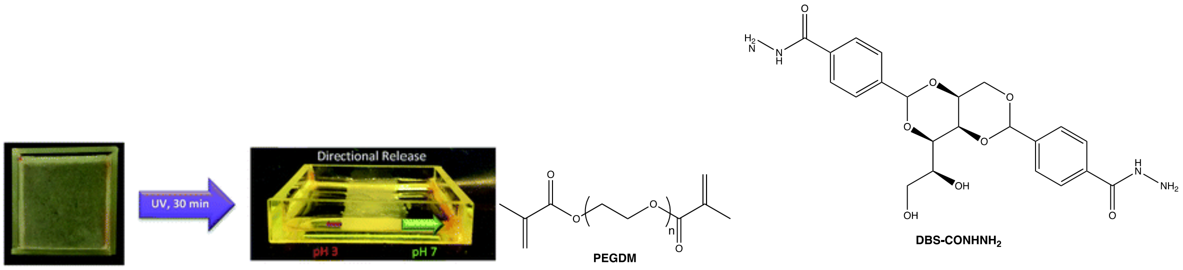


Recent developments in super-resolution microscopy have significantly expanded the requirements for switchable dyes, leading to demand for specially designed molecular switches. We report the **synthesis and characterization of a spironaphthoxazine photochromic switch** (a derivative of palatinate purple) **displaying high photoconversion** (85–95%) **under readily accessible 405 nm light, broad absorption in the visible, and excellent fatigue resistance**. The indole substituent on this spironaphthoxazine is twisted out of conjugation with the naphthalene unit, yet it is crucial for activation with visible light. The open colored merocyanine form of the spironaphthoxazine reverts to the closed form with a lifetime of 4.7 s in dichloromethane at 20 °C; this thermal reversion is even faster in more polar solvents. The photochemical quantum yields for ring-opening and ring-closing are approximately 8% and 1%, respectively, in dichloromethane. The ring-opening and ring-closing reactions have been characterized by time-resolved infrared and transient absorption spectroscopies. Ring opening occurs rapidly (τ = 2.1 ns) and efficiently (~90%) from the singlet excited state to form an intermediate (assigned as a cisoid merocyanine), which returns to the closed ground state (τ = 4.5 ns) in competition with relaxation to the transoid open form (τ = 40 ns). Photochemical ring closing is a faster and simpler process: the excited state proceeds to the closed spirooxazine with a time constant of 0.28 ns. This photochromic switch can be used in conjunction with commercial fluorescent dyes to create a small-molecule switchable fluorescent dyad that shows high contrast and good fatigue resistance in living cells. These properties make the dyads suitable for application in RESOLFT microscopy.

Comment: This paper allows to get a better understanding of the spirooxazine systems and their photochemistry. Moreover, a deep spectroscopic analysis has been realized with some commonly used methods (UV/Vis absorption, fluorescence) but also with more unusual techniques (Ultrafast photochemistry: Time-resolved infrared (TRIR) and transient absorption (TA) spectroscopy. Thus, this paper may be useful to anyone who would like to perform thorough spectroscopic analysis of their compounds.

Spatially-resolved Soft materials for Controlled Release – Hybrid Hydrogels Combining a Robust Photo-activated Polymer Gel with an Interactive Supramolecular Gel

Chivers, P. R. A.; Smith, D. K.* *Chem. Sci.* **2017**, *8*, 7218-7227.

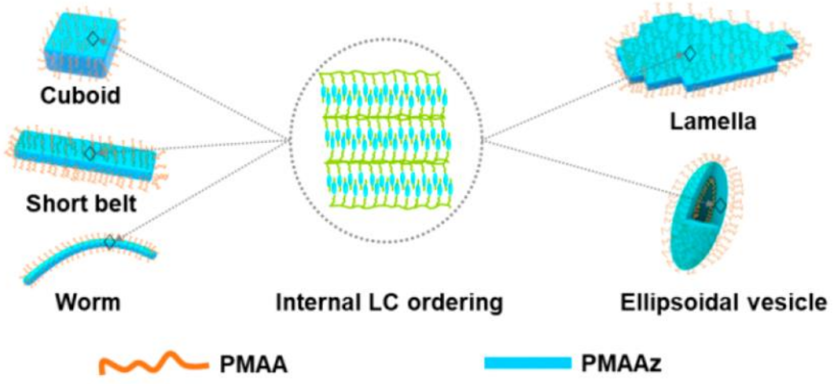


Hybrid hydrogels based on self-assembling low-molecular-weight gelator (LMWG) DBS-CONHNH$_2$ (DBS = 1,3;2,4-dibenzylidene-D-sorbitol) and crosslinked polymer gelator (PG) PEGDM (poly(ethyleneglycol) dimethacrylate) are reported, and an active pharmaceutical ingredient (naproxen, NPX) is incorporated. **The use of PEGDM as PG enhances the mechanical stiffness of the hybrid gel** (*G*′ increases from 400 to 4500 Pa) **– the LMWG enhances its stability to very high frequency. Use of DBS-CONHNH$_2$ as LMWG enables interactions with NPX and hence allows pH-mediated NPX release** – the PG network is largely orthogonal and only interferes to a limited extent. **Use of photo-activated PEGDM as PG enables spatially-resolved photo-patterning of robust hybrid gel domains within a preformed LMWG network** – the presence of the LMWG enhances the spatial resolution. The photo-patterned multi-domain gel retains pH-mediated NPX release properties and directionally releases NPX into a compartment of higher pH. The two components within these hybrid PG/LMWG hydrogels therefore act largely independently of one another, although they do modify each other's properties in subtle ways. Hybrid hydrogels capable of spatially controlled unidirectional release have potential applications in tissue engineering and drug-delivery.

Comment: This is a very interesting paper for whoever would like to work with a gel and to characterize it. A lot of characterization techniques have been used to determine the physical and chemical properties of the gel (NMR on gel, IR spectroscopy, SEM, rheology).

Formation of Anisotropic Liquid Crystalline Nanoparticles via Polymerization-Induced Hierarchical Self-Assembly

Guan, S.; Zhang, C.; Wen, W.; Qu, T.; Zheng, X.; Zhao, Y.; Chen, A.* *ACS Macro Lett.* **2018**, *7*, 358–363.

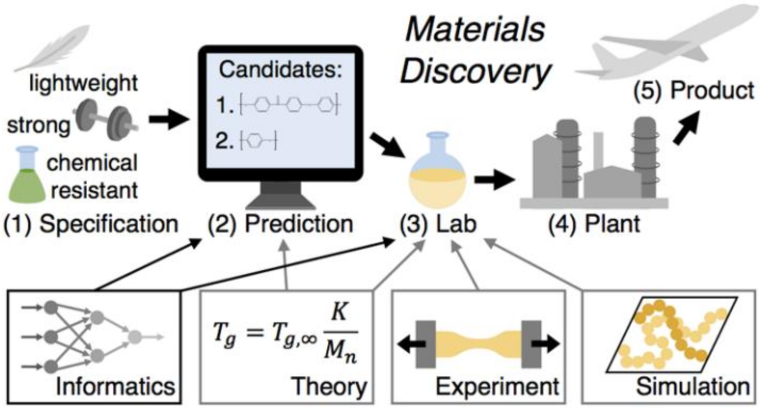


Polymeric nanoparticles (NPs) containing liquid crystalline (LC) mesogens with tunable anisotropic morphologies have applications in various fields, but their preparation typically suffers from tedious and low-throughput approaches. Here we present an efficient route to the preparation of **anisotropic morphologies of azobenzene-containing block copolymers (BCPs)** at high solids content via a polymerization-induced hierarchical self-assembly in ethanol. Various anisotropic NPs, including cuboids, short belts, lamellae, and ellipsoidal vesicles, have been obtained in a remarkably broad range of BCP compositions. The NPs exhibit a smectic phase with ordered stripes when observed under TEM. This internal LC ordering plays a significant role on the formation of these intriguing anisotropic morphologies. **Morphological transitions from anisotropic to isotropic spheres can be obtained** upon UV illumination due to the photoresponsive properties of the azobenzene mesogens. This work significantly expands the scope of accessible morphologies in PISA and suggests that the under explored LC BCPs may have an impactful role in the PISA field.

Comment: While the use of azobenzene moieties in the synthesis of photoresponsive polymers is not new, combining it with PISA forms a variety of nanostructures depending on the copolymer composition (a **phase diagram** was established). Some of these structures (cuboid, mainly) are, according to the authors, rarely reported.

Polymer Informatics: Opportunities and Challenges

Audus, D. J.*; de Pablo, J. J.* *ACS Macro Lett.* **2017**, *6*, 1078–1082.

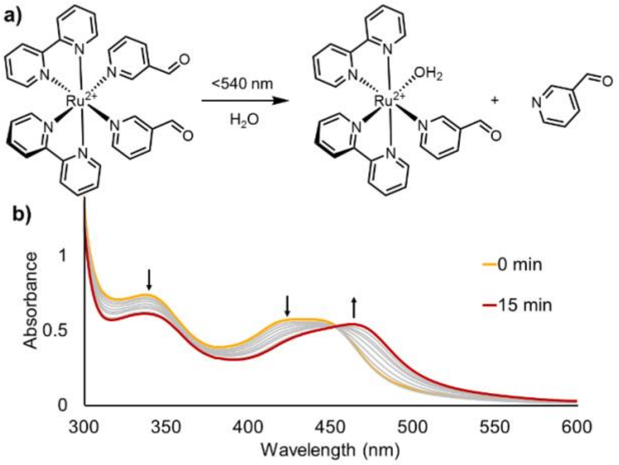


We are entering an era where large volumes of scientific data, coupled with algorithmic and computational advances, can reduce both the time and cost of developing new materials. This emerging field known as **materials informatics** has gained acceptance for a number of classes of materials, including metals and oxides. In the particular case of polymer science, however, there are important challenges that must be addressed before one can start to deploy advanced machine learning approaches for designing new materials. These challenges are primarily related to the manner in which polymeric systems and their properties are reported. In this viewpoint, we discuss the opportunities and challenges for making materials informatics as applied to polymers, or equivalently polymer informatics, a reality.

Comment: The authors first discuss **the integration and the use of machine learning** in the ways science is done nowadays, and the challenges that need to be addressed if we want to apply it to polymer sciences. These problems arise from the complexity of polymeric materials (tacticity, processing history, and so on) and it is interesting to compare it to “small molecules” referencing.

Ruthenium-Crosslinked Hydrogels with Rapid, Visible-Light Degradation

Rapp, T; Highley, C; Manor, B; Burdick, J; Dmochowski, I. J.* *Chem. Eur. J.* **2018**, ASAP.

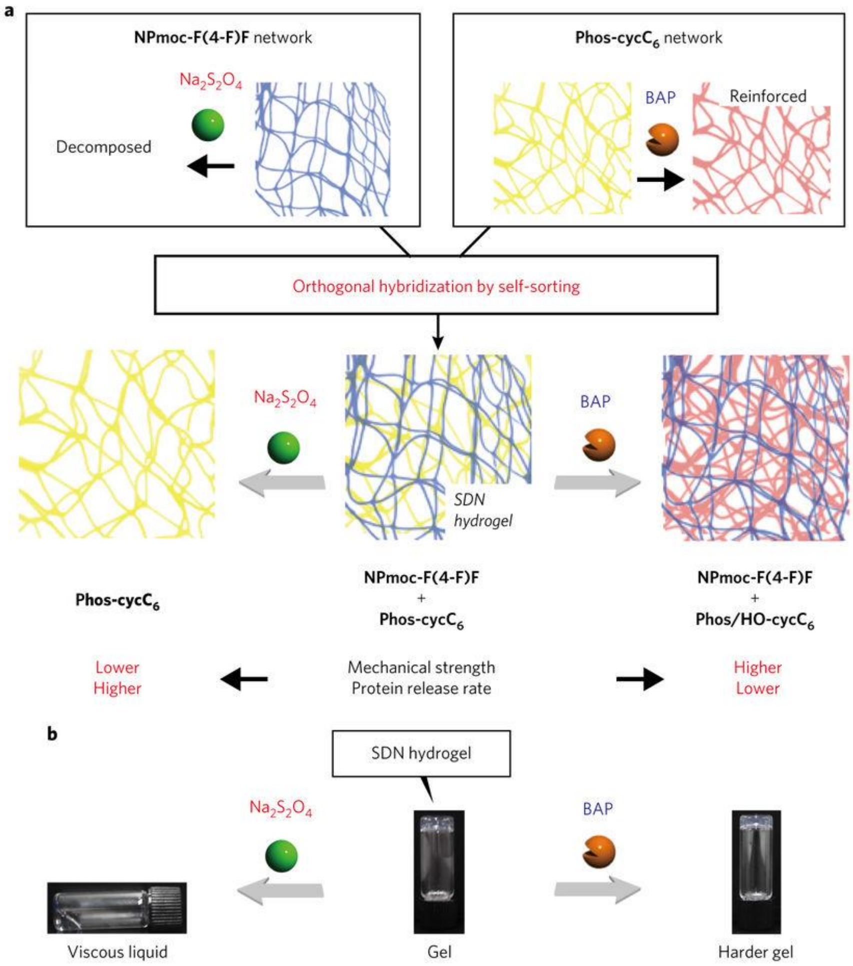


Incorporation of photoresponsive molecules within soft materials can provide spatiotemporal control over bulk properties, and address challenges in targeted delivery and mechanical variability. However, the kinetics of in situ photochemical reactions are often slow and typically employ ultraviolet wavelengths. Here, we present a novel photoactive crosslinker Ru(bipyridine)$_2$(3-pyridinaldehyde)$_2$ (RuAldehyde), which was reacted with hydrazide-functionalized hyaluronic acid to form hydrogels capable of encapsulating protein cargo. Visible light irradiation (400 – 500 nm) initiated rapid ligand exchange on the ruthenium center, which degraded the hydrogel within seconds to minutes, depending on gel thickness. An exemplar enzyme cargo, TEM1 beta-lactamase, was loaded into and photoreleased from the Ru-hydrogel. To expand their applications, Ru-hydrogels were also processed into microgels using a microfluidic platform.

Comment: The idea of incorporating a photo-responsive linker into a supramolecular structure allows the formation of materials with interesting properties. Considering that in our group the study of photo-responsive gel is widely used, I think that this system could be interesting.

An Adaptive Supramolecular Hydrogel Comprising Self-sorting Double Nanofibre Networks

Shigemitsu, H.; Fujisaku, T.; Tanaka, W.; Kubota, R.; Minami, S.; Urayama, K., Hamachi, I.*
Nat. Nanotechnol. **2018**, *13*, 165.

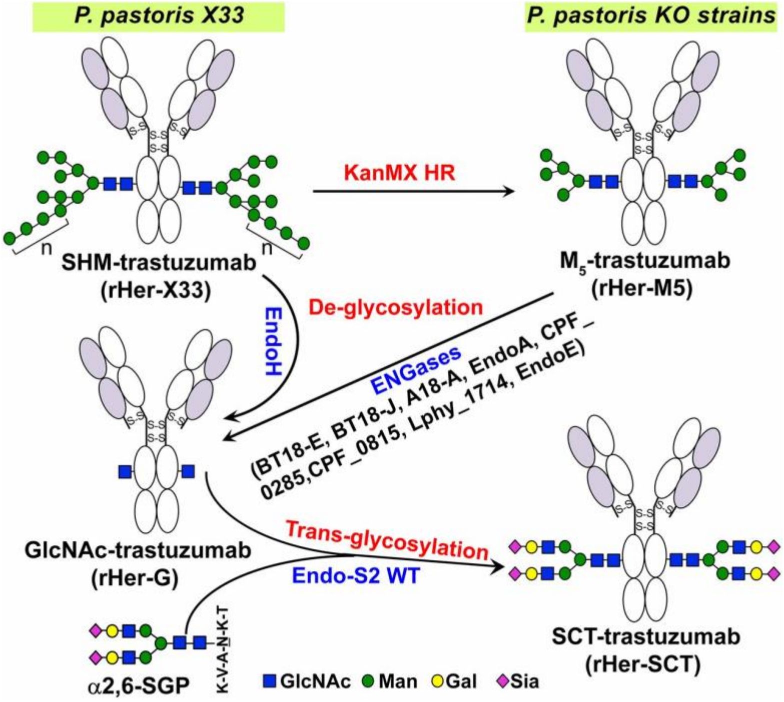


Novel soft materials should comprise multiple supramolecular nanostructures whose responses (for example, assembly and disassembly) to external stimuli can be controlled independently. Such multicomponent systems are present in living cells and control the formation and break-up of a variety of supramolecular assemblies made of proteins, lipids, DNA and RNA in response to external stimuli; however, artificial counterparts are challenging to make. Here, we present a hybrid hydrogel consisting of a self-sorting double network of nanofibres in which each network responds to an applied external stimulus independent of the other. The hydrogel can be made to change its mechanical properties and rates of release of encapsulated proteins by adding $Na_2S_2O_4$ or bacterial alkaline phosphatase. Notably, the properties of the gel depend on the order in which the external stimuli are applied. Multicomponent hydrogels comprising orthogonal stimulus-responsive supramolecular assemblies would be suitable for designing novel adaptive materials.

Comment: A new artificial soft materials built from diverse and orthogonal assemblies – namely peptide- and lipid-type hydrogelators has been developed by the Hamachi group. This hybrid self-sorting hydrogels responds differently towards two assigned stimuli leading to two very different materials.

Glycoengineering of Antibody (Herceptin) through Yeast Expression and In Vitro Enzymatic Glycosylation

Liu, C.-H.; Tsai, T.-I.; Cheng, T.; Shivatare, V. S.; Wu, C.-Y.; Wu, C.-Y.; Wong, C.-H.* *Proc. Nat. Acad. Sci. USA* **2018**, *115*, 720.

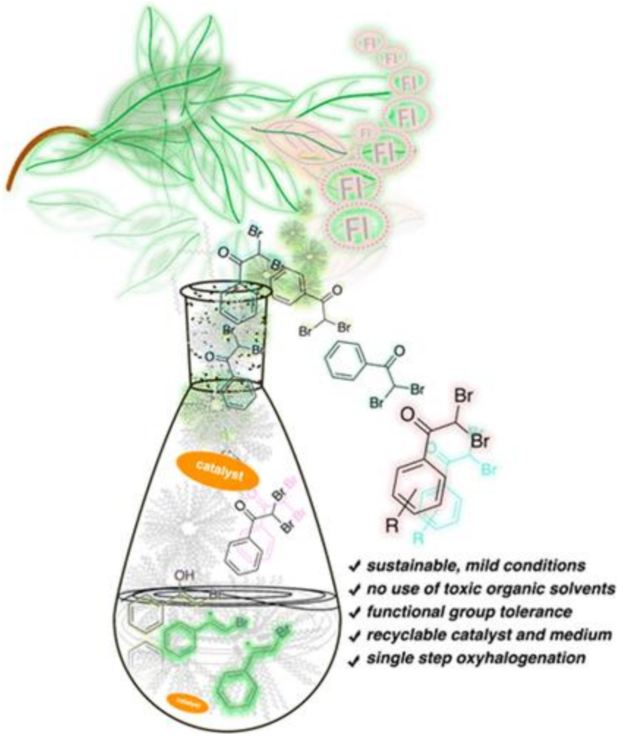


Monoclonal antibodies (mAbs) have been developed as therapeutics, especially for the treatment of cancer, inflammation, and infectious diseases. Because **the glycosylation of mAbs in the Fc region influences their interaction with effector cells** that kill antibody-targeted cells, and **the current method of antibody production is relatively expensive**, efforts have been directed toward the development of alternative expressing systems capable of large-scale production of mAbs with desirable glycoforms. In this study, we demonstrate that **the mAb trastuzumab expressed in glycoengineered *P. pastoris* can be remodeled through deglycosylation by endoglycosidases** identified from the Carbohydrate Active Enzymes database **and through transglycosylation using glycans** with a stable leaving group to generate a homogeneous antibody designed to optimize the effector functions. The 10 newly identified recombinant bacterial endoglycosidases are complementary to existing endoglycosidases (EndoA, EndoH, EndoS), two of which can even accept sialylated tri- and tetraantennary glycans as substrates.

Comment: This is an interesting biotechnology research paper. The workhorse for therapeutic monoclonal antibody production is Chinese Hamster Ovary (CHO) cell line. Using mammal cell lines is for now the best way to express a protein containing the right glycoforms. Why is glycosylation important? Well, once an antibody attaches to a target cell, the glycosylation pattern makes the therapy effective by offering a signal to nearby immune cells to finish the immune attack. This paper shows that a yeast-based approach coupled with deglycosylation-transglycosylation can be a cheaper alternative to current mAb production.

Micelle-Enabled Photoassisted Selective Oxyhalogenation of Alkynes in Water under Mild Conditions

Finck, L.; Brals, J.; Pavuluri, B.; Gallou, F.; Handa, S.* *J. Org. Chem.* **2018**, Article ASAP.

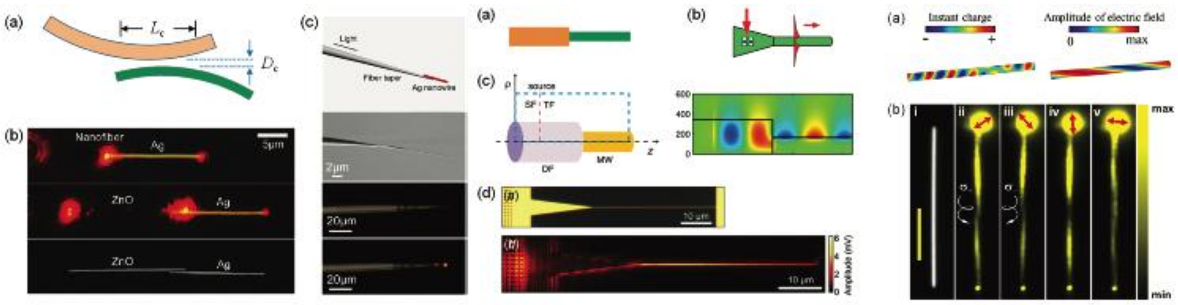


Using **micelles of FI-750-M, visible light, photocatalysts, and inexpensive halogenating reagents,** such as *N*-bromosuccinimide and *N*-chlorosuccinimde, selective oxyhalogenations of alkynes were achieved **in water under very mild conditions**. No halogenation at the aromatic rings was detected, and control experiments revealed the radical pathway. The easily conducted protocol exhibited high reproducibility, was readily adjusted to gram scale, and allowed for recycling of reaction medium and catalyst.

Comment: Organic chemistry "making the switch" – the story continues. This paper is another example of the transition that organic chemistry can make from being a discipline highly dependent on organic solvents to one that will be sustainable, based on water as the reaction medium… and micelles.

Plasmon Waveguiding in Nanowires

Wei, H.; Pan, D.; Zhang, S.; Li, Z.; Li, Q.; Liu, N.; Wang, W.; Xu, H.* *Chem. Rev.* **2018**, ASAP.

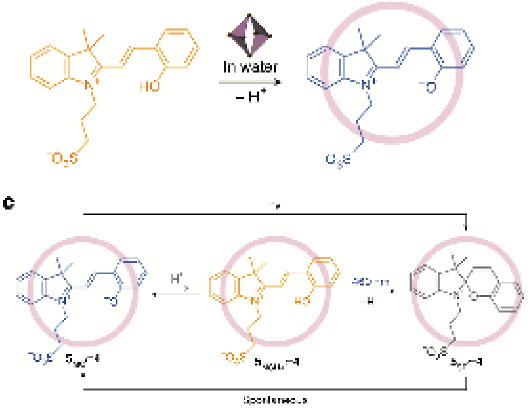


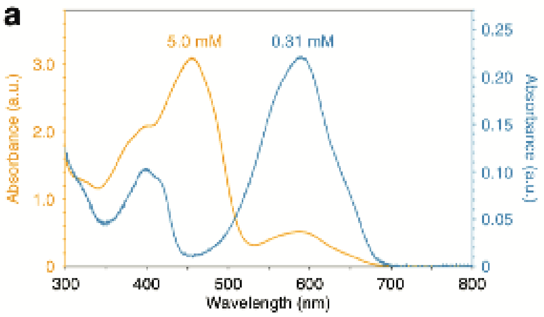
Nanowires supporting propagating surface plasmons can function as nanowaveguides to realize the light guiding with field confinement beyond the diffraction limit, providing fundamental building blocks for nanophotonic integrated circuits. This review covers the recent developments of plasmon waveguiding in nanowires, mainly including plasmon waveguiding in metal nanowires, coupling of nanowire plasmons and emitters, hybrid nanowire waveguides and plasmonic gain, and nanowire photonic devices. We first introduce the main techniques for fabricating metal nanowires, the plasmon modes in metal nanowires and the excitation/detection methods. **We then discuss the fundamental properties of plasmon propagation and emission, including zigzag, chiral and spin-dependent propagation**, mode conversion, loss and propagation length, group velocity, terminal emission, and leaky radiation. Then the interactions between nanowires and emitters are reviewed, especially the coupling of single nanowires and single quantum emitters. Finally, we briefly introduce the hybrid nanowire waveguide composed of a semiconductor nanowire and a metal film with an intervening thin insulator and highlight a few nanophotonic devices based on plasmonic nanowire networks or plasmonic-photonic hybrid nanowire structures.

Comment: While the review only focuses on metal nanorods, the concepts are obviously general. They briefly describe many ways to test plasmon waveguiding, which is cool on itself and even more so because of cool ideas like using evanescence waves (to the left of the figure). Moreover: chiral waveguiding!

Reversible Chromism of Spiropyran in the Cavity of a Flexible Coordination Cage

Samanta, D.; Galaktionova, D.; Gemen, J.; Shimon, L. J. W.; Diskin-Posner, Y.; Avram, L.; Král, P.; Klajn, R.* *Nat. Commun.* **2018**, *9*, 641.



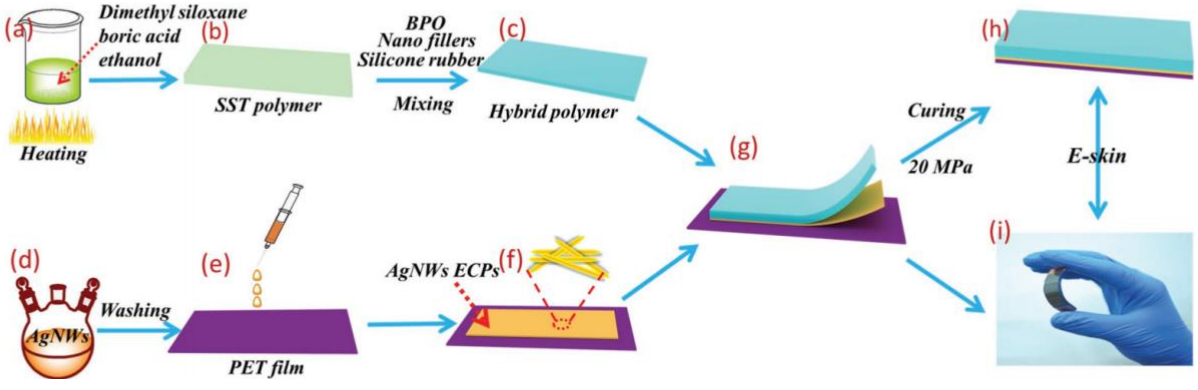


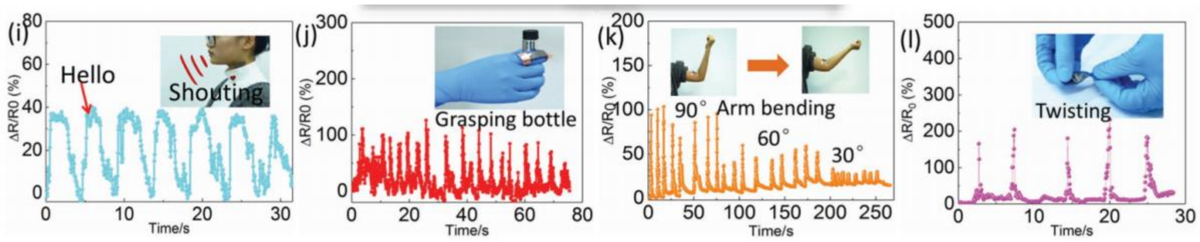
Confining molecules to volumes only slightly larger than the molecules themselves can profoundly alter their properties. Molecular switches—entities that can be toggled between two or more forms upon exposure to an external stimulus—often require conformational freedom to isomerize. Therefore, placing these switches in confined spaces can render them non-operational. To preserve the switchability of these species under confinement, we work with a water-soluble coordination cage that is flexible enough to adapt its shape to the conformation of the encapsulated guest. We show that owing to its flexibility, the cage is not only capable of accommodating—and solubilizing in water—several light-responsive spiropyran-based molecular switches, but, more importantly, it also provides an environment suitable for the efficient, reversible photoisomerization of the bound guests. Our findings pave the way towards studying various molecular switching processes in confined environments.

Comment: Molecular switching in confined spaces, is there really need to say more? And it is an article from Rafal Klajn's group. It is great to see how simple concepts are applied: The caging of a spiropyran shifts its equilibrium among the possible forms (open, closed, and tautomers) and thus it is possible to add one extra dimension to the ways to drive the system. I particularly like the dilution-induced chromism shown in the figure to the right (which is also, probably, thermochromism depending on the entropic contribution).

Novel Safeguarding Tactile e-Skins for Monitoring Human Motion Based on SST/PDMS–AgNW–PET Hybrid Structures

Wang, S.; Gong, L.; Shang, Z.; Ding, L.; Yin, G.*; Jiang, W.; Gong, X.; Xuan, S.* *Adv. Funct. Mater.* **2018**, 1707538.



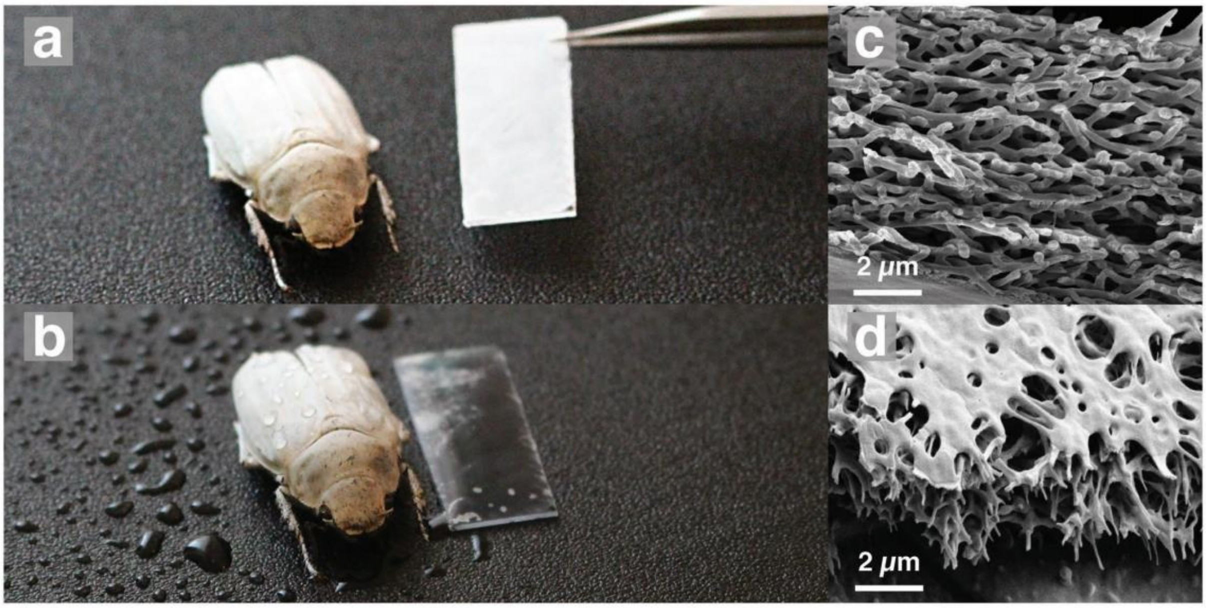


A novel versatile electrical skin (e-skin) with **safeguarding** and **multisensing** properties based on hybrid structures is developed by assembling Ag nanowires (AgNWs), polyester (PET) film with hybrid shear stiffening polymer/polydimethylsiloxane (SST/PDMS) matrix. The hybrid SST/PDMS polymer shows stable configuration. Storage modulus of the SST/PDMS increases from 5.5 kPa to 0.39 MPa when the shear frequency changes from 0.1 to 100 Hz, exhibiting typical rate-dependent behavior. e-Skin functions as a human-monitoring device by detecting various motions such as gentle touching, stroking, elbow bending, as well as speaking. More importantly, due to the **shear stiffening** characteristic, e-skin with high damping capacity exhibits **safeguarding performance**, which can dissipate impact force from 720 to 400 N and increase buffer time (from 0.9 to 2 ms). Meanwhile, distinguishable resistance values can reveal the level of harsh impact applied on the e-skin. In addition, the visible thermosensation effect of e-skin similar to chameleon epidermis is convenient for assessing environmental temperature. e-Skin arrays can precisely map the dynamic impact location and pressure distribution. Finally, the high electrical sensitivity and shear stiffening performance are attributed to the disturbance of AgNW effective conductive paths and **dynamic B-O bonds**, respectively.

Comment: a) An investigation of e-skins with safeguarding and sensing properties, which mimics the skin's function to feel the impact and to protect the human body against external damage by incorprating shear stiffening (SST) polymers into the composite e-skin. b) The dynamic B-O bonds play the key role in the SST polymer which impede the slippage of polymer chains in short time but can be broke when the external loaded force is under a low rate. c) The device with the resulting hybrid polymer can reveal the amplitude and distribution of impact force, which is quite appealing for developing smart devices.

Bio-inspired Highly Scattering Networks via Polymer Phase Separation

Syurik, J.; Jacucci, G.; Onelli, O. D.; Hölscher, H.*; Vignolini, S.* *Adv. Funct. Mater.* **2018,** 1706901.



A common strategy to optimize whiteness in living organisms consists in using 3D random networks with dense and polydisperse scattering elements constituted by relatively low refractive index materials. Inspired by these natural architectures, **a fast and scalable method to produce highly scattering porous polymer films via phase separation is developed.** By varying the molecular weight of the polymer, the morphology of the porous films is modified, and therefore their scattering properties are tuned. The achieved transport mean free paths are in the micrometer range, improving the scattering strength of analogous low refractive index systems, e.g., standard white paper, by an order of magnitude. The produced porous films show a broadband reflectivity of ≈75% while only 4 μm thick. In addition, the films are flexible and can be readily index-matched with water (i.e., they become transparent when wet), allowing for various applications such as coatings with tunable transmittance and responsive paints.

Comment: An interesting bio-inspired study on highly scattering porous polymer materials. The preparation is simple and scalable, and the PMMA film is flexibile, lightweight and processable. The film loses the high scattering properties when wet and is thus responsive to humidity. It seems that for the structural design, the order is important (e.g. iridescent coloration of butterfly), but sometimes disorder is also playing an important role (protection? cut off the information transmission?).

Dye-conjugated Complementary Lipophilic Nucleosides as Useful Probes to Study Association Processes by Fluorescence Resonance Energy Transfer

Mayoral, M. J.*; Camacho-Garcia, J.; Magdalena-Estirado, E.; Blanco-Lomas, M.; Fadaei, E.; Montoro-Garcia, C.; Serrano-Molina, D.; Gonzalez-Rodriguez, D.* *Org. Biomol. Chem.* **2017**, *15*, 7558.

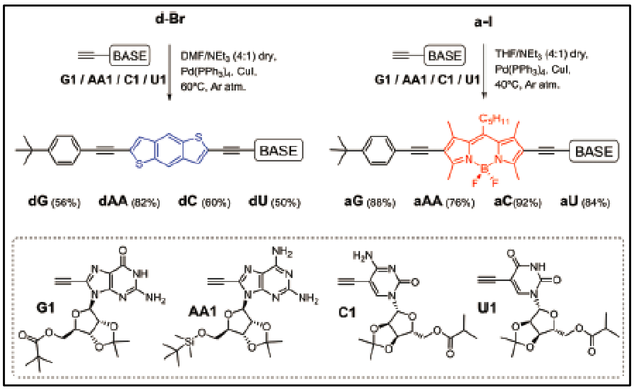


Figure1. Synthesis of nucleosides dG, dAA, dC, dU, aG, aAA, aC and aU via the Sonogashira coupling reaction between d-Br or a-I and ethynyl-nucleobases G1, AA1, C1 and U1.(d: donor, a: acceptor)

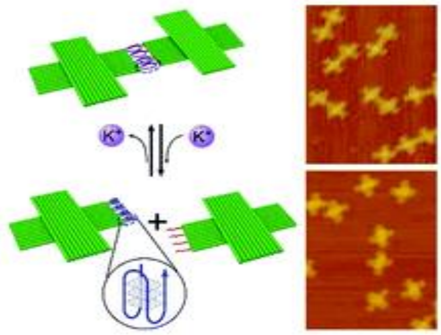
Modern supramolecular chemistry relies on the combination of diverse analytical techniques that can provide complementary information on complex self-assembly landscapes. Among them, resonance energy transfer, monitored by fluorescence emission spectroscopy, arises as a sensitive and convenient phenomenon to report binding intermolecular interactions. The use of molecular probes labelled with suitable complementary energy-transfer pairs can provide valuable information about the thermodynamics, kinetics and self-sorting characteristics of a particular self-assembled system. The objective of this work is to generate a set of nucleoside FRET probes that can be reliably employed to prove and analyse quantitatively H-bonding interactions between complementary Watson-Crick pairs. We first describe the preparation of a set of lipophilic nucleosides that are linked to a p-conjugated functional fragment. The bases include guanosine and 2-aminoadenosine as purine heterocycles, and cytidine and uridine as complementary pyrimidine bases. The p-conjugated moiety comprises either a short phenylene- ethynylene oligomer, a bithiophene, or a BODIPY dye. We then demonstrate that the last two chromophores constitute an energy donor-acceptor couple and that donor emission quenching can be related to the ratio of molecules bound to the complementary acceptor pair. Hence, fluorescence spectroscopy in combination with resonance energy transfer, is shown here to be a useful tool to study and quantify the association and self-sorting events between complementary and non-complementary nucleosides in apolar aromatic solvents, where the binding strength is considerably high, and sensitive techniques that employ low concentrations are demanded.

Comment: This work studies the Förster resonance energy transfer (FRET) between donor-acceptor dimers (D-A) based on Watson-Crick pairs and calculate the association constants between the G–C ($K_{G–C}$) and AA–U ($K_{AA–U}$) in toluene with low concentration (10^{-5} M). It is important for investigating the Watson-Crick pairing in toluene and chloroform.

Metal-ion Responsive Reversible Assembly of DNA Origami Dimers: G-Quadruplex Induced Intermolecular Interaction

Yang, S.; Liu, W.; Nixon, R.; Wang, R.* *Nanoscale* **2018**, *10*, 3626.

Chair-type G-quadruplex-driven assembly/disassembly of DNA origami dimers.



We present a novel metal-ion stimulated organization of DNA origami nanostructures by employing G-quadruplexes as stimuli-responsive bridges. The reversible assembly process of DNA origami was the result of conformational changes between the G-quadruplex and its single-strand state induced by monovalent cations. This study might stimulate a new design of responsive DNA-based intelligent nanomaterials.

Comment: This work studies G-quadruplexes-assisted reversible assembly and disassembly of DNA origami. The idea is not new but can be applied to guanine-decorated molecules or nanostructures to form organized materials.