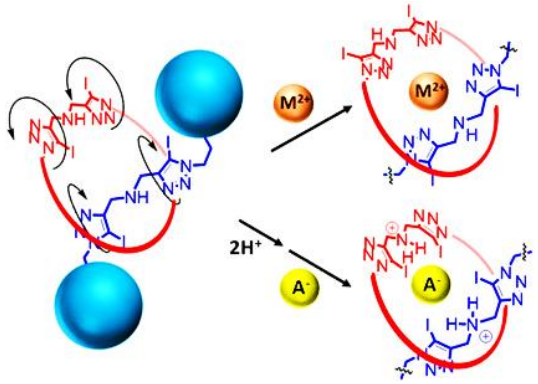
Acid-Regulated Switching of Metal Cation and Anion Guest Binding in Halogen-Bonding Rotaxanes

Li, X.; Lim, J. Y. C.; Beer, P. D.* *Chem. Eur. J.* **2018**, 24, 17788–17795

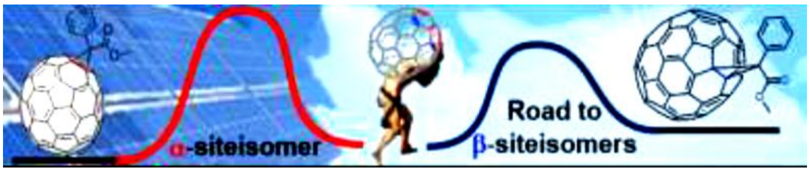


The ability of natural enzymes to regulate their guest binding affinities and preferences through the use of co-ligands which alter the features of the binding site is fundamental to biological homeostatic control. Herein, the rarely exploited orthosteric control of guest binding is demonstrated using neutral halogen bonding [2]rotaxanes, in which a chemical stimulus (acid) interacting with the interlocked host binding site switches the host's native guest preference from metal cations to anions. **When neutral, the rotaxanes exhibit pronounced transition metal cation affinity and comparatively weak anion binding properties**. However, the addition of acid attenuates the rotaxanes' ability to coordinate cations, while concurrently enabling strong binding of halides through charge assisted halogen bonding and hydrogen bonding interactions in competitive aqueous solvent media. **The appendage of a fluorescent anthracene reporter group to the rotaxane framework also enables diagnostic sensory responses to cation/anion binding.**

Comment: The authors highlight the *high* yield (60%) obtained in the formation of a macrocycle without the presence of a template, which is commonly used to facilitate the macrocyclization over the formation of acyclic oligomers. On the other hand, the photophysical properties of one of the rotaxanes were studied in the presence of metal cations (Zn^{2+}, Cu^{2+}) and Cl^{-} anions, finding different responses in the fluorescence emissions. For the **determination of the host-guest 1:1 association constants** between the rotaxanes and the anions, a program called **WinEQNMR2** was employed.

Site-selective Synthesis of β-[70]PCBM-like Fullerenes: Efficient Application in Perovskite Solar Cells

Vidal, S.; Izquierdo, M.; Filippone, S.; Fernández, I.; Akin, S.; Seo, J-Y.; Zakeeruddin, S. M.; Graetzel, M.; Nazario M.* *Chem. Eur. J.* **2019**, ASAP.

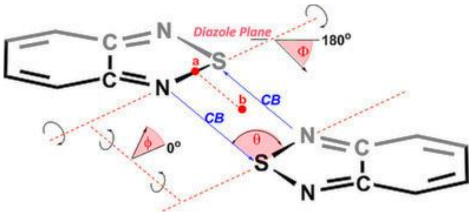


We report on the site-selective synthesis of PCBM-like [70]fullerene site-isomers, where the elusive **β-site-isomers are, for the first time, the major product in an (cyclo)addition chemical reaction involving [70]fullerene**. The reaction involves an straightforward cyclopropanation of [70]fullerene from sulfonium salts, affording a mixture of α and β site-isomers in good yields. Amazingly, the preference for the α- or β-site-isomer can be efficiently controlled by means of the solvent polarity! DFT theoretical calculations (DMF and toluene) nicely predict that, although the formation of the α-adduct is, as expected, thermodynamically favored, the selectivity of the process is determined by the energy difference of the respective transition states. Furthermore, **the employ of α or/and β site-isomers, as pure materials or as a mixture of them, used as templating agent, has been evaluated in perovskites solar cells**. The positive influence of the [70]fullerenes by passivating the voids/pin-holes and/or deep slits, is reflected in highly efficient and stable bulk heterojunction perovskite solar cells, whose performance (around 20%) is slightly but consistently depending on the isomeric fullerene composition. **These experimental findings pave the way to investigate a new reactivity on C70 and to explore the properties of the less-known β-derivatives**.

Comment: This article presents the selective synthesis of C70 fullerene isomers modulated by the solvent polarity (confirmed also by DFT calculations), being the first time that a β-site isomer is obtained as the main product of an addition reaction on C70. On the other hand, this paper made me curious about different concepts related to the surface morphology of perovskite films in solar cells.

Chalcogen Bonding "2S–2N Squares" versus Competing Interactions: Exploring the Recognition Properties of Sulfur

Ams, M. R.;* Trapp, N.; Schwab, A.; Milić, J.V.; Diederich, F.* *Chem. Eur. J.* **2018**, *25*, 323–333

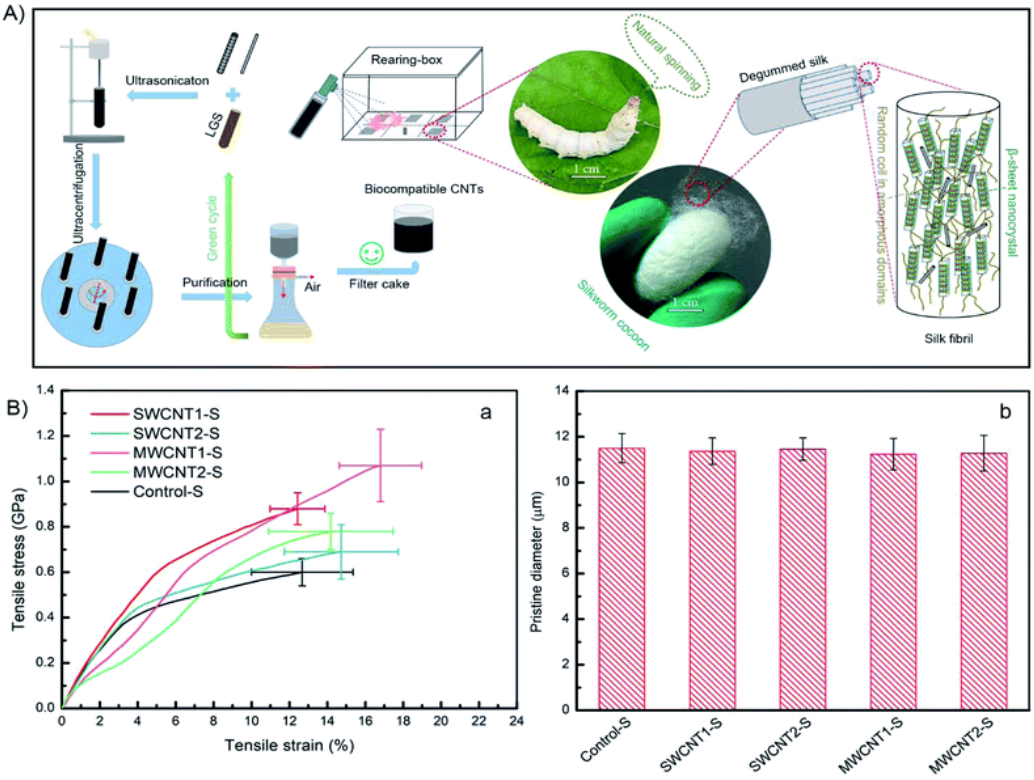


Chalcogen bonding (CB) is the focus of increased attention for its applications in medicinal chemistry, materials science, and crystal engineering. However, the origin of sulfur's recognition properties remains controversial, and experimental evidence for supporting theories is still emerging. Here, a comprehensive evaluation of sulfur CB interactions is presented by investigating 2,1,3-benzothiadiazole X-ray crystallographic structures gathered from the Cambridge Structure Database (CSD), Protein Data Bank (PDB), and own laboratory findings. Through the systematic analysis of substituent effects on a subset library of over thirty benzothiadiazole derivatives, **the competing interactions have been categorized into four main classes, namely 2S–2N CB square, halogen bonding (XB), S···S, and hydrogen-bonding (HB)**. A geometric model is employed to characterize the 2S–2N CB square motifs and discuss the role of electrostatic, dipole, and orbital contributions toward the interaction.

Comment: This article fits in the computational chemistry field, so it is a bit hard to understand specially if one is not related with theoretical calculations but, personally, I found this article very interesting from the perspective of learning new concepts. This is particularly true for me, because I did not know about chalcogen bonds, how it occurs, and that it is gaining more attention due to its potential applications in different fields of chemistry: ranging from medicinal chemistry to supramolecular chemistry and crystal engineering.

Obtaining High Mechanical Performance Silk Fibers by Feeding Purified Carbon Nanotube/Lignosulfonate Composite to Silkworms

Xu, H.; Yi, W.; Li, D.; Zhang, P.; Yoo, S.; Bai, L.; Hou, J.; Hou, X.* *RSC Advances* **2019**, *9*, 3558. RSC Adv., 2019,9, 3558-3569

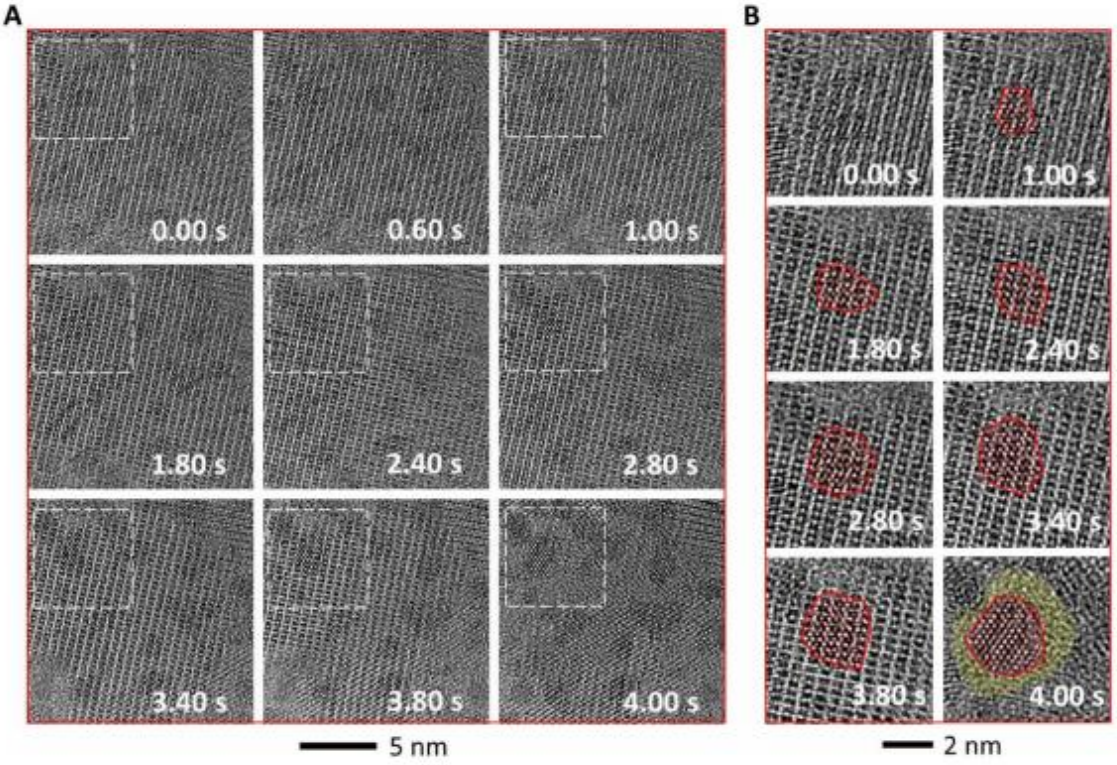


Silkworm fibers have attracted widespread attention for their superb glossy texture and promising mechanical performance. The mechanical properties can be reinforced with carbon nanofillers, particularly carbon nanotubes (CNTs), depending on the CNT content in the silk fibers. In order to increase the CNT content, lignosulfonate (LGS) was used as a surfactant to ameliorate the CNT solubility, dispersibility, and biocompatibility. The resulting CNT/LGS nano-composite was further processed through an additional purification method to remove excess surfactant and enhance the CNT/LGS ratio. Then the **purified biocompatible single and multiple-walled CNTs were fed to silkworms**, leading to a large CNT content in the resulting silk fibers. Reinforced silk fibers were produced with a mechanical strength as high as 1.07 GPa and a strain of 16.8%. **The toughness modulus is 1.69 times than that of the unpurified group**. The CNT-embedded silk fibers were characterized *via* Raman spectrometry and thermogravimetric analysis (TGA), demonstrating that the CNT content in the silk fibers increased 1.5-fold in comparison to the unpurified group. The increased CNT content not only contributed to the self-assembly into buffering knots of silk fibers, but it also enhanced the conductivity of graphitized silk. Our coating and purification strategies provide a potential facile way to obtain natural silk fibers with high mechanical performance.

Comment: SWCNT and MWCNT have been successfully fed to silk worms. The authors reached a good level of mechanical performance of the fibers. Fortunately, the ethics of animal research do not care about insects.

Probing the Dynamics of Nanoparticle Formation from a Precursor at Atomic Resolution

Gao, W.; Tieu, P.; Addiego, C.; Ma, Y.; Wu, J.*; Pan, X.* *Sci. Adv.* **2019**, *5*, eaau9590.



Control of reduction kinetics and nucleation processes is key in materials synthesis. However, understanding of the reduction dynamics in the initial stages is limited by the difficulty of imaging chemical reactions at the atomic scale; the chemical precursors are prone to reduction by the electron beams needed to achieve atomic resolution. Here, we study **the reduction of a solid-state Pt precursor** compound in an aberration-corrected transmission electron microscope by combining low-dose and in situ imaging. The beam-sensitive Pt precursor, K_2PtCl_4, is imaged at atomic resolution, **enabling determination of individual (K, Pt, Cl) atoms**. The transformation to Pt nanoclusters is captured in **real time**, showing a three-stage reaction including the breaking of the ionic bond, formation of $PtCl_2$, and the reduction of the dual-valent Pt to Pt metal. Deciphering the atomic-scale transformation of chemicals in real time using combined low-dose and in situ imaging brings new possibility to study reaction kinetics in general.

Comment: The author visualized nanoparticles formation in solid state.

Molecular Dynamics Simulation of Four Typical Surfactants in Aqueous Solution

Shi, P.; Zhang, H.; Lin, L.; Song, C.; Chen, Q.*; Li, Z. *RSC Advances* **2019**, *9*, 3224.

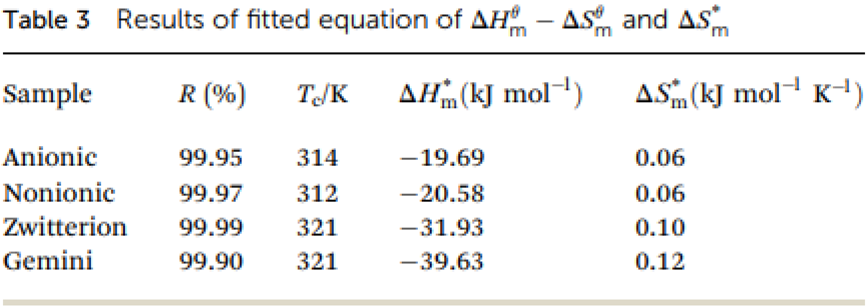


Table 3 Results of fitted equation of $\Delta H^{\theta}_{m} - \Delta S^{\theta}_{m}$ and ΔS^{*}_{m}

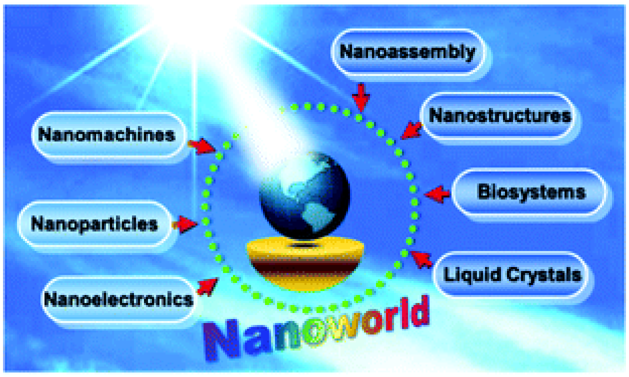
Sample	R (%)	T_c/K	ΔH^{*}_{m}(kJ mol^{-1})	ΔS^{*}_{m}(kJ mol^{-1} K^{-1})
Anionic	99.95	314	−19.69	0.06
Nonionic	99.97	312	−20.58	0.06
Zwitterion	99.99	321	−31.93	0.10
Gemini	99.90	321	−39.63	0.12

The thermodynamic values of the four surfactants, anionic surfactants, nonionic surfactants, zwitterion surfactants and gemini surfactants, were calculated by molecular dynamics simulation. The calculated results of thermodynamic parameters showed that the four surfactant can form micelles spontaneously. The mainly force for micellization process is entropy-driven, and as the temperature increases, the entropy-driven contribution is gradually reduced. There are linear enthalpy–entropy compensation phenomena for the four surfactants. Among the studied four surfactants, the gemini surfactant is the easiest to form micelles and has good stability, the zwitterion surfactant is the second, and the anionic surfactant is the least stable.

Comment: Revisiting the basics of surfactant thermodynamics. The current work provides theoretical background for the use of surfactants.

Photochromism into Nanosystems: Towards Lighting up the Future Nanoworld

Wang, L.; Li, Q.* *Chem. Soc. Rev.* **2018**, *47*, 1044–1097.



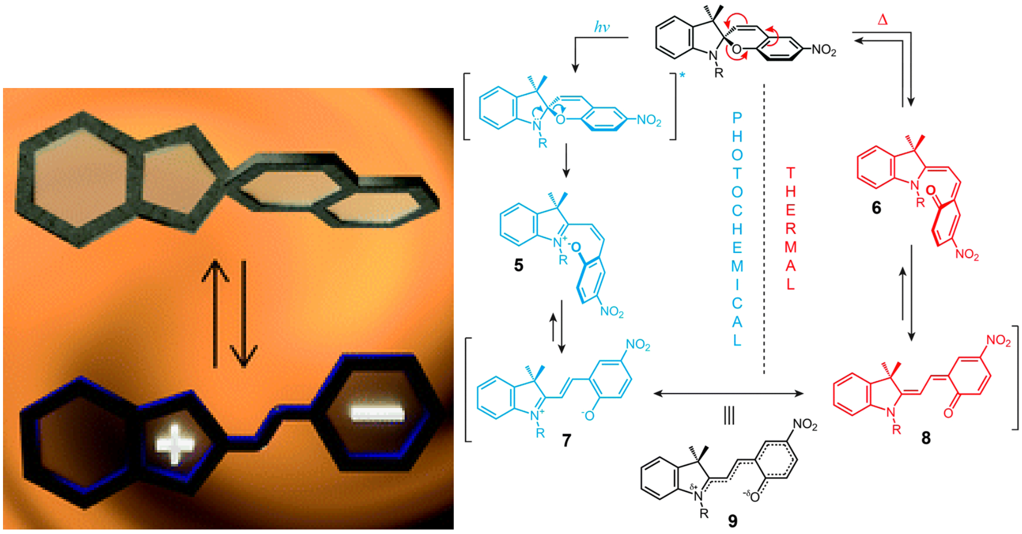
The ability to manipulate the structure and function of promising nanosystems *via* energy input and external stimuli is emerging as an attractive paradigm for developing reconfigurable and programmable nanomaterials and multifunctional devices. Light stimulus manifestly represents a preferred external physical and chemical tool for *in situ* remote command of the functional attributes of nanomaterials and nanosystems due to its unique advantages of high spatial and temporal resolution and digital controllability. Photochromic moieties are known to undergo reversible photochemical transformations between different states with distinct properties, which have been extensively introduced into various functional nanosystems such as nanomachines, nanoparticles, nanoelectronics, supramolecular nanoassemblies, and biological nanosystems. The integration of photochromism into these nanosystems has endowed the resultant nanostructures or advanced materials with intriguing photoresponsive behaviors and more sophisticated functions.

In this Review, we provide an account of the recent advancements in reversible photocontrol of the structures and functions of photochromic nanosystems and their applications. The important design concepts of such truly advanced materials are discussed, their fabrication methods are emphasized, and their applications are highlighted. The Review is concluded by briefly outlining the challenges that need to be addressed and the opportunities that can be tapped into. We hope that the review of the flourishing and vibrant topic with myriad possibilities would shine light on exploring the future nanoworld by encouraging and opening the windows to meaningful multidisciplinary cooperation of engineers from different backgrounds and scientists from the fields such as chemistry, physics, engineering, biology, nanotechnology and materials science.

Comment: This complete review from 2018 is a **must-read**. This paper covers the majority of the systems that exist in the fascinating world of nanomachines; the authors give an insight of what could be achieved in the relatively close future.

Spiropyran-Based Dynamic Materials

Klajn, R.* *Chem. Soc. Rev.* **2014**, *43*, 148–184

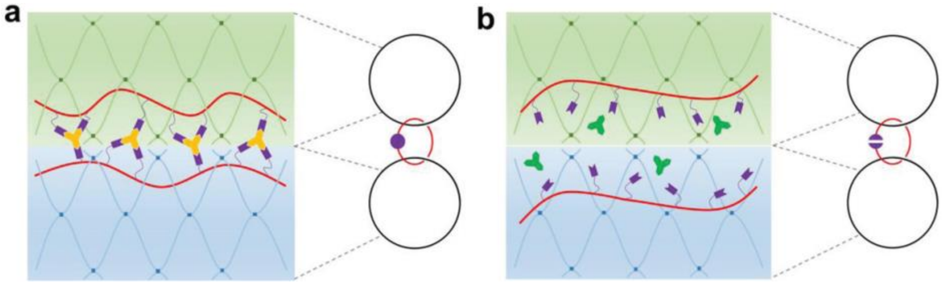


In the past few years, spiropyran has emerged as the molecule-of-choice for the construction of novel dynamic materials. This unique molecular switch undergoes structural isomerisation in response to a variety of orthogonal stimuli, e.g. light, temperature, metal ions, redox potential, and mechanical stress. Incorporation of this switch onto macromolecular supports or inorganic scaffolds allows for the creation of robust dynamic materials. This review discusses the synthesis, switching conditions, and use of dynamic materials in which spiropyran has been attached to the surfaces of polymers, biomacromolecules, inorganic nanoparticles, as well as solid surfaces. The resulting materials show fascinating properties whereby the state of the switch intimately affects a multitude of useful properties of the support. The utility of the spiropyran switch will undoubtedly endow these materials with far-reaching applications in the near future.

Comment: This less recent review is also mandatory for anyone who would like to work with spiropyran. The author is clear and comprehensible; the different systems accurately described and the main issues well explained. So far, I didn't find a better review on this subject.

Photodetachable Adhesion

Gao, Y.; Wu, K.; Suo, Z.* *Adv. Mater.* **2018**, 1806948

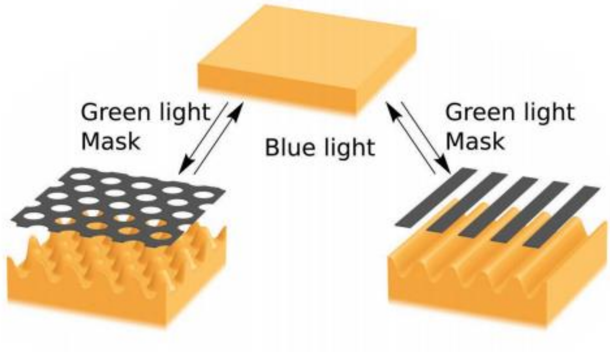


Peeling from strong adhesion is hard, and sometimes painful. Herein, an approach is described to achieve both strong adhesion and easy detachment. The latter is triggered, on-demand, through an exposure to light of a certain frequency range. The principle of photodetachable adhesion is first demonstrated using two hydrogels as adherends. Each hydrogel has a covalent polymer network, but does not have functional groups for bonding, so that the two hydrogels by themselves adhere poorly. The two hydrogels, however, adhere strongly when an aqueous solution of polymer chains is spread on the surfaces of the hydrogels and is triggered to form a stitching polymer network in situ, in topological entanglement with the pre-existing polymer networks of the two hydrogels. The two hydrogels detach easily when the stitching polymer network is so functionalized that it undergoes a gel–sol transition in response to a UV light. For example, two pieces of alginate–polyacrylamide hydrogels achieve adhesion energies about 1400 and 10 J m−2, respectively, before and after the UV radiation. Experiments are conducted to study the physics and chemistry of this strong and photodetachable adhesion, and to adhere and detach various materials, including hydrogels, elastomers, and inorganic solids.

Comment: I really like the idea of photodetachable materials, it opens a wide range of applications. This proof-of-concept lays the foundations for futures studies. The adhesion is based on interpenetrations of polymer networks and the reduction of Fe(III) ions acting as crosslinkers into Fe(II).

Re- and Preconfigurable Multistable Visible Light Responsive Surface Topographies

Hendrikx, M.; ter Schiphorst, J.; van Heeswijk, E. P. A.; Koçer, G.; Knie, C.; Bléger, D.; Hecht, S.; Jonkheijm, P.; Broer, D. J.*; Schenning, A. P. H. J.* *Small* **2018**, *14*, 1803274.

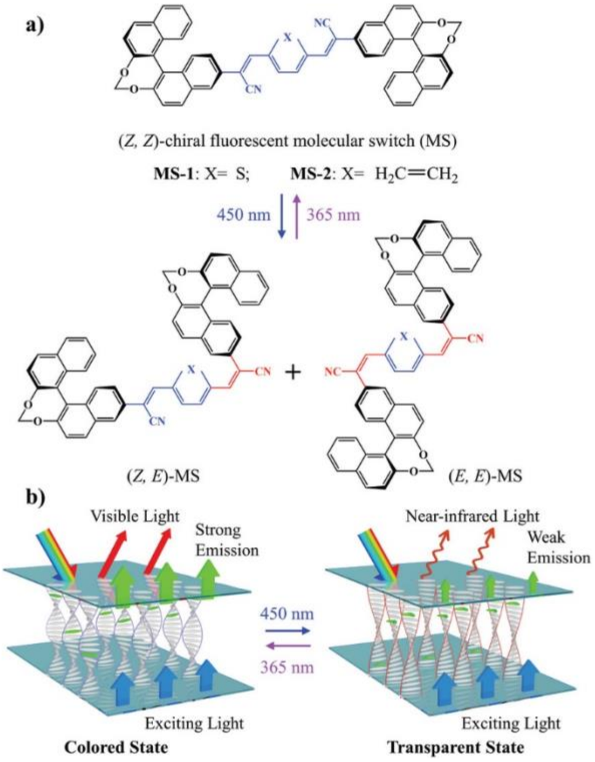


Light responsive materials that are able to change their shape are becoming increasingly important. However, preconfigurable bistable or even multistable visible light responsive coatings have not been reported yet. Such materials will require less energy to actuate and will have a longer lifetime. Here, it is shown that **fluorinated azobenzenes** can be used to create rewritable and pre-configurable responsive surfaces that show multi-stable topographies. These surface structures can be formed and removed by using low intensity green and blue light, respectively. **Multistable preconfigured surface topographies can also be created in the absence of a mask**. The method allows for full control over the surface structures as the topographical changes are directly linked to the molecular isomerization processes. Preliminary studies reveal that these light responsive materials are suitable as adaptive biological surfaces.

Comment: Surface topographies can also be attained when an azobenzene-containing material is irradiated through a mask (or an interference pattern), because of the mass migration towards the irradiated areas. Here, the authors use a **fluorinated azobenzene in a liquid-crystalline matrix**, lowering the light intensity necessary to achieve motion.

Optically Rewritable Transparent Liquid Crystal Displays Enabled by Light-Driven Chiral Fluorescent Molecular Switches

Li, J.; Bisoyi, H. K.; Tian, J.; Guo J.; Li, Q.; *Adv. Mater.* **2019**, 1807751

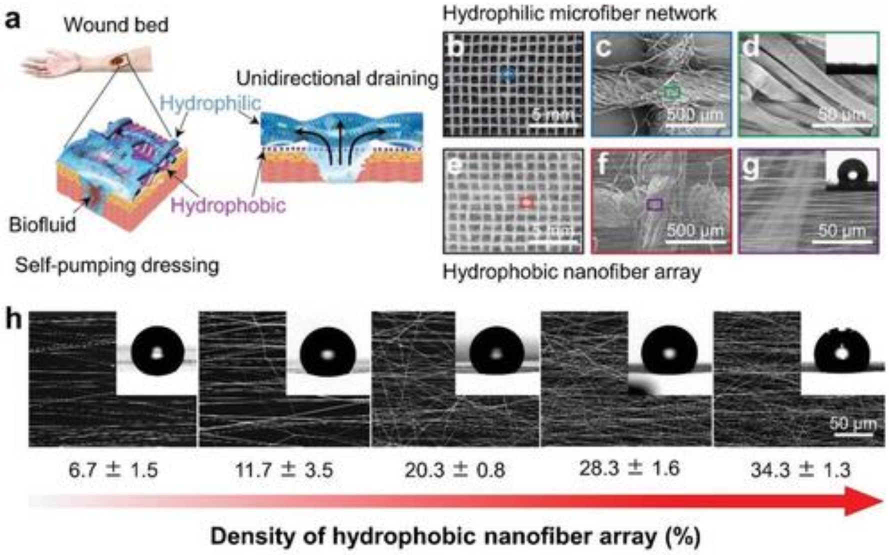


Functional soft materials exhibiting distinct functionalities in response to a specific stimulus are highly desirable towards the fabrication of advanced devices with superior dynamic performances. Herein, two novel light-driven chiral fluorescent molecular switches have been designed and synthesized that are able to exhibit unprecedented reversible Z/E photoisomerization behavior along with tunable fluorescence intensity in both isotropic and anisotropic media. Cholesteric liquid crystals fabricated using these new fluorescent molecular switches as chiral dopants exhibit reversible reflection color tuning spanning the visible and infrared region of the spectrum. Transparent display devices have been fabricated using both low chirality and high chirality cholesteric films that operate either exclusively in fluorescent mode or in both fluorescent and reflection mode, respectively. The dual mode display device employing short pitch cholesteric film is able to function on demand under all ambient light conditions including daylight and darkness with fast response and high resolution. Moreover, the proof-of-concept for a "remote-writing board" using cholesteric films containing one of the light-driven chiral fluorescent molecular switches with ease of fabrication and operation is disclosed herein. Such optically rewritable transparent display devices enabled by light-driven chiral fluorescent molecular switches pave a new way for developing novel display technology under different lighting conditions.

Comment: I find this proof-of-concept interesting for the molecule itself. The yield of the isomerization is good, and the role of display is fulfilled as long as we don't examine too closely the time of response.

A Self-Pumping Dressing for Draining Excessive Biofluid around Wounds

Shi, L.; Liu, X.; Wang, W.; Jiang, L.; Wang, S.* *Adv. Mater.* **2019**, 1804187

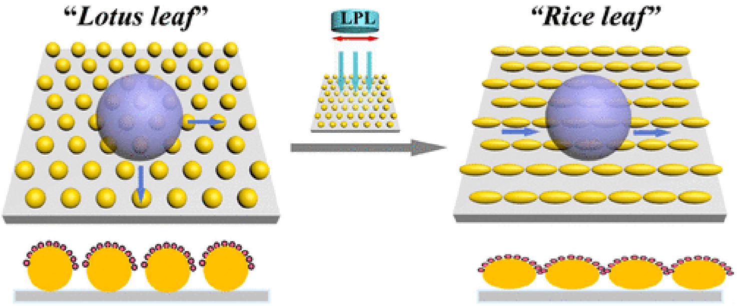


Excessive biofluid around wounds often causes infection and hinders wound healing. However, the intrinsic hydrophilicity of the conventional dressing inevitably retains excessive biofluid at the interface between the dressing and the wound. Herein, a self-pumping dressing is reported, by electrospinning a hydrophobic nanofiber array onto a hydrophilic microfiber network, which can unidirectionally drain excessive biofluid away from wounds and finally accelerate the wound healing process. The hydrophilic microfiber network offers a draining force to pump excessive biofluid through the hydrophobic nanofiber array, which can further keep those pumped biofluids from rewetting the wounds. In the proof of concept, the self-pumping dressing unidirectionally drains the biofluid from murine dorsum wounds, thereby resulting in faster wound healing than conventional dressings. This unique self-pumping dressing has enormous potential to be a next-generation dressing for healing wounds clinically.

Comment: The dressing of the future may be designed. By combining two networks with radically opposed hydrophilicity, the material exhibits very good self-pumping properties and thus healing rate.

Light-Driven Transformation of Bio-Inspired Superhydrophobic Structure via Reconfigurable PAzoMA Microarrays: From Lotus Leaf to Rice Leaf

Gao, F.; Yao, Y.; Wang, W.; Wang, X.; Li, L.; Zhuang, Q.; Lin, S.* [*Macromolecules* **2018**, *51*, 2742–2749.]

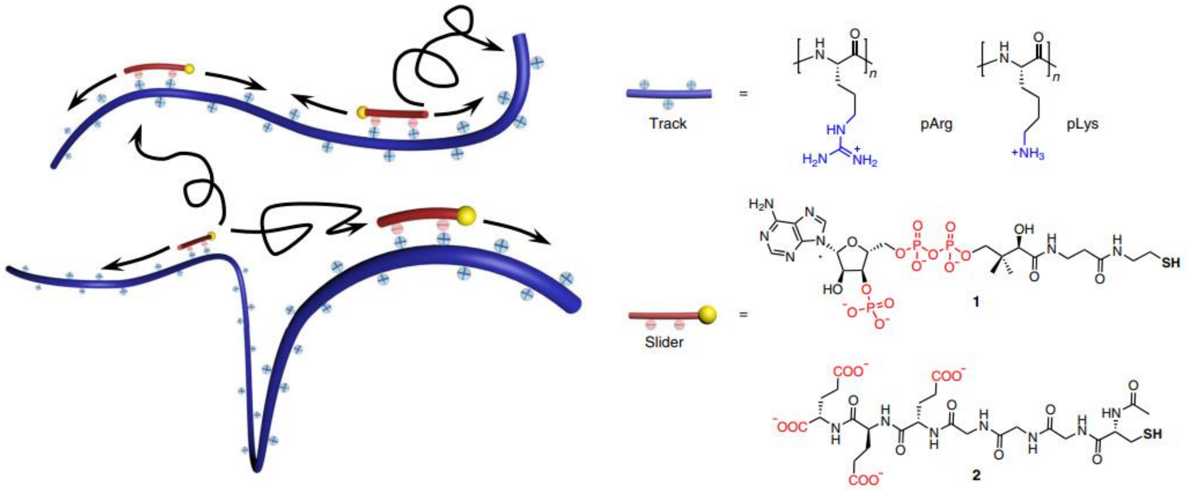


Light-driven transformation from isotropic superhydrophobicity to anisotropic superhydrophobicity was accomplished through bio-inspired modification and reconfiguration on poly[6-(4-methoxy-4'-oxyazobenzene)hexyl methacrylate] (PAzoMA) microarrays. In this study, ordered PAzoMA microarray film was fabricated via the reverse breath figure (RBF) method. After gold nanoparticles sputtering and subsequent modification with self-assembly of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (FSH), the obtained lotus-leaf-inspired film showed **isotropic superhydrophobicity** with self-cleaning property due to the hierarchical structure and low surface free energy. Upon irradiation with **linearly polarized light** (LPL), the microspheres were elongated along the direction of polarization and exhibited **anisotropic superhydrophobicity** resembling rice leaf. With the increase of illumination time, the axis ratio became larger, and anisotropy sliding was more obvious. This research enriches responsive bio-inspired superhydrophobicity and further provides a promising candidate for smart water harvesting.

Comment: I think that everyone is familiar with the Lotus effect of superhydrophobicity, mainly caused by the surface topography (if you are not, you should have come to the "Fête de la Science"). When irradiated with linearly polarized light, **azobenzene-containing polymers deform because of the orientation of the azobenzene moiety**. The authors take advantage of this phenomenon with microarrays to achieve anisotropic superhydrophobicity.

Catalytic Transport of Molecular Cargo Using Diffusive Binding along A Polymer Track

Zheng, L.*; Zhao, H.; Han, Y.; Qian, H.; Vukovic, L.; Mecinović, J.; * Huck, W. T.* [*Nat. Chem* **2018**, ASAP.]

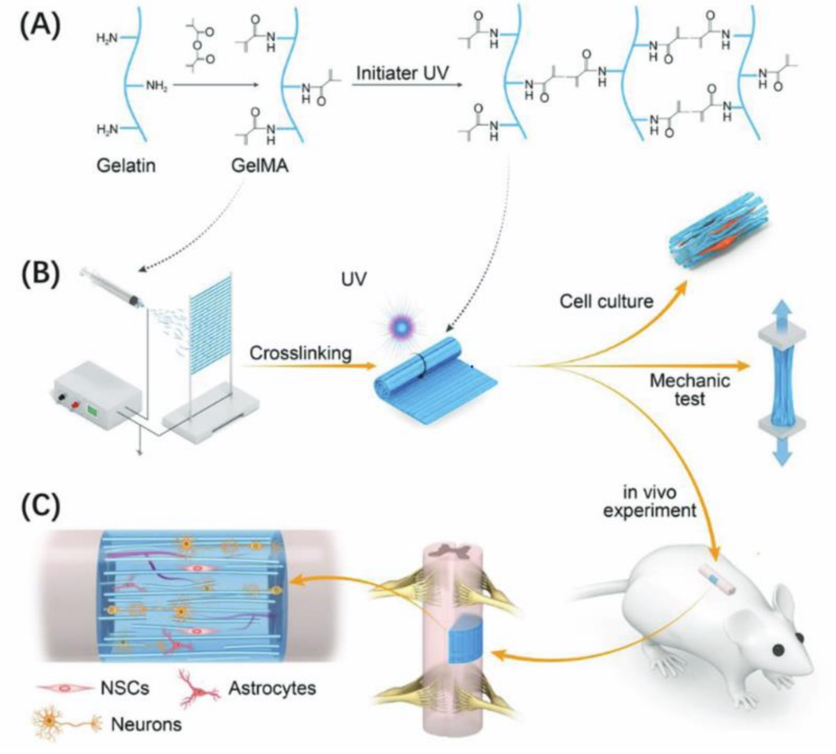


Transport at the molecular scale is a prerequisite for the development of future molecular factories. Here, we have designed oligoanionic molecular sliders on polycationic tracks that exploit Brownian motion and diffusive binding to transport cargo without using a chemical fuel. The presence of the polymer tracks increases the rate of bimolecular reactions between modified sliders by over two orders of magnitude. Molecular dynamics simulations showed that the sliders not only diffuse, but also jump and hop surprisingly efficiently along polymer tracks. Inspired by acetyl-coenzyme A transporting and delivering acetyl groups in many essential biochemical processes, we developed a new and unconventional type of catalytic transport involving sliders (including coenzyme A) picking up, transporting and selectively delivering molecular cargo. Furthermore, we show that the concept of diffusive binding can also be utilized for the spatially controlled transport of chemical groups across gels. This work represents a new concept for designing functional nanosystems based on random Brownian motion.

Comment: A very interesting transport system, on a molecular scale, by polypeptide and oligoanion.

Bioinspired Hydrogel Electrospun Fibers for Spinal Cord Regeneration

Chen, C.; Tang, J.; Gu, Y.; Liu, L.; Liu, X.; Deng, L.; Martins C,; Sarmento B,; * Cui W,; * Chen, L.**Adv. Funct. Mater.***2019*, *29*, 1806899

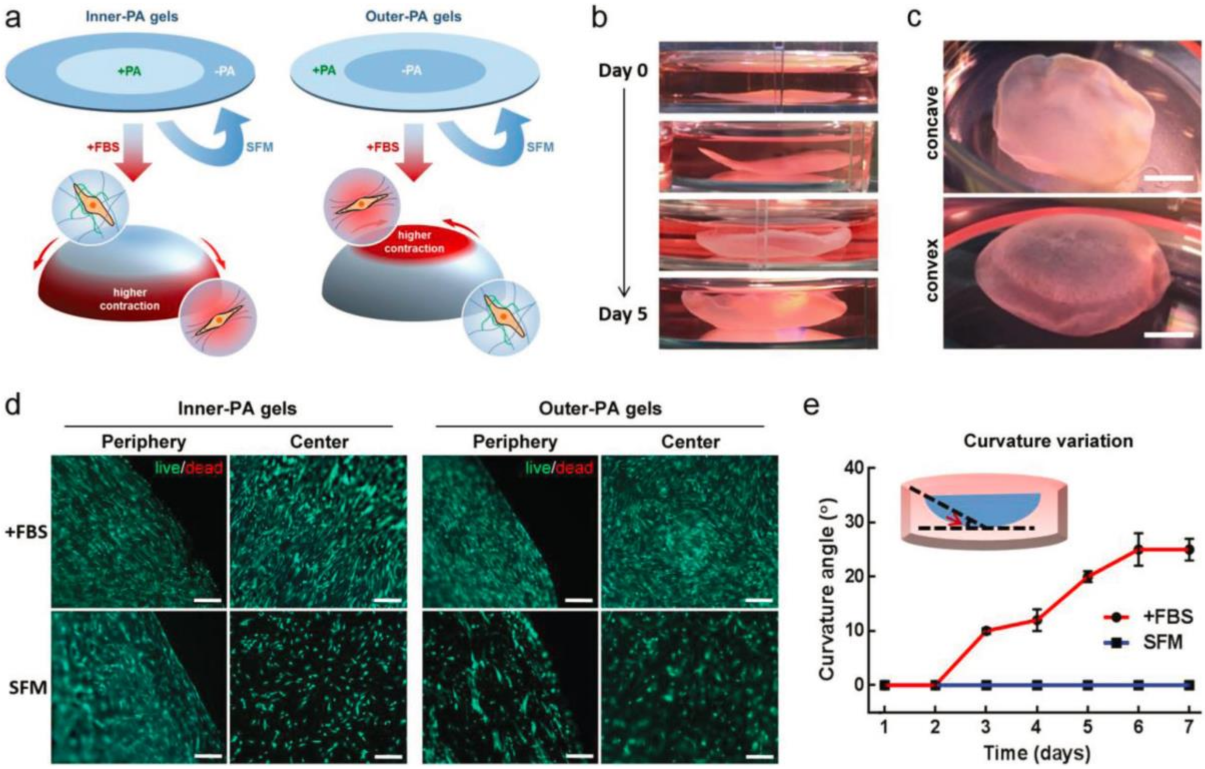


Fully simulating the components and microstructures of soft tissue is a challenge for its functional regeneration. A new aligned hydrogel microfiber scaffold for spinal cord regeneration is constructed with photocrosslinked gelatin methacryloyl (GelMA) and electrospinning technology. The directional porous hydrogel fibrous scaffold consistent with nerve axons is vital to guide cell migration and axon extension. The GelMA hydrogel electrospun fibers soak up water more than six times their weight, with a lower Young's modulus, providing a favorable survival and metabolic environment for neuronal cells. GelMA fibers further demonstrate higher antinestin, anti-Tuj-1, antisynaptophysin, and anti-CD31 gene expression in neural stem cells, neuronal cells, synapses, and vascular endothelial cells, respectively. In contrast, anti-GFAP and anti-CS56 labeled astrocytes and glial scars of GelMA fibers are shown to be present in a lesser extent compared with gelatin fibers. The soft bionic scaffold constructed with electrospun GelMA hydrogel fibers not only facilitates the migration of neural stem cells and induces their differentiation into neuronal cells, but also inhibits the glial scar formation and promotes angiogenesis. Moreover, the scaffold with a high degree of elasticity can resist deformation without the protection of a bony spinal canal. The bioinspired aligned hydrogel microfiber proves to be efficient and versatile in triggering functional regeneration of the spinal cord..

Comment: This paper introduces a microfiber scaffold promoted migration and further differentiation of endogenous neural stem cells into neurons, while forming significantly more newly functional synaptic connections.

4D Corneal Tissue Engineering: Achieving Time-Dependent Tissue Self-Curvature through Localized Control of Cell Actuators

Miotto, M.; Gouveia, R. M.; Ionescu, A. M.; Figueiredo, F.; Hamley, I. W.; Connon, C. J.*;
Adv. Func. Mater **2019**, 1807334

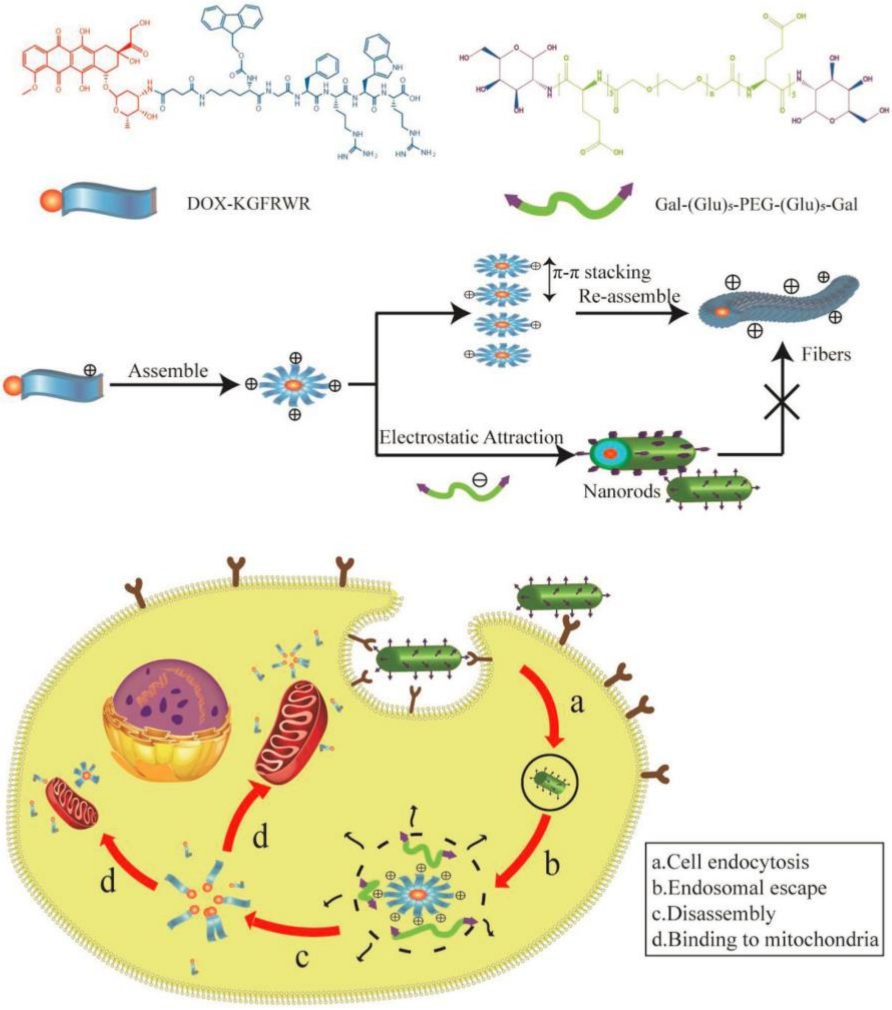


While tissue engineering is widely used to construct complex tridimensional biocompatible structures, researchers are now attempting to extend the technique into the fourth dimension. Such fourth dimension consists in the transformation of 3D materials over time, namely, by changing their shape, composition, and/or function when subjected to specific external stimuli. Herein, producing a 4D biomaterial with an internal mechanism of stimulus, using contractile cells as bio-actuators to change tissue shape and structure, is explored. Specifically, producing cornea-shaped, curved stromal tissue equivalents via the controlled, cell-driven curving of collagen-based hydrogels. This is achieved by modulating the activity of the bio-actuators in delimited regions of the gels using a contraction-inhibiting peptide amphiphile. The self-curved constructs are then characterized in terms of cell and collagen fibril reorganization, gel stiffness, cell phenotype, and the ability to sustain the growth of a corneal epithelium in vitro. Overall, the results show that the structural and mechanical properties of self-curved gels acquired through a 4D engineering method are more similar to those of the native tissue, and represent a significant improvement over planar 3D scaffolds. In this perspective, the study demonstrates the great potential of cell bio-actuators for 4D tissue engineering applications. Cell actuators are used to produce 4D curved corneal stromal tissue equivalents. The control over the contraction of cell actuators via their localized interaction with peptide amphiphiles (PA) in composite collagen-based hydrogels results in the progressive curvature of the constructs over time. Such 4D tissue equivalents show a hierarchical organization and shape resembling the native human corneal stromal tissue.

Comment: Very interesting work. They report using peptide amphiphiles as contraction-inhibiting factor to construct differentiated Young modulus gels after cell culturing. What if the contraction is reversible?

From Nanofibers to Nanorods: Nanostructure of Peptide-Drug Conjugates Regulated by Polypeptide-PEG Derivative and Enhanced Antitumor Effect

Chen, R.; Wang, J.; Qian, C.; Ji, Y.; Zhu, C.; Wu, L.; Li, W.; Bi, X.; Wang, Y.; Cao, G.*; Chen, Z.*; *Adv. Func. Mater* **2019**, *1806058*

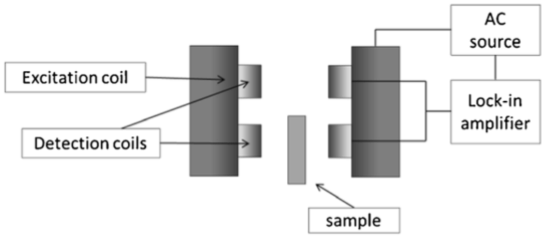


Peptide-drug conjugates (PDCs) are a type of self-assembled prodrug with good potential for drug delivery due to their excellent biocompatibility, high drug loading, and permanent controllable release. However, most PDCs tend to self-assemble into filamentous nanostructures in water and under physiological conditions, making them unsuitable as intravenous formulations due to the entanglement of long fibers and the risk of thrombus. Injected PDCs also face challenges in overcoming the complex physiological environment to reach the target site. To expand their clinical use, it is necessary to control the properties of PDC, including the self-assembled structure and physiological performance, to avoid the above problems. Based on assembly mechanism studies of PDCs, a new method for regulating PDC morphology is developed by controlling intermolecular interactions in the assembly process. This method can alter the final morphology of PDCs from nanofibers to nanorods, and the introduced macromolecules endow the PDC with new characteristics that facilitate stable and high-efficiency access to the target site. An entirely new strategy for regulating peptide-drug conjugates (PDCs) morphology by controlling intermolecular interactions in the assembly process is developed. This method can not only alter the final morphology of PDCs from nanofibers to nanorods, but also endow the PDCs with new characteristics that facilitate stable and high-efficiency access to the target site.

Comment: Co-assembly is nice way to construct functional materials; the authors are rather ingenious.

Magnetic Particle Nanorheology

Roeben, E.; Roeder, L.; Teusch, S.; Effertz, M.; Deiters, U. K.; Schmidt, A. M. *Colloid Polym. Sci.* **2014**, *292*, 2013.



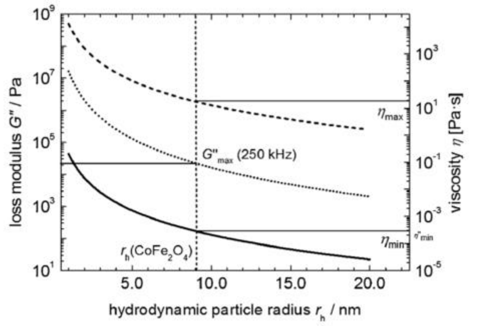
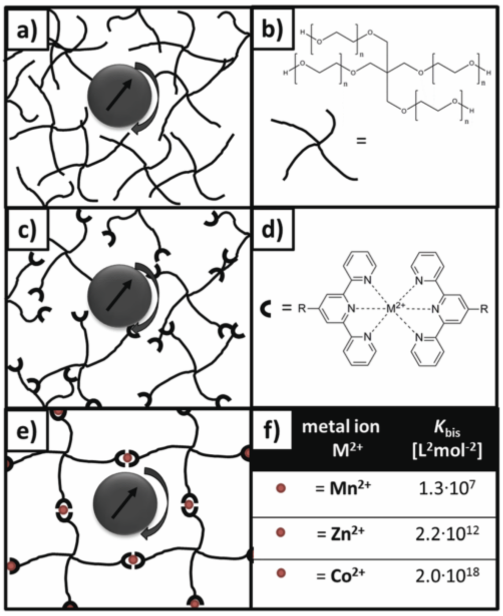


Fig. 2 Detection limits for the magnetic particle nanorheology (1 Hz–250 kHz) vs. particle radius r_h. Minimum viscosity η_{min} (*solid line*), maximum viscosity η_{max} (*dashed line*), maximum loss modulus G''_{max} at 250 kHz (*dotted line*)

We investigate the employment of AC susceptometry as **a novel method to extract frequency- and scale-dependent rheological properties of soft materials**. The approach makes use of the interrelation between the magnetic susceptibility of magnetically blocked tracer particles and the mechanical modulus of the matrix as experienced on the particle scale. We report susceptibility measurements on aqueous solutions of ethylene glycol, triethylene glycol, or poly-(ethylene glycol), using $CoFe_2O_4$ nanoparticles as tracer particles, in the frequency range of 1 Hz–250 kHz. Frequency- dependent rheological properties, including viscosity and loss moduli, of the solutions were obtained by applying an extended Debye relaxation model and a method analogous to the Gemant-DiMarzio-Bishop approach.

Local Dynamics in Supramolecular Polymer Networks Probed by Magnetic Particle Nanorheology

Hess, M.; Roeben, E.; Habicht, A.; Seiffert, S.; Schmidt, A. M.* *Soft Matter* **2019**, *15*, 842.



Transient supramolecular polymer networks are promising candidates as soft self-healing or stimuli-sensitive materials. In this paper, we employ a novel nanorheological approach, magnetic particle nanorheology (MPN), in order to better understand the local dynamic properties of model supramolecular networks from a molecular point of view. Hence, the bond strength between four-arm star-shaped polyethylene glycol (PEG) functionalized at the four extremities with terpyridine ligands is tuned by implementing different metal ions with variable complexation affinities for the ligand. **We show that MNP allows for the evaluation of the strength and connectivity of the polymer networks by the estimation of relaxation times, mesh size, and also the viscoelastic properties of these materials.** These results are compared and complemented to former outcomes on these systems that were obtained by macroscopic analytical methods. A clear dependence between the strength of the metal-ligand complex and the local dynamics of the polymeric network is observed by the nanorheological approach, which is in good agreement with previous predictions related to the complex formation constants.

Comment: Both papers report on “magnetic particle nanorheology” (MPN) and I find the concept intriguing. Probably one of the reasons is because given the dynamic nature of non-covalent interactions, it is usually “wrong” to measure rheology of supramolecular polymers and gels using standard set-ups. Of course, that is not really avoidable, and not really wrong, because the whole formalism necessary is not available. I still want to read the maths presented on the first paper to understand if they account for it or not?