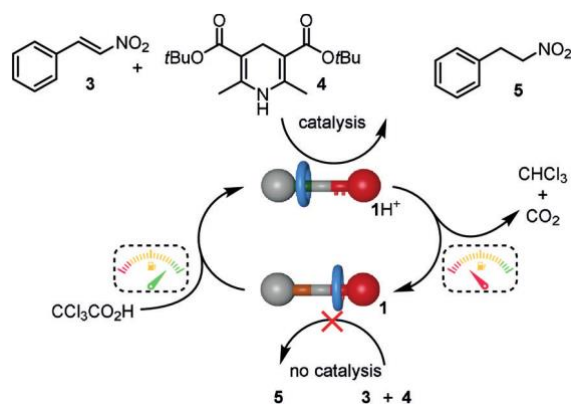


Dissipative Catalysis with a Molecular Machine

Biagini, C.; Fielden, S. D. P.; Leigh, D. A.*; Schaufelberger, F.; Di Stefano, S.; Thomas, D.
[Angew. Chem. Int. Ed. 2019, ASAP.](#)



We report on catalysis by a fuel-induced transient state of a synthetic molecular machine. A [2]rotaxane molecular shuttle containing secondary ammonium/amine and thiourea stations is converted between catalytically inactive and active states by pulses of a chemical fuel (trichloroacetic acid), which is itself decomposed by the machine and/or the presence of additional base. The ON-state of the rotaxane catalyzes the reduction of a nitrostyrene by transfer hydrogenation. By varying the amount of fuel added, the lifetime of the rotaxane ON-state can be regulated and temporal control of catalysis achieved. **The system can be pulsed with chemical fuel several times in succession, with each pulse activating catalysis for a time period determined by the amount of fuel added.** Dissipative catalysis by synthetic molecular machines has implications for the future design of networks that feature communication and signaling between the components.

Comment: The thing is that on the TOC they dared to use “An out-of-equilibrium state of a synthetic molecular machine is used to control catalysis” and I cannot agree with that, certainly not for a rotaxane with two station, which are by definition thermodynamic states. But that is the state of things: even good groups are reduced to have to use catchy words... The paper though is as nice as one would expect.

Moving Towards the Market

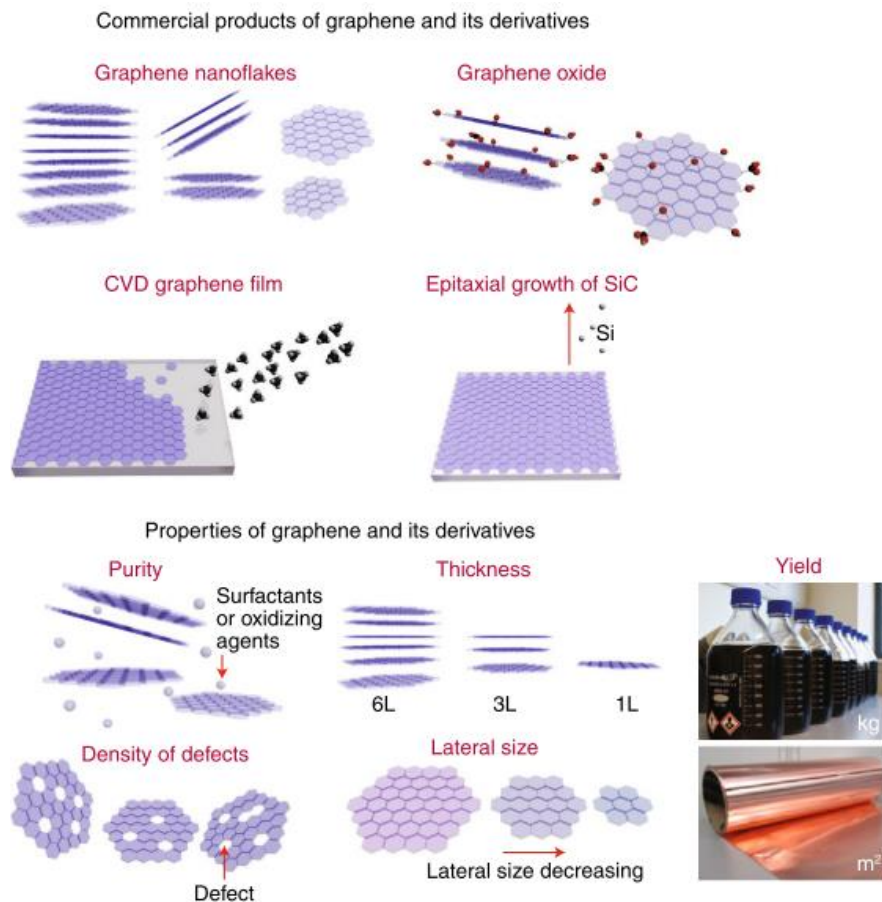
Editorial, [Nat. Mater. 2019, 18 \(6\), 519–519](#)



2D materials face challenges along the road to **commercialization**, with increasing efforts being made in order to **satisfy industrial needs**.

Synthesis Challenges for Graphene Industry

Lin, L.; Peng, H.; Liu, Z. *Nat. Mater.* **2019**, *18* (6), 520–524

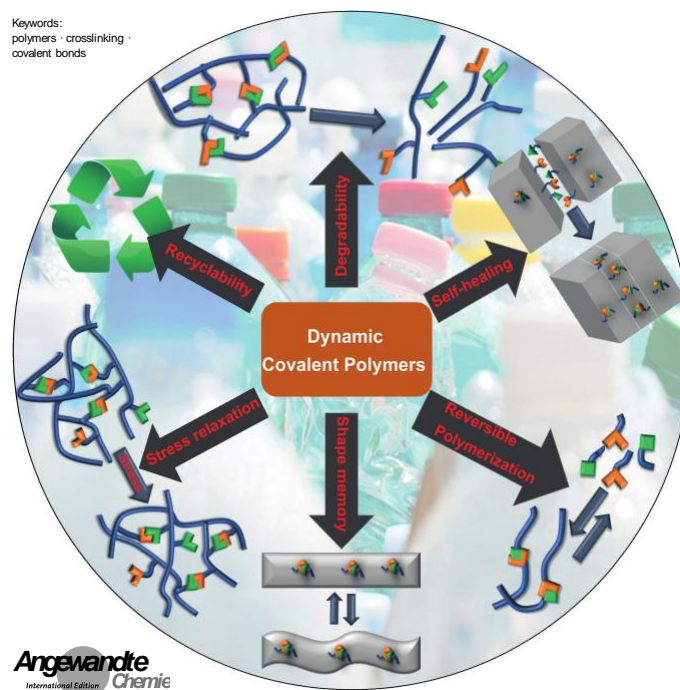


The past few years have witnessed significant **development in graphene research**, yet a number of challenges remain for its **commercialization** and **industrialization**. This Comment discusses relevant issues for **industrial-scale graphene synthesis**, one of the critical aspects for the future graphene industry.

Comment: These two articles focus on the graphene industry and on the different issues concerning the development of industrial-scale synthesis of this material. These papers are particularly interesting insofar as it is necessary for researchers working on fundamental sciences to keep in mind that even if a material possesses the most promising properties, it will remain useless if no scalable synthesis is developed. The example of graphene is all the more striking when we learn that its first uses were in elaboration of fishing rods and golf clubs.

Dynamic Covalent Bonds in Polymeric Materials

Chakma, P.; Konkolewicz, D.* [Angew. Chem. Int. Ed. 2019, ASAP.](#)

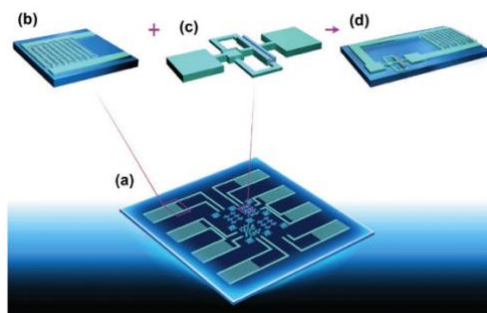


Dynamic covalent bonds (DCBs) have received significant attention over the past decade. These are covalent bonds that are capable of exchanging or switching between several molecules. Particular focus has recently been on utilizing these DCBs in polymeric materials. Introduction of DCBs into a polymer material provides it with powerful properties including self-healing, shape-memory properties, increased toughness, and ability to relax stresses as well as to change from one macromolecular architecture to another. **This Minireview summarizes commonly used powerful DCBs formed by simple, often “click” reactions, and highlights the powerful materials that can result.** Challenges and potential future developments are also discussed.

Comment: Just trying to be useful here: if you missed this mini-review and you happen to work on the polymer project, you probably would want to have a careful read. Also, have you noticed how Angew is pushing again on the reviews?

Integration of Electrochemical Microsupercapacitors with Thin Film Electronics for On-Chip Energy Storage

Hota, M. K.; Jiang, Q.; Wang, Z.; Wang, Z. L.; Salama, K. N.*; Alshareef, H. N.* [Adv. Mater. 2019, 31, 1807450.](#)

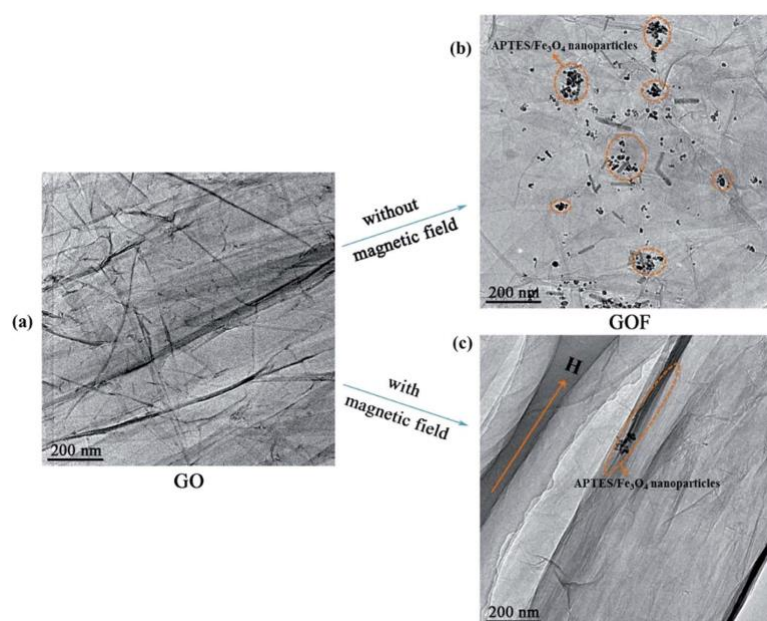


The development of self-powered electronic systems requires integration of on-chip energy-storage units to interface with various types of energy harvesters, which are intermittent by nature. Most studies have involved **on-chip electrochemical microsupercapacitors** that have been interfaced with energy harvesters through bulky Si-based rectifiers that are difficult to integrate. This study demonstrates **transistor-level integration of electrochemical microsupercapacitors** and **thin film transistor rectifiers**. In this approach, the thin film transistors, thin film rectifiers, and electrochemical microsupercapacitors share the same electrode material for all, which allows for a highly integrated electrochemical on-chip storage solution. The thin film rectifiers are shown to be **capable of rectifying AC signal input** from either triboelectric nanogenerators or standard function generators. In addition, electrochemical microsupercapacitors exhibit exceptionally **slow self-discharge rate** ($\approx 18.75 \text{ mV h}^{-1}$) and **sufficient power** to drive various electronic devices. This study opens a new avenue for developing compact on-chip electrochemical micropower units integrated with thin film electronics.

Comment: If you are unexperienced in the field of batteries and capacitors, I would recommend you to read this article, or at least the introduction and the conclusion. This paper is indeed quite complex but remains clear enough to understand the main challenges when it comes to the elaboration of such devices. Although I have to admit that for an organic chemist the results and discussion part is really difficult to follow.

Self-Assembly of Chemically Modified Graphene Sheets in an External Magnetic Field

Tong, M.; Cao, J.; Chen, X.; Zhang, H.; Wu, W.; Ma, H. [RSC Adv. 2019, 9, 19457–19464.](#)



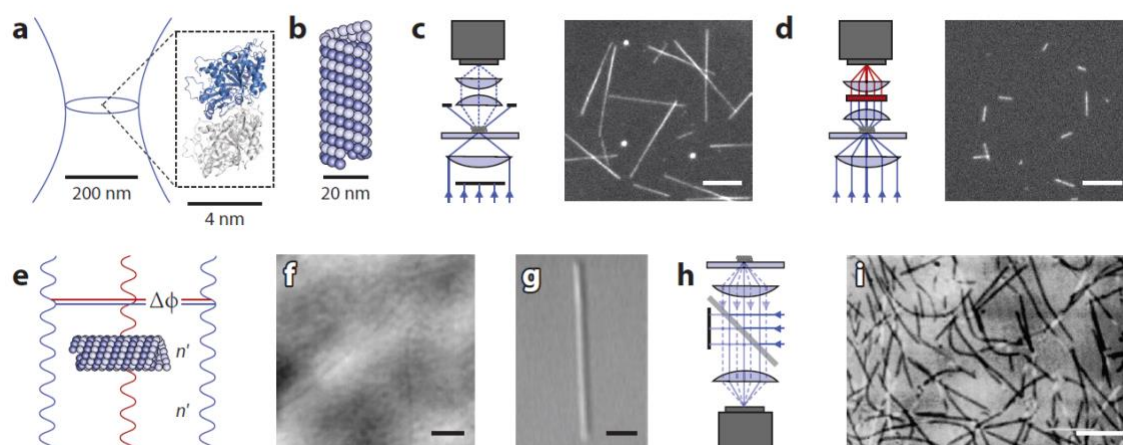
The rapid developments of effective self-assembly technologies indicated that ordered structures could be produced using external field inducement. We designed the alignment of graphene oxide nanosheets grafted with the modified ferroferric oxide by the application of a magnetic field. The results indicated that the morphologies of graphene oxide went through some changes from disordered to semi-ordered in the final and, highly oriented wrinkled structures. The orientation mechanism of graphene oxide demonstrated that the geometric features of the wrinkles were related to the edge stresses and the elastic stiffness of the sheets, magnetic force of magnetic field

to magnetic-particles. The prepared reduced graphene oxide fibers indicated that the sheets with magnetic precipitates underwent shrinkage in the radial direction when an external magnetic field was exerted and the interior sheets aligned along the direction of the magnetic field, which was supported by the proposed theories. It is expected that the research could contribute to the applications of flexible graphene-based materials in preparation and controlling the formation of wrinkles in single layer graphene.

Comment: A nice example in which control over the morphology of the self-assembled structures is achieved by applying an external magnetic field.

Interferometric Scattering Microscopy

Young, G.; Kukura, P. *Annu. Rev. Phys. Chem.* **2019**, *70* (1), 331–352.

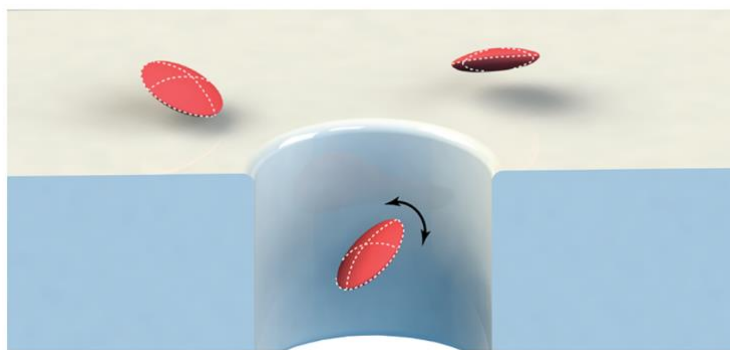


Interferometric scattering microscopy (iSCAT) is an extremely sensitive imaging method based on the efficient detection of light scattered by nanoscopic objects. The ability to, at least in principle, maintain high imaging contrast independent of exposure time or scattering cross section of the object imaged allows for unique applications in single-particle tracking, label-free imaging of nanoscopic (dis)assembly, and quantitative single-molecule characterization. We illustrate these capabilities in areas as diverse as mechanistic studies of motor protein function, viral capsid assembly, and single-molecule mass measurement in solution. We anticipate that iSCAT will become a widely used approach to unravel previously hidden details of biomolecular dynamics and interactions.

Comment: An optical microscopy technique which was for me almost unknown but in the recent times is really growing, especially for its application in biology.

Estimation of Shape, Volume, and Dipole Moment of Individual Proteins Freely Transiting a Synthetic Nanopore

Houghtaling, J.; Ying, C.; Eggenberger, O. M.; Fennouri, A.; Nandivada, S.; Acharjee, M.; Li, J.; Hall, A. R.; Mayer, M.* *ACS Nano* **2019**, *13*, 5231–5242.

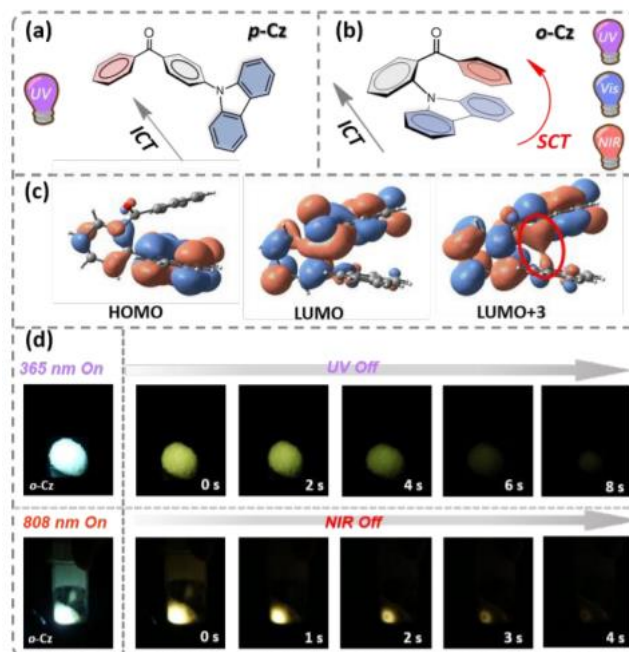


This paper demonstrates that high-bandwidth current recordings in combination with low-noise silicon nitride nanopores make it possible to **determine the molecular volume, approximate shape, and dipole moment of single native proteins in solution** without the need for labeling, tethering, or other chemical modifications of these proteins. The analysis is based on current modulations caused by the translation and rotation of single proteins **through a uniform electric field inside of a nanopore**. We applied this technique to nine proteins and show that the measured protein parameters agree well with reference values but only if the nanopore walls were coated with a nonstick fluid lipid bilayer. One potential challenge with this approach is that an untethered protein is able to diffuse laterally while transiting a nanopore, which generates increasingly asymmetric disruptions in the electric field as it approaches the nanopore walls. These “off-axis” effects add an additional noise-like element to the electrical recordings, which can be exacerbated by nonspecific interactions with pore walls that are not coated by a fluid lipid bilayer. We performed finite element simulations to quantify the influence of these effects on subsequent analyses. Examining the size, approximate shape, and dipole moment of unperturbed, native proteins in aqueous solution on a single-molecule level in real time while they translocate through a nanopore may enable applications such as **identifying or characterizing proteins in a mixture**, or **monitoring the assembly or disassembly** of transient protein complexes based on their shape, volume, or dipole moment.

Comment: Three issues in determining physical properties of proteins are circumvented in this work: First, the detection of diffusion events through nanopores can be tedious due to the low signal-to-noise ratio. The authors designed an experimental setup **increasing the sensitivity of the detection**. Second, proteins are often chemically modified to ensure a proper detection. In their system, **the authors do not need to functionalize their macromolecules, ensuring the detection of the native configuration of the proteins**. Third, the diffusion process of proteins has to be slowed down for detection. The authors achieved this by functionalizing the nanopore with a **lipid bilayer that ensures the molecules can be properly detected**. Overall, it seems **they have developed an improved technique that could greatly facilitate the characterization of proteins**.

Two-Photon-Excited Ultralong Organic Room Temperature Phosphorescence by Operating Dual-Channel Triplet Harvesting

Mao, Z. N.; Yang, Z.; Xu, C.; X, Z.; Jiang, L.; Gu, F. L.; Zhao, J.*; Zhang, Y.; Aldred, M. P.; Chi, Z.* [Chem. Sci. 2019, ASAP.](#)



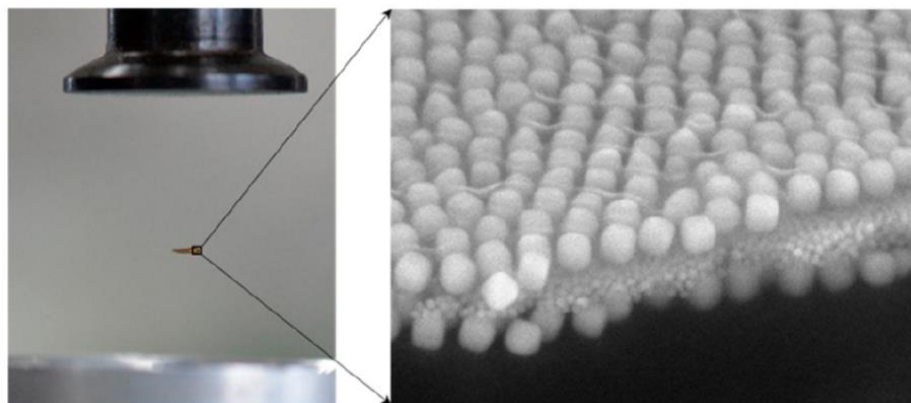
Due to inefficient molecular design strategy, two-photon-excited ultralong organic room temperature phosphorescence (TPUOP) have not yet been reported in single-component materials. Herein, we present an innovative design method by operating dual-channel triplet harvesting to obtain the first bright TPUOP molecule with a lifetime of 0.84 s and quantum efficiency of 16.6%. In compound *o*-Cz the donor and acceptor units are connected at the ortho position of benzophenone, showing intramolecular space charge transfer. Therefore, the two-photon absorption ability is improved due to the enhanced charge transfer character. Moreover, the small energy gap boosts dual-channel triplet harvesting via ultralong thermally activated delayed fluorescence and H-aggregation phosphorescence, which suppresses the long-lived triplet concentration quenching. Through two-photon absorption, a near-infrared laser (808 nm) is able to trigger the obvious ultralong emission under ambient conditions. This research work provides valuable guidance for designing near-infrared-excited ultralong organic room temperature phosphorescence materials.

Comment: Unlike fluorescence, phosphorescence shows longer lifetimes from microseconds to milliseconds. This article demonstrates ultralong (seconds timescale) organic, room temperature phosphorescence in a single component that could be excited by a two-photon process.

A General Approach to Free-Standing Nanoassemblies via Acoustic Levitation Self-Assembly

Shi, Q.; Di, W.; Dong, D.; Yap, L. W.; Li, L.; Zang, D.*; Cheng, W.* [ACS Nano 2019, 13, 5243–5250.](#)

Acoustic levitation self-assembly of free-standing 2D nanoassemblies

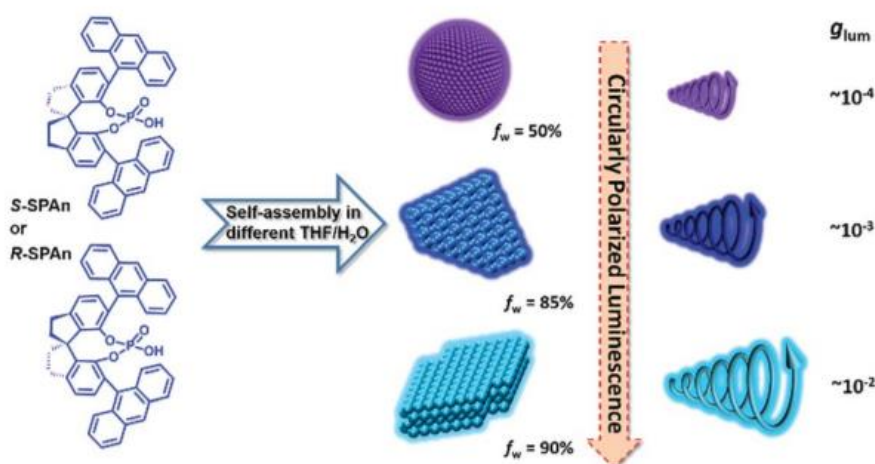


Droplets suspended by acoustic levitation provide genuine substrate-free environments for understanding unconventional fluid dynamics, evaporation kinetics, and chemical reactions by circumventing solid surface and boundary effects. Using a fully levitated air–water interface by **acoustic levitation** in conjunction with drying-mediated nanoparticle self-assembly, here, we demonstrate a general approach to fabricating **free-standing nanoassemblies**, which can totally avoid solid surface effects during the entire process. This strategy has no limitation for the sizes or shapes of constituent metallic nanoparticle building blocks and can also be applied to fabricate free-standing bilayered and trilayered nanoassemblies or even three-dimensional hollow nanoassemblies. We believe that our strategy may be further extended to quantum dots, magnetic particles, colloids, *etc.* Hence, it may lead to a myriad of homogeneous or heterogeneous free-standing nanoassemblies with programmable functionalities.

Comment: First, **acoustic levitation looks like magic** and that is why science is amazing. In this case, using acoustic levitation for self-assemblies **avoids interfacial interactions** with the substrate. As the authors state, this technique can, in principle, be applied to any nanoobject.

Boosting the circularly polarized luminescence of small organic molecules via multi-dimensional morphology control

Ma, K.; Chen, W.; Jiao, T. *; Jin, X.; Sang, Y.; Yang, D.; Zhou, J.; Liu, M.*; Duan, P.* [Chem. Sci. 2019, ASAP](#)

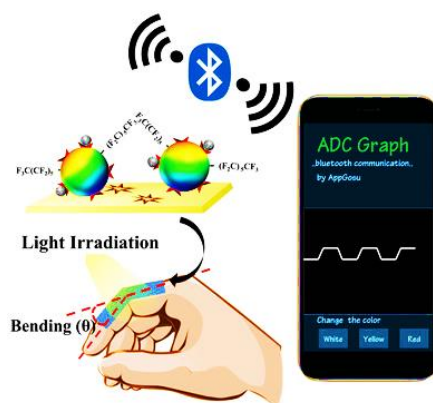


Achieving a higher dissymmetry factor is a crucial issue in developing circularly polarized luminescence (CPL) materials. Here, by tailoring the solvent composition and the morphology of the same chiral emissive small molecules (R- or S-SPAN), circularly polarized emission with a boosted dissymmetry factor (two orders) was realized. It was found that by regulating the water fraction in the mixed THF/H₂O, we were able to achieve kinetic control over association of chiral emissive R- or S-SPAN into various nanostructures with 0D nanospheres, 2D nanoflakes and 3D stacked nanoflakes. These nanostructures are all CPL active. Remarkably, the dissymmetry factors of the nanostructures were significantly enhanced compared to those of the molecules and further boosted in different morphologies, from $\sim 10^4$ (0D nanospheres) to 10^3 (2D flake) to $\sim 10^2$ (3D nanoflakes). The enlarged g_{lum} value could be assigned to a good packing induced strong luminescence of an excimer. This strategy provides an efficient way to fabricate higher dissymmetry factor CPL organic nanomaterials by only changing the supramolecular architectures while using the same chiral small molecules.

Comment: This paper is similar to Flavio's project, they also could control the intensity of CPL by modulating the morphology of self-assemblies. We should keep in mind that the solvent also could affect the supramolecular structure.

Light-Induced Swelling-Responsive Conductive, Adhesive, and Stretchable Wireless Film Hydrogel as Electronic Artificial Skin

Ryplida, B.; Lee, K.; In, I.;* Park, S. Y.* *Adv. Funct. Mater.* **2019**, 1903209



Light-induced wireless soft electronic skin hydrogels with excellent mechanical and electronic properties are important for several applications, such as soft robotics and intelligent wearable devices. Precise control of reversible stretchability and capacitive properties depending on intermolecular interaction and surface characteristics remains a challenge. Here, a thin-film hydrogel is designed based on titanium oxide (TiO₂) polydopamine–perfluorosilica carbon dot-conjugated chitosan–polyvinyl alcohol-loaded tannic acid with controllable hydrophobic–hydrophilic transition in the presence of UV–vis light irradiation. The shifting of surface wettability from hydrophobic to hydrophilic by irradiation affects thin-film water permeability and swelling ratio. This allows the penetration of water into the matrix to change its mechanical strength, electronic properties, and adhesive behaviour. Specifically, the hydrogel displays mechanical strain as high as 278% in response to light stimuli and demonstrates the ability to regain its initial state determining the elasticity of the fabricated material. Moreover, the thin-film hydrogel shows an increase in conductivity to 1.096×10^{-3} and 1.026×10^{-3} S cm⁻¹ when irradiated with UV and visible light, respectively. **The hydrogel exhibits capacitive reversibility that follows finger motion**

which can be identified directly or remotely using wireless connection, indicative of its possible applications as an artificial electronic skin.

Comment: Soft materials are influencing more and more modern technologies. This time, a controlled hydrophobic-hydrophilic adhesive film hydrogel was obtained as a soft and conductive skin in the presence of UV-Vis light irradiation, which also affects the swelling ratio of the material.

Elementary Women

Murray, C. [Nat. Chem. 2019, 11, 602-603.](#)

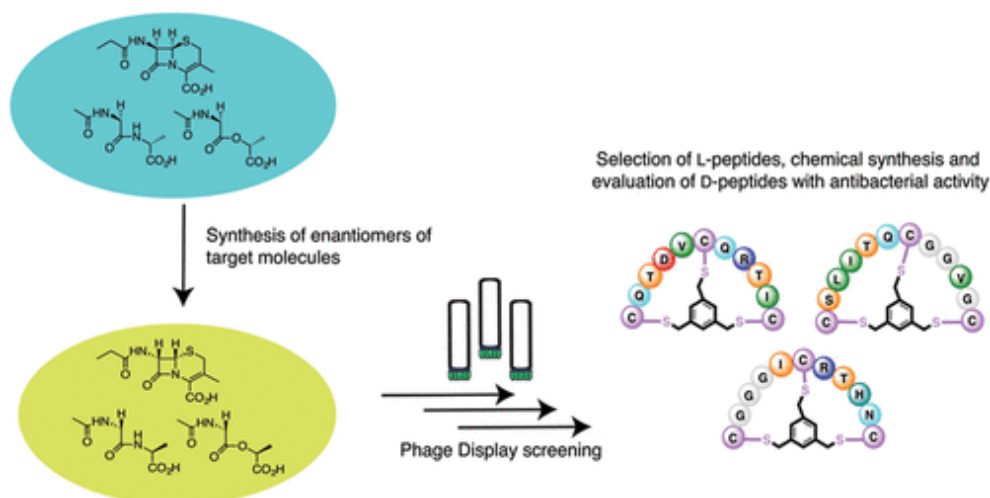


The contributions of women to the development of the periodic table have long been overlooked.

Comment: In this meeting report, the author highlight the most important topics that were mentioned in the international symposium “Setting their table: Women and the periodic table of elements”. For instance, the contribution of other women (besides Marie Skłodowska-Curie) to the discovery of new elements for the periodic table and the lack of visibility of women in science, among other topics. **Interesting!**

Discovery of Peptide Antibiotics Composed of D-Amino Acids

Adaligil, E.; Patil, K.; Rodenstein, M.; Kumar, K.* [ACS Chem. Biol. 2019, ASAP](#)

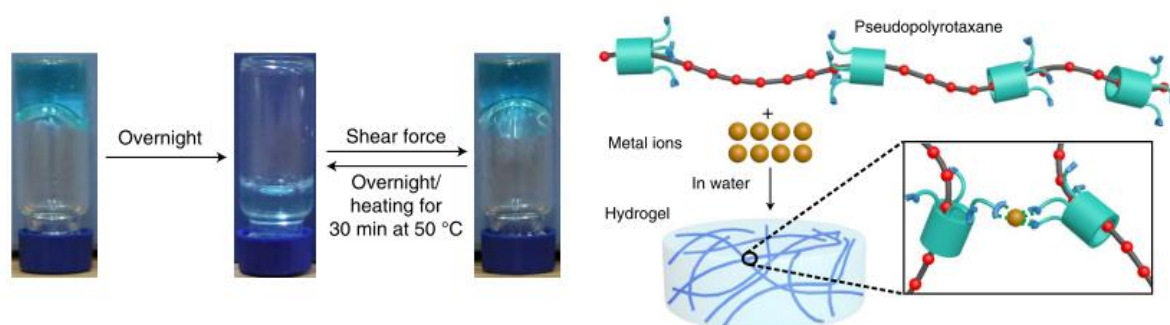


A paucity of viable programs and pipelines for the discovery of new antibiotics poses a significant public health threat. The emergence of resistant strains against vancomycin is particularly dangerous in hospital settings. Here, we report the design of enantiomeric targets based on bacterial cell wall biosynthesis precursors that allow for selection and identification of short linear, cyclic and bicyclic peptides that are composed of d-amino acids. These compounds are active against *Staphylococcus aureus*, Methicillin-resistant *S. aureus*, and vancomycin-resistant *Enterococci* that possess moderately high antibacterial activity and furthermore display no toxicity to both human red blood cells and mammalian cells at these concentrations. This ‘mirror image phage display’ approach yielded templates that can serve as scaffolds for further improvements in activity-based structural modifications. This strategy has the potential to provide a new class of antimicrobials that are metabolically stable and have the promise for oral delivery. **The use of this platform combined with traditional medicinal chemistry approaches could rapidly yield large numbers of new therapeutic lead compounds.**

Comment: An article that could be interesting for people involved in peptide chemistry. The main topic of this paper fits in the field of medicinal chemistry and show the relevance of peptides in the development of new antibiotics.

Shear-Induced Assembly of a Transient Yet Highly Stretchable Hydrogel Based on Pseudopolyrotaxanes

Ke, H.; Yang, L. P.; Xie, M.; Chen, Z.; Yao, H.; Jiang, W.* [*Nat. Chem.* **2019**, *11* \(5\), 470–477.](#)

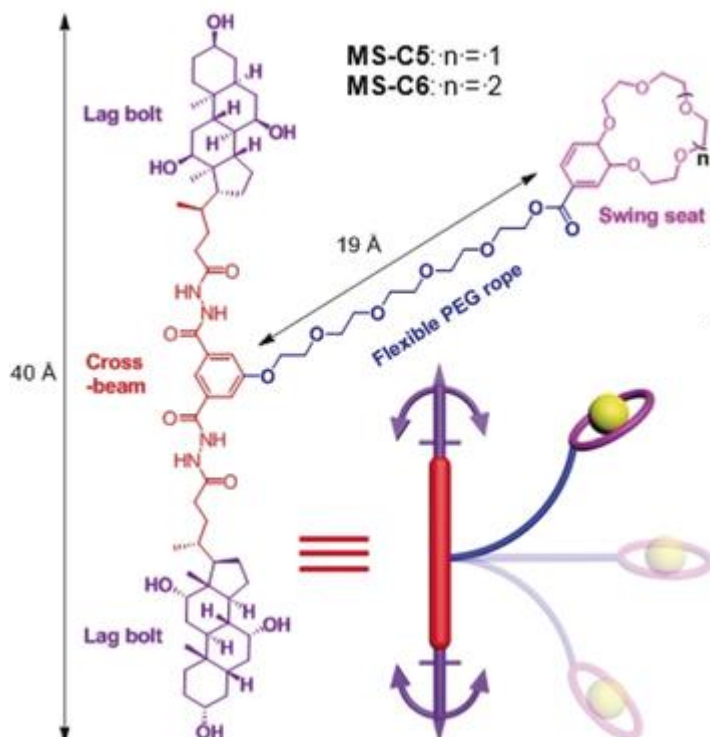


Dissipative self-assembly is common in biological systems, where it serves to maintain a far-from-equilibrium functional state through fuel consumption. Synthetic dissipative systems have been prepared that can mimic some of the properties of biological systems, but they often show poor mechanical performance. Here, we report a shear-induced transient hydrogel that is highly stretchable. The system is constructed by adding Cu(ii) into the aqueous solution of a pseudopolyrotaxane, which is itself formed by threading molecular tubes on polyethylene glycol chains. Vigorous shaking transforms the solution into a gel, which gradually relaxes back to the sol state over time. This cycle can be repeated at least five times. A mechanism is proposed that relies on a shear-induced transition from intrachain to interchain coordination and subsequent thermal relaxation. The far-from-equilibrium hydrogel is highly stretchable, which is probably due to ‘frictional’ sliding of the molecular tubes on the polyethylene glycol chains. On shaking, the hydrogel undergoes fast self-healing.

Comment: An example of dissipative self-assembly using shear force as the fuel, with some interesting host-guest chemistry and decent elasticity.

Molecular Swings as Extremely Active Ion Transporters

Ren, C.; Chen, F.; Ye, R.; Ong, Y. S.; Lu, H.; Lee, S. S.; Ying, J. Y.; Zeng, H.* [Angew. Chemie - Int. Ed.](#) **2019**, *ASAP*

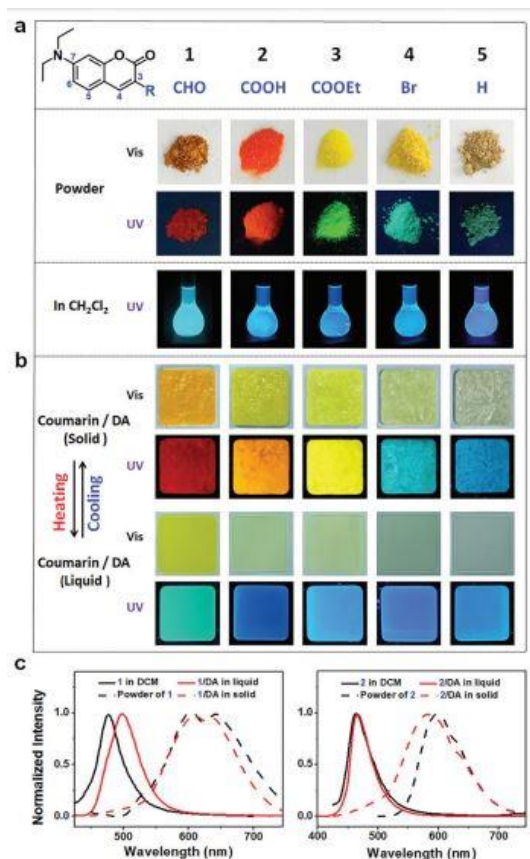


Ions get transported across membrane mostly via carrier or channel mechanisms. We report herein a unique class of molecular machine-inspired membrane transporters, termed molecular swings that utilize a previously unexplored swing mechanism for promoting ion transport in a highly efficient manner. In particular, the molecular swing, which carries a 15-crown-5 unit as the ion-binding and transporting unit, exhibits extremely high ion transport activities with EC_{50} values of 46 nM (a channel:lipid molar ratio of 1:4800 or 0.021 mol% relative to lipid) and 110 nM for K^+ and Na^+ ions, respectively. Remarkably, such ion transport activities remain high in cholesterol-rich environment, with EC_{50} values of 130 (0.045 mol% relative to lipid/cholesterol) and 326 nM, respectively, for K^+ and Na^+ ions.

Comment: An effective use of a molecular machine as an ion transporter, with some biological studies showing promising anti-cancer activities for diseases that require ion transport regulation.

Simple and General Platform for Highly Adjustable Thermochromic Fluorescent Materials and Multi-feasible Applications

Du, J.; Sheng, L.; Chen, Q.; Xu, Y.; Li, W.; Wang, X.; S. X. A.* [Mater Horiz.](#) **2019**, *ASAP*



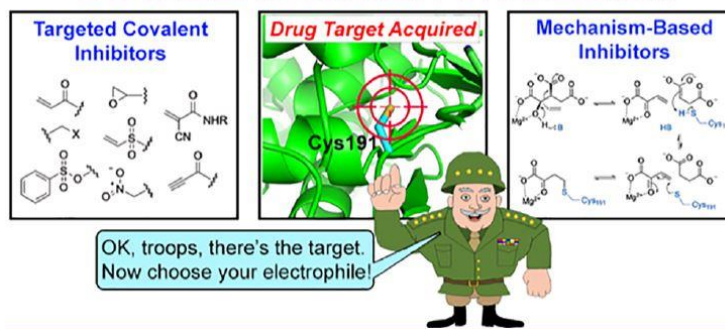
Even though numerous thermochromic fluorescent materials (TFMs) have been reported, effective and universal strategies for the development of ideal TFMs with simple preparation, low cost, excellent performance and practicability are still urgently required. Herein, we report a simple and general platform for such TFMs via taking biomimetic lipid like fatty acids (FAs) as an effective matrix which is applicable to abundant simple fluorophores. Change of crystallinity of FAs induced by phase transition regulates the reversible interconversion between non-dispersion and dispersion states of fluorescent dyes (e.g., coumarins), thus leading to obvious fluorescence (FL) change of the TFMs based on both. The reaction mechanism was proved in detail by FL spectra, XRD and SEM techniques. **The substituent effect of coumarins and the nature of FAs play important roles in adjusting the properties of the TFMs,** such as FL colour and responsive temperature. Additionally, their multiple feasible potential applications (i.e., in situ thermometers, thermal response FL papers, FL colour change crayon, anti-counterfeiting and encryption, erasable or long-preservative thermal printing) with selective multi-mode (i.e., groove-fill, writable pen, loading on paper substrate) were developed. These TFMs with the merit of easy preparation, low cost, obvious colour change (ca. 100 nm shifts), fast response speed, good reversibility and high adjustability are very close to industrial application requirements. The design and preparation principles from this work should facilitate the development of other novel stimuli-responsive fluorescent materials.

Comment: It is always an interesting topic: the development of different multi-stimulated fluorescent materials. Here is the introduction for thermochromic fluorescent materials.

New Electrophiles and Strategies for Mechanism-Based and Targeted Covalent Inhibitor Design

Ray, S.; Murkin, A. S.* [Biochem. 2019](#)

COVALENT INHIBITOR DESIGN



Covalent inhibitors are experiencing a growing resurgence in drug design and are an increasingly useful tool in molecular biology. The ability to attach inhibitors to their targets by a covalent linkage offers pharmacodynamic and pharmacokinetic advantages, but this can also be a liability if undesired off-target reactions are not mitigated. The discovery of new electrophilic groups that react selectively with specific amino acid residues is therefore highly desirable in the design of targeted covalent inhibitors (TCIs). Additionally, the ability to control the reactivity through exploitation of the target enzyme's machinery, as in mechanism-based inhibitors (MBIs), greatly benefits from the discovery of new strategies. This Perspective showcases recent advances in electrophile development and their application in TCIs and MBIs, exhibiting high selectivity for their targets.

Comment: The interaction between inhibitors and the intended protein targets can be divided into non-covalent and covalent interaction. So, the investigation of new electrophilic groups which specifically bind with different amino acids is highly desirable in the design of targeted covalent inhibitors.