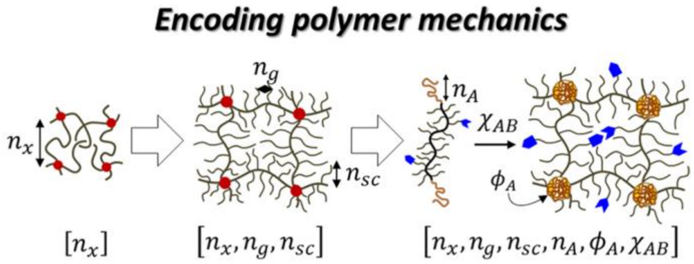
Architectural Code for Rubber Elasticity: From Supersoft to Superfirm Materials

Sheiko, S. S.;* Dobrynin, A. V.* *Macromolecules* **2019**, *52*, 7531−7546

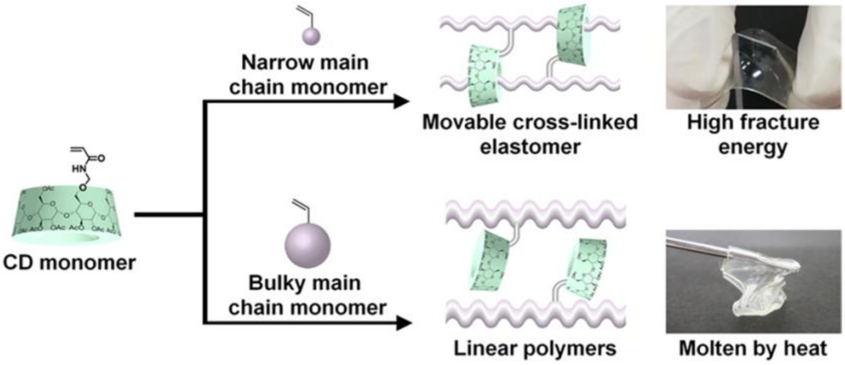


The current approach to regulating mechanical properties of elastomeric materials is predominately based on the exploratory mixing of different polymers, solvents, and fillers -- which is both inflexible in application and imprecise in property control. Here we overview a new materials design approach that harnesses well-defined molecular codes of independently controlled architectural parameters to program grand variation of mechanical “phenotypes”. This design-by architecture approach generates a set of universal correlations between the molecular architecture and the physical behavior of elastomers. In turn, this will lead to novel solvent-free materials that closely mimic the mechanical behavior of biological tissues, ranging from soft fat tissue to firm skin, and fundamentally change high-impact technologies such as soft robotics, wearable electronics, and biomedical devices.

Comment: A innovative way of designing polymers: By tuning simple physical parameters of bottle brush polymers, the authors achieved to control the mechanical properties of their material. It provided another additional tool to the physico-chemists for the design of smart materials.

Supramolecular Elastomers with Movable Cross-Linkers Showing High Fracture Energy Based on Stress Dispersion

Ikura, R.; Park, J.; Osaki, M.; Yamaguchi, H.; Harada, A.* and Takashima Y.* *Macromolecules* **2019**, *52*, 6953−6962



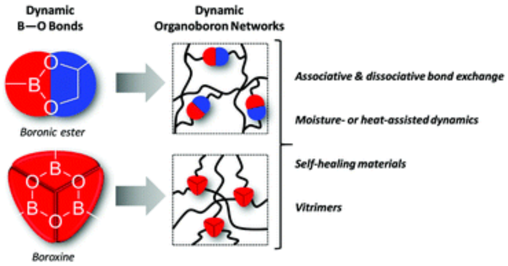
Highly flexible and tough elastomers were obtained from the bulk copolymerization of a peracetylated cyclodextrin (CD) monomer and small alkyl acrylate main chain monomers without a guest monomer. The main chains penetrated the cavity of the CD units, and the CD units on the polymer chain acted as movable cross-linking points in the obtained elastomer. In contrast, the copolymerization using a bulky main chain monomer with bulky side groups gave linear polymers.

The CD units with the bulky main chain polymer cannot serve as movable cross-linking points. Introducing movable cross-linking into poly(ethyl acrylate) resulted in a higher fracture energy comparable to that of conventional rubbers because of the stress-dispersion properties related to the sliding motion of the movable cross-linking points. The movable cross-linkers disperse applied external stresses more effectively than an elastomer with reversible cross-linking at a high Young's modulus (150 MPa). Movable cross-linking can be introduced to enhance the fracture energy of polymeric materials.

Comment: I really like this novel crosslinking method. It is a combination of entanglement and physical crosslinking, like daisy chains in a melt. It is as simple to set up as polyacrylates and enhances their mechanical properties.

Bulk Network Polymers with Dynamic B–O Bonds: Healable and Reprocessable Materials

Bapat, A. P.*; Sumerlin, B. S.*; Sutti, A.* *Mater. Horizons* **2019**, Advanced article.

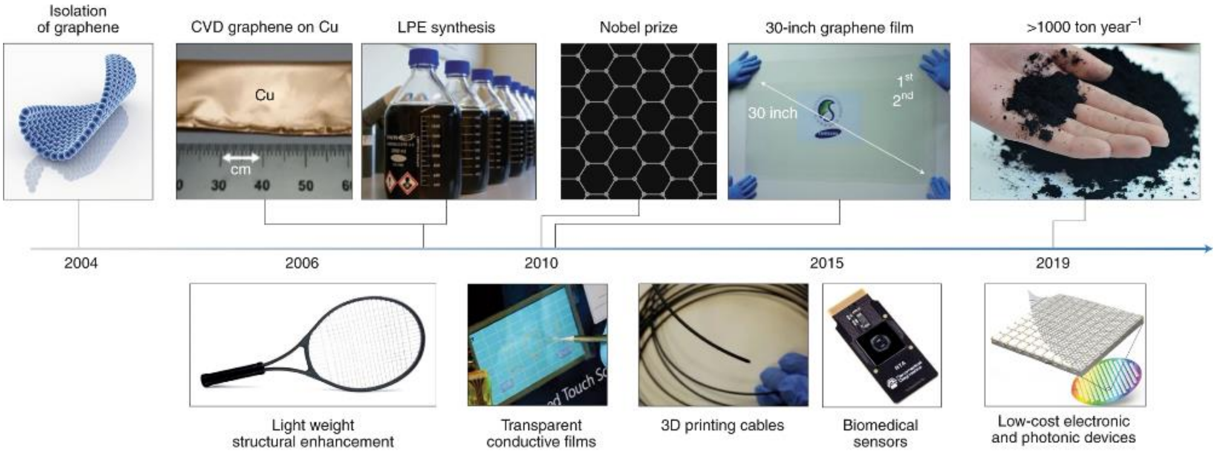


The need to minimize the amount of polymeric waste entering landfills and oceans has led to several research avenues in the field of polymer science. Particularly, the development of **intrinsically self-healing** and **reprocessable thermoset polymers** containing **dynamic crosslinks** has garnered significant interest in the recent years. **Reversible B–O bonds** in certain orgonoboron compounds have shown great versatility and promise as dynamic crosslinks for the design of self-healing and reprocessable bulk polymer networks. This **review** provides an **overview of the chemistry of organoboron species with dynamic B–O bonds** amenable to the design of healable/reprocessable thermosets. Recent developments in this fairly young and interesting research topic are highlighted, along with a critical commentary on the scope and future challenges in designing robust dynamic materials with reversible B–O bonds.

Comment: This review is perfectly complementary to the presentation from our last group meeting. The main challenges are well addressed, as are the different strategies developed so far and their intrinsic limitations which are all well described. The authors managed to keep the discussion understandable even to a non-polymer chemist.

Path towards Graphene Commercialization from Lab to Market

Kong, W.; Kum, H.; Bae, S.-H.; Shim, J.; Kim, H.; Kong, L.; Meng, Y.; Wang, K.; Kim, C.; Kim, J.* *Nat. Nanotechnol.* **2019**, *14*, 927–938.

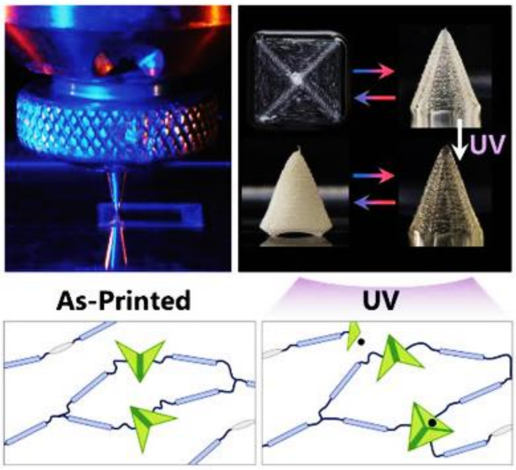


The ground-breaking demonstration of the electric field effect in graphene reported more than a decade ago prompted the strong push towards the commercialization of graphene as evidenced by a wealth of graphene research, patents and applications. **Graphene flake production** capability has reached **thousands of tonnes per year**, while **continuous graphene sheets of tens of metres in length** have become available. Various graphene technologies developed in laboratories have now transformed into commercial products, with the very first demonstrations in sports goods, automotive coatings, conductive inks and touch screens, to name a few. Although challenges related to quality control in graphene materials remain to be addressed, the advancement in the understandings of graphene will propel the commercial success of graphene as a compelling technology. **This Review discusses the progress towards commercialization of graphene** for the past decade and future perspectives.

Comment: This review allows us to have an insight to all the challenges that need to be addressed when a novel material, even one with such amazing properties as graphene, tries to find a place in industry. I find this article useful and well written. **I definitely recommend reading it.**

3D Printable and Reconfigurable Liquid Crystal Elastomers with Light-Induced Shape Memory via Dynamic Bond Exchange

Davidson, E; Kotikian, A.; Li, S.; Aizenberg, J.; Lewis, J.* *Adv. Mater*. **2019**, ASAP

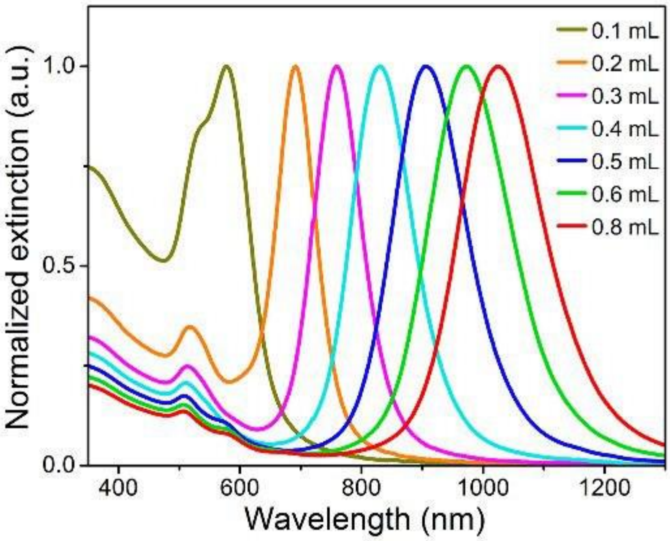


3D printable and reconfigurable liquid crystal elastomers (LCEs) that reversibly shape-morph when cycled above and below their nematic-to-isotropic transition temperature (T_{NI}) are created, whose actuated shape can be locked-in via high-temperature UV exposure. By synthesizing LCE-based inks with light-triggerable dynamic bonds, printing can be harnessed to locally program their director alignment and UV light can be used to enable controlled network reconfiguration without requiring an imposed mechanical field. Using this integrated approach, 3D LCEs are constructed in both monolithic and heterogenous layouts that exhibit complex shape changes, and whose transformed shapes could be locked-in on demand.

Comment: The authors are able to design and synthesize a liquid crystal elastomer whose shape can be modified by heating and cooling it, and it could also be locked in by dynamic covalent bond exchange due to UV light exposure. The degree of lock-in is controlled by the UV exposure time, so full lock-in was achieved after 3 min. Also, the relevance of using allyl dithiol due to the efficient bond exchange capacity in the presence of radicals, and ethylenedioxydiethanethiol to diminish the nematic-to-isotropic transition temperature and avoiding crystallization at room temperature is mentioned.

High-yield synthesis of monodisperse gold nanorod with tunable plasmon wavelength using 3-aminophenol as the reducing agent

Wu, Z. *; Liang, Y.; Cao, L.; Guo, Q. ; Jiang, S. ; Mao, F.; Sheng, J.; Xiao, Q.* *Nanoscale* **2019**, ASAP.

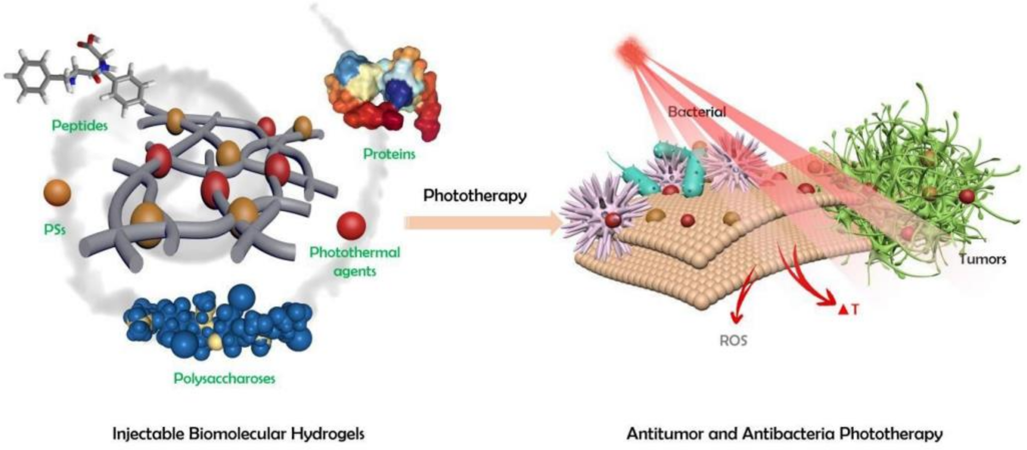


Facile synthesis of high quality gold nanorods (AuNRs) with tunable size is of great value for application of AuNR in various fields as well as study on growth mechanism of such anisotropic nanostructure. However, limitations usually exist in a specific synthesis protocol. In this work, using 3-aminophenol as the reducing agent, we present an AuNR synthesis strategy with an excellent comprehensive performance, which includes an exceptional monodispersity, an AuNR shape purity of around 99%, a conversion ratio of gold precursor of about 91%, and an easily tuned longitudinal surface plasmon resonance wavelength ranging from 580 to 1050 nm. Studies on impacts of the experimental parameters including silver ions, gold seeds, reducing agent, and cetyltrimethylammonium bromide (CTAB) revealed a profound recognition of the significant effect of the reductive atmosphere, in synergy with other parameters, on directing the growth and structural evolution of the gold seeds, thus deeply affecting the size, shape yield, monodispersity, and morphology of the final structure. These results could be immensely useful for the application and the growth mechanism revelation of AuNR.

Comment: This paper described a high-yield synthesis of gold nanorods. They could easily get the rods with tuneable longitudinal ratio by adjusting the amount sliver ions.

Self-Assembled Injectable Biomolecular Hydrogels towards Phototherapy

Xing, R.; Liu, Y.; Zhou, Q.; Yan, X.* *Nanoscale* **2019**, DOI: 10.1039/C9NR06266A.

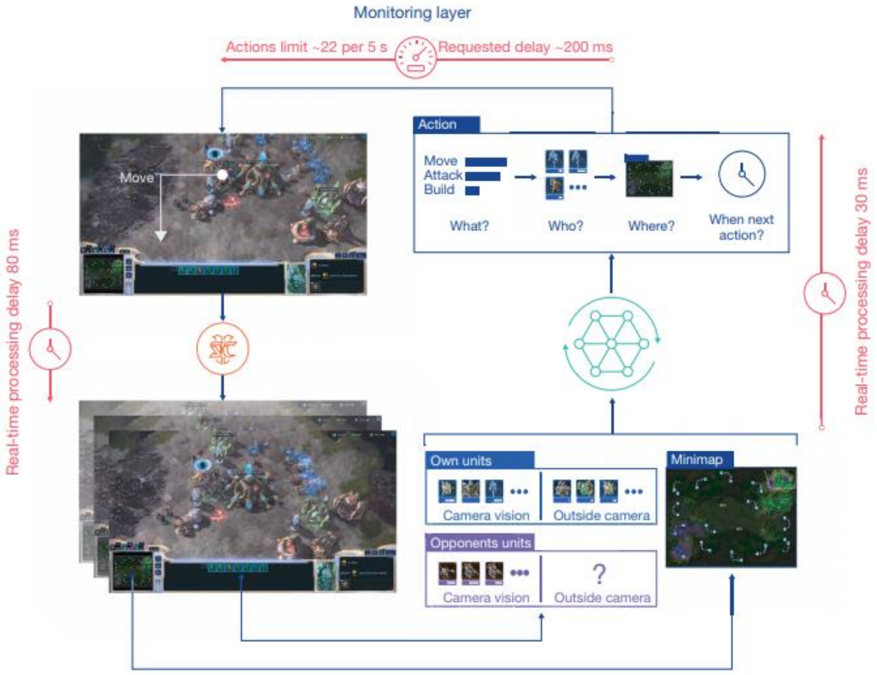


Biomolecular hydrogels assembled from biomolecules, such as proteins, peptides, and polysaccharides, are promising candidates for facilitating biomedical applications due to their advantages of high biocompatibility, adjustable mechanical properties, functional diversity, and good degradability. This review focuses on current progress in the field of supramolecular injectable biomolecular hydrogels and their applications for antitumor photodynamic therapy (PDT), photothermal therapy (PTT), combined PDT&PTT, as well as antibacterial phototherapy with emphasis on the biomolecular hydrogelators, injectable behaviors, phototherapeutic functions, and the remaining challenges. We hope that this review can provide useful inspiration for the construction and biological applications of novel photo-functional hydrogels as well as phototherapies.

Comment: Biomolecules-based supramolecular self-assemblies are attracting increasing attention due to their special biocompatibility. The paper describes several examples in which the biomaterials are used for phototherapy.

Grandmaster Level in StarCraft II Using Multi-Agent Reinforcement Learning

Vinyals, O.*; Babuschkin, I.; Czarnecki, W. M.; Mathieu, M; Dudzik, A.; Chung, J.; Choi, D. H.; Powell, R.; Ewalds, T.; Georgiev, P.; Oh, J.; (…) Apps, C.; Silver D.* *Nature* **2019** *(ASAP).*

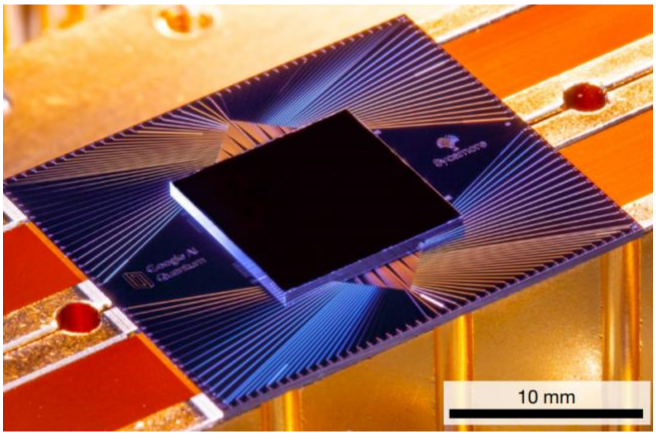


Many real-world applications require artificial agents to compete and coordinate with other agents in complex environments. As a stepping stone to this goal, the domain of StarCraft has emerged as an important challenge for artificial intelligence research, owing to its iconic and enduring status among the most difficult professional esports and its relevance to the real world in terms of its raw complexity and multi-agent challenges. Over the course of a decade and numerous competitions, the strongest agents have simplified important aspects of the game, utilized superhuman capabilities, or employed hand-crafted sub-systems. Despite these advantages, no previous agent has come close to matching the overall skill of top StarCraft players. We chose to address the challenge of StarCraft using general-purpose learning methods that are in principle applicable to other complex domains: a multi-agent reinforcement learning algorithm that uses data from both human and agent games within a diverse league of continually adapting strategies and counter-strategies, each represented by deep neural networks. We evaluated our agent, AlphaStar, in the full game of StarCraft II, through a series of online games against human players. AlphaStar was rated at Grandmaster level for all three StarCraft races and above 99.8% of officially ranked human players.

Comment: Look at all these authors! No need to count them, there are 42. On a more serious note, the most 'gamers' of us may enjoy this article. I personally never played StarCraft (way too complicated), but it is interesting to note that scientists not only try to create AI for chess or the Go game. One of the main points for StarCraft, which is a real-time game, is the time management; the authors had to slower the AI response in order to hide the fact that it was not a human playing. Still, as for chess, it could not beat the best players.

Quantum Supremacy Using a Programmable Superconducting Processor

Arute, F.; Arya, K.; Babbush, R.; Bacon, D.; Bardin, J. C.; Barends, R.; Biswas, R.; Boixo, S.; Brandao, F. G. S. L.; Buell, D. A.; (…) Vainsencher, A.; Villalonga, B.; White, T.; Yao, Z. J.; Yeh, P.; Zalcman, A.; Neven, H.; Martinis, J. M.* *Nature* **2019**, *574* (7779), 505–510.

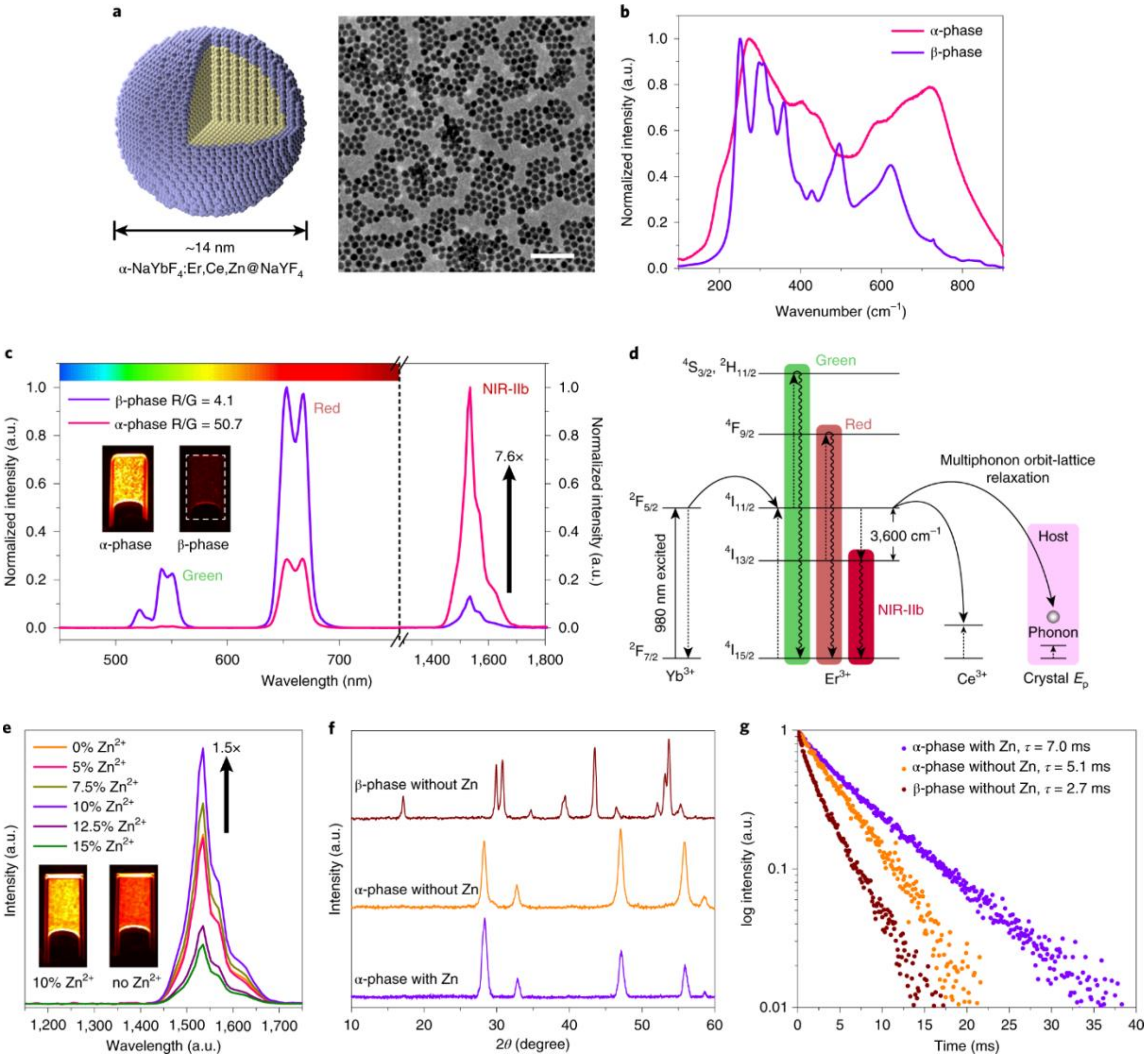


The promise of quantum computers is that certain computational tasks might be executed exponentially faster on a quantum processor than on a classical processor[1]. A fundamental challenge is to build a high-fidelity processor capable of running quantum algorithms in an exponentially large computational space. Here we report the use of a processor with programmable superconducting qubits to create quantum states on 53 qubits, corresponding to a computational state-space of dimension 2^{53} (about 10^{16}). Measurements from repeated experiments sample the resulting probability distribution, which we verify using classical simulations. Our Sycamore processor takes about 200 seconds to sample one instance of a quantum circuit a million times—our benchmarks currently indicate that the equivalent task for a state-of-the-art classical supercomputer would take approximately 10,000 years. This dramatic increase in speed compared to all known classical algorithms is an experimental realization of quantum supremacy for this specific computational task, heralding a much-anticipated computing paradigm.

Comment: Again, do not count; there are 77 authors. I am quite sure you heard about this breakthrough if you read about general scientific news, and also the controversy around this result. Even if you have not, I still think it is a good read!

In Vivo Molecular Imaging for Immunotherapy Using Ultra-bright Near-Infrared-Iib Rare-earth Nanoparticles

Zhong, Y.; Ma, Z.; Wang, F.; Wang, X.; Yang, Y.; Liu, Y.; Cui, Q.* *Nat. Biotechnol.* **2019**, *ASAP*.

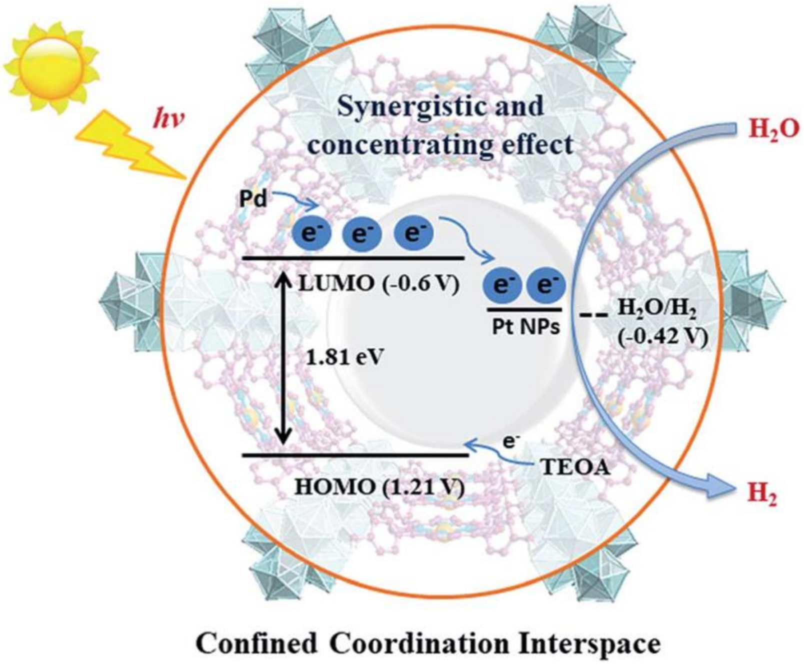


The near-infrared-IIb (NIR-IIb) (1,500–1,700 nm) window is ideal for deep-tissue optical imaging in mammals, but lacks bright and biocompatible probes. Here, we developed biocompatible cubic-phase (α-phase) erbium-based rare-earth nanoparticles (ErNPs) exhibiting bright downconversion luminescence at ~1,600 nm for dynamic imaging of cancer immunotherapy in mice. We used ErNPs functionalized with cross-linked hydrophilic polymer layers attached to anti-PD-L1 (programmed cell death-1 ligand-1) antibody for molecular imaging of PD-L1 in a mouse model of colon cancer and achieved tumor-to-normal tissue signal ratios of ~40. The long luminescence lifetime of ErNPs (~4.6 ms) enabled simultaneous imaging of ErNPs and lead sulfide quantum dots emitting in the same ~1,600 nm window. In vivo NIR-IIb molecular imaging of PD-L1 and CD8 revealed cytotoxic T lymphocytes in the tumor microenvironment in response to immunotherapy, and altered CD8 signals in tumor and spleen due to immune activation. The cross-linked functionalization layer facilitated 90% ErNP excretion within 2 weeks without detectable toxicity in mice.

Comment: The near-infrared-IIb treatment is a hot topic. Even this article applies this technology to nanoparticles. I believe small molecules or supramolecules still have a chance to use this technology in biothechnology.

Well-Distributed Pt-nanoparticles within Confined Coordination Interspaces of Self-sensitized Porphyrin Metal–organic Frameworks: Synergistic Effect Boosting Highly Efficient Photocatalytic Hydrogen Evolution Reaction

Li, S.; Mei, H. M.; Yao, S. L.; Chen, Z.; Lu, Y. L.; Zhang, L.; Su, C. Y. * *Chem Sci.* **2019**, *ASAP.*

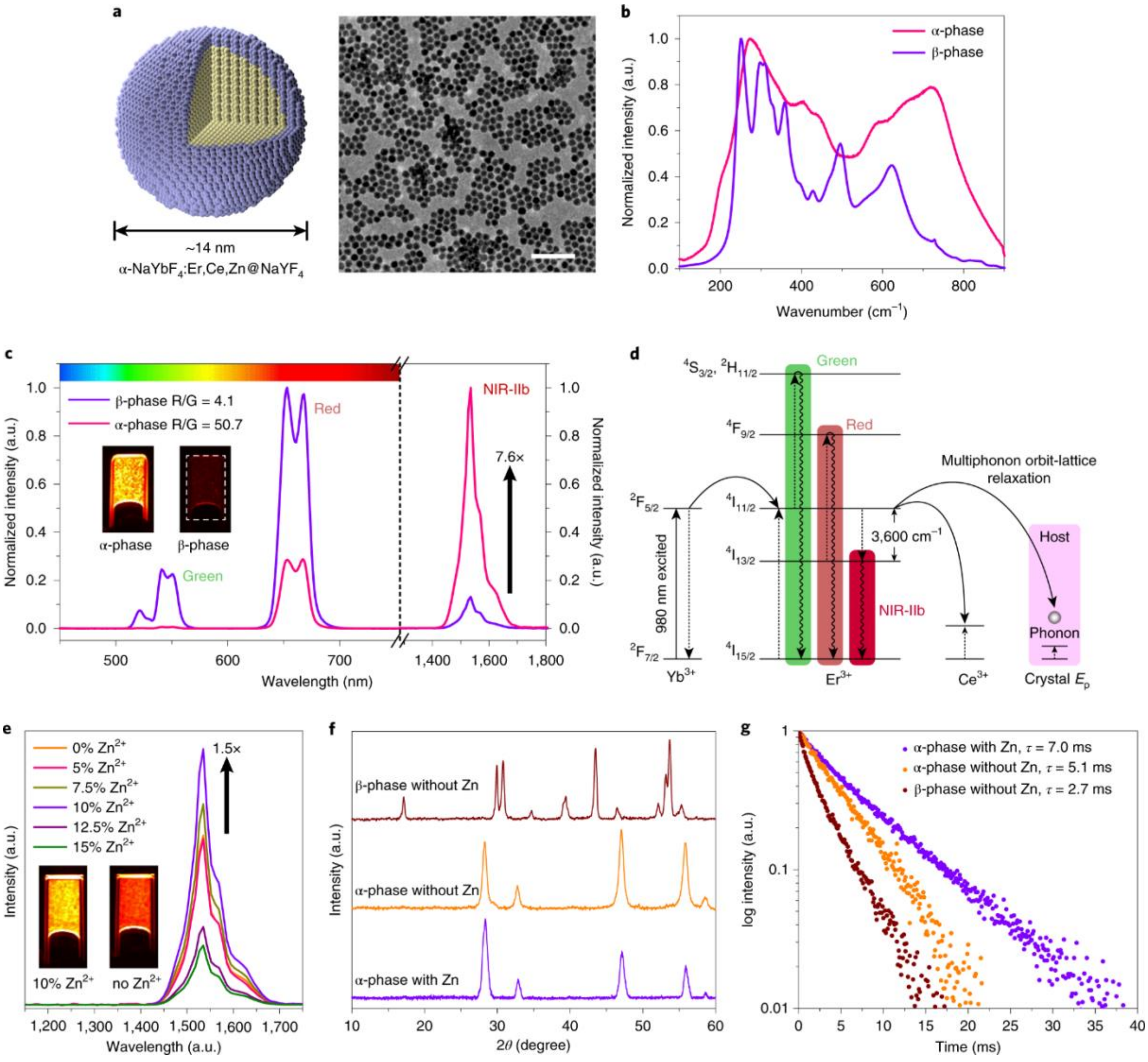


Effective conversion of solar energy into chemical energy by visible light represents a potential strategy for sustainable development. Among which, photocatalytic hydrogen evolution reaction (HER) with a relatively small activation energy (1.23 eV, around 1000 nm light irradiation) is especially attractive. In this work, well-distributed platinum nanoparticles (Pt-NPs) with a width of about 3 nm have been successfully immobilized into the confined coordination interspaces of 3.7 nm diameter, which are facilitated by early transition metal Hf(IV)-based clusters of a self-sensitized palladium porphyrin metal–organic framework. Under visible light irradiation, the resultant Pt@Pd-PCN-222(Hf) (which is also denoted as Pt@Pd-PMOF-2(Hf)) displays superb photocatalytic activity, achieving an unprecedented maximum H2 evolution rate of 22 674 μmol g−1 h−1 with a turn-over number (TON) of 4131.2 in 32 h and the highest turn-over frequency (TOF) of 482.5 h−1 based on Pt-NPs. This photocatalyst can be recycled and reused for three successive runs without significant loss of catalytic activity. This effective strategy takes advantage of the synergetic effect between Pd-porphyrin photosensitizers and Pt-NP co-catalysts confined within nanoscale coordination interspaces incorporating hydrophilic Hf(IV)-oxo clusters.

Comment: A good application employing MOF.

In Vivo Molecular Imaging for Immunotherapy Using Ultra-bright Near-Infrared-Iib Rare-earth Nanoparticles

Zhong, Y.; Ma, Z.; Wang, F.; Wang, X.; Yang, Y.; Liu, Y.; Cui, Q.* *Nat. Biotechnol.* **2019**, *ASAP.*

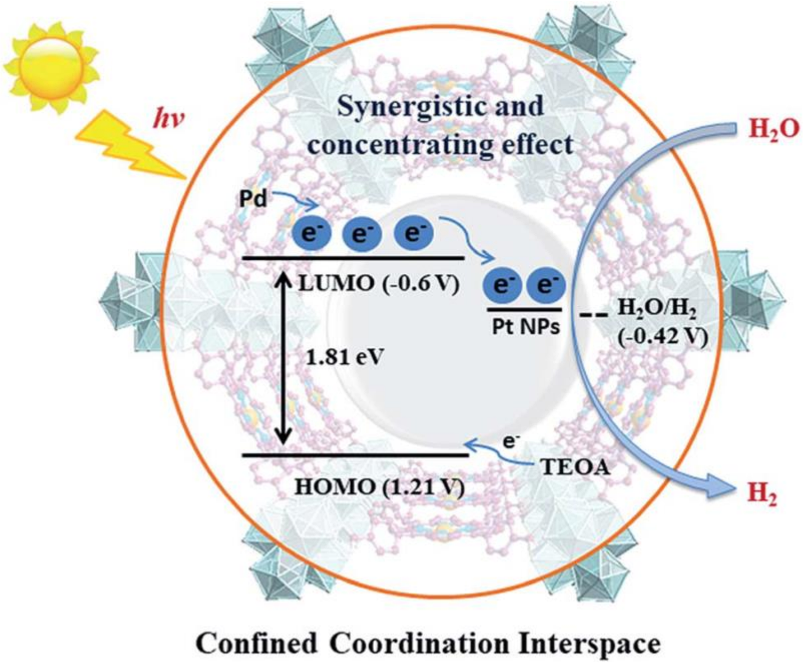


The near-infrared-IIb (NIR-IIb) (1,500–1,700 nm) window is ideal for deep-tissue optical imaging in mammals, but lacks bright and biocompatible probes. Here, we developed biocompatible cubic-phase (α-phase) erbium-based rare-earth nanoparticles (ErNPs) exhibiting bright downconversion luminescence at ~1,600 nm for dynamic imaging of cancer immunotherapy in mice. We used ErNPs functionalized with cross-linked hydrophilic polymer layers attached to anti-PD-L1 (programmed cell death-1 ligand-1) antibody for molecular imaging of PD-L1 in a mouse model of colon cancer and achieved tumor-to-normal tissue signal ratios of ~40. The long luminescence lifetime of ErNPs (~4.6 ms) enabled simultaneous imaging of ErNPs and lead sulfide quantum dots emitting in the same ~1,600 nm window. In vivo NIR-IIb molecular imaging of PD-L1 and CD8 revealed cytotoxic T lymphocytes in the tumor microenvironment in response to immunotherapy, and altered CD8 signals in tumor and spleen due to immune activation. The cross-linked functionalization layer facilitated 90% ErNP excretion within 2 weeks without detectable toxicity in mice.

Comment: The near-infrared-IIb treatment is a hot topic. Even this article applies this technology to nanoparticles. I believe small molecules or supramolecules still have a chance to use this technology in biothechnology.

Well-Distributed Pt-nanoparticles within Confined Coordination Interspaces of Self-sensitized Porphyrin Metal–organic Frameworks: Synergistic Effect Boosting Highly Efficient Photocatalytic Hydrogen Evolution Reaction

Li, S.; Mei, H. M.; Yao, S. L.; Chen, Z.; Lu, Y. L.; Zhang, L.; Su, C. Y. * *Chem Sci.* **2019**, *ASAP.*

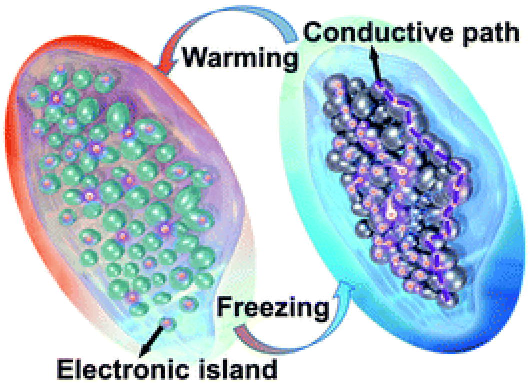


Effective conversion of solar energy into chemical energy by visible light represents a potential strategy for sustainable development. Among which, photocatalytic hydrogen evolution reaction (HER) with a relatively small activation energy (1.23 eV, around 1000 nm light irradiation) is especially attractive. In this work, well-distributed platinum nanoparticles (Pt-NPs) with a width of about 3 nm have been successfully immobilized into the confined coordination interspaces of 3.7 nm diameter, which are facilitated by early transition metal Hf(IV)-based clusters of a self-sensitized palladium porphyrin metal–organic framework. Under visible light irradiation, the resultant Pt@Pd-PCN-222(Hf) (which is also denoted as Pt@Pd-PMOF-2(Hf)) displays superb photocatalytic activity, achieving an unprecedented maximum H2 evolution rate of 22 674 μmol g−1 h−1 with a turn-over number (TON) of 4131.2 in 32 h and the highest turn-over frequency (TOF) of 482.5 h−1 based on Pt-NPs. This photocatalyst can be recycled and reused for three successive runs without significant loss of catalytic activity. This effective strategy takes advantage of the synergetic effect between Pd-porphyrin photosensitizers and Pt-NP co-catalysts confined within nanoscale coordination interspaces incorporating hydrophilic Hf(IV)-oxo clusters.

Comment: A good application employing MOF.

Generalized way to make temperature tunable conductor–insulator transition liquid metal composites in a diverse range

Chen, C.; Wang, H-W.; Sun, X-Y.; Wang, Q.; Wang, X-J.; Chen, L-B.; Zhang, L-J.; Guo, R.; Liu, J.* *Mater. Horiz.*, **2019**, *6*, 1854-1861

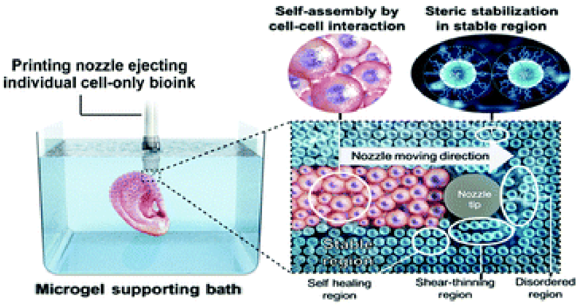


Liquid materials with the ability to transit between conductor and insulator are of great scientific and practical significance. However, achieving the conduction of a liquid metal droplet network is still a challenge. To solve these problems, a generalized method is proposed to fabricate temperature tunable liquid conductor–insulator transition composites, which is achieved firstly via freezing and thawing liquid metal droplets dispersed in dimethicone. Such composites also impart conductivity to the dispersed liquid metal droplet network. To illustrate the typical application of the thus realized materials, a visualized circuit is constructed based on the relationship between the color and the conduction. In addition, reconfigurable and repairable circuits are fabricated depending on the inherent liquid properties of these materials. Furthermore, this universal mechanism has been revealed via the abnormal volume expansion ratio of the liquid metal droplets during the phase change. By calculating the volume change ratio of all metals, we speculate and confirm that gallium-based alloys and bismuth-based alloys can be used to prepare such conductive transition materials. Accordingly, we identify more eligible materials with suitable phase transition points, which significantly extend the transition temperature from insulator to conductor. The liquid material preparation strategy proposed here provides a novel paradigm for achieving the conductor–insulator transition at a wide temperature range and offers promising potential for future applications.

Comment: The idea behind this is so basic – I mean that the conductivity of metals decreases with increasing temperature – that I am surprised that it has not yet been investigated… Although it is nice that depending on the alloy used, the transition point occurs in a large temperature range, which makes it applicable for electronic devices operating a very wide range of environments (outer space, earth, volcanoes..).

Individual cell-only bioink and photocurable supporting medium for 3D printing and generation of engineered tissues with complex geometries

Jeon, O.; Lee, Y. B.; Jeong, H.; Lee, S. J.; Wells, D.; Alsberg, E.* *Mater. Horiz.*, **2019**, *6*, 1625-1631

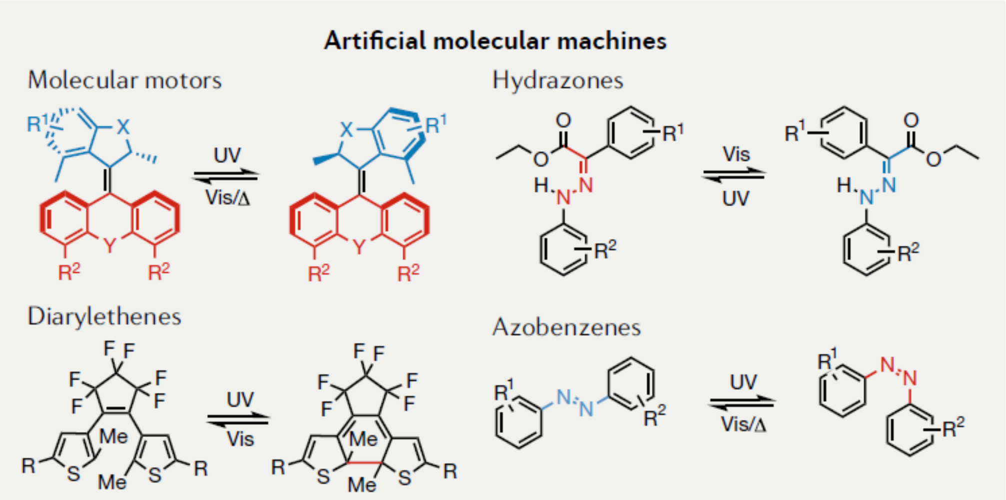


Scaffold-free engineering of three-dimensional (3D) tissue has focused on building sophisticated structures to achieve functional constructs. Although the development of advanced manufacturing techniques such as 3D printing has brought remarkable capabilities to the field of tissue engineering, **creating and culturing individual cell-only based high-resolution tissues with complex geometries without an intervening biomaterial scaffold while maintaining the resulting constructs' shape and architecture over time** has not been achieved to date. In this report, we introduce a cell printing platform which addresses the aforementioned challenge and permits 3D printing and long-term culture of a living cell-only bioink lacking a biomaterial carrier for functional tissue formation. A biodegradable and photocrosslinkable microgel supporting bath serves initially as a fluid, allowing free movement of the printing nozzle for high-resolution cell extrusion, while also presenting solid-like properties to sustain the structure of the printed constructs. The printed human stem cells, which are the only component of the bioink, couple together via transmembrane adhesion proteins and differentiate down tissue-specific lineages while being cultured in a further photocrosslinked supporting bath to form bone and cartilage tissue with precisely controlled structure. Collectively, this system, which is applicable to general 3D printing strategies, is a paradigm shift for printing of scaffold-free individual cells, cellular condensations and organoids, and may have far reaching impact in the fields of regenerative medicine, drug screening, and developmental biology.

Comment: This is one of those topics where they describe things that I thought could only be done in science-fiction for me (probably because I am not in this field and I do not know how fast the field is developing). But they actually printed human stem cells that once printed, differentiate, and formed a real-life femur! I think the use of their microgel is a simple yet brilliant idea. In short, it normally displays solid-like properties, giving support to the printed cellular structure. However, it behaves as a fluid in the regions where the nozzle and cell-only bioink causes shear thinning by their motion. Thus, once cells are printed and the nozzle moves away, the microgel rapidly flows into the region, self-heals and gives support.

Life-like motion driven by artificial molecular machines

Lancia, F.; Ryabchun, A.; Katsonis, N.* *Nat. Rev. Chem.* **2019**, *3*, 536-551.

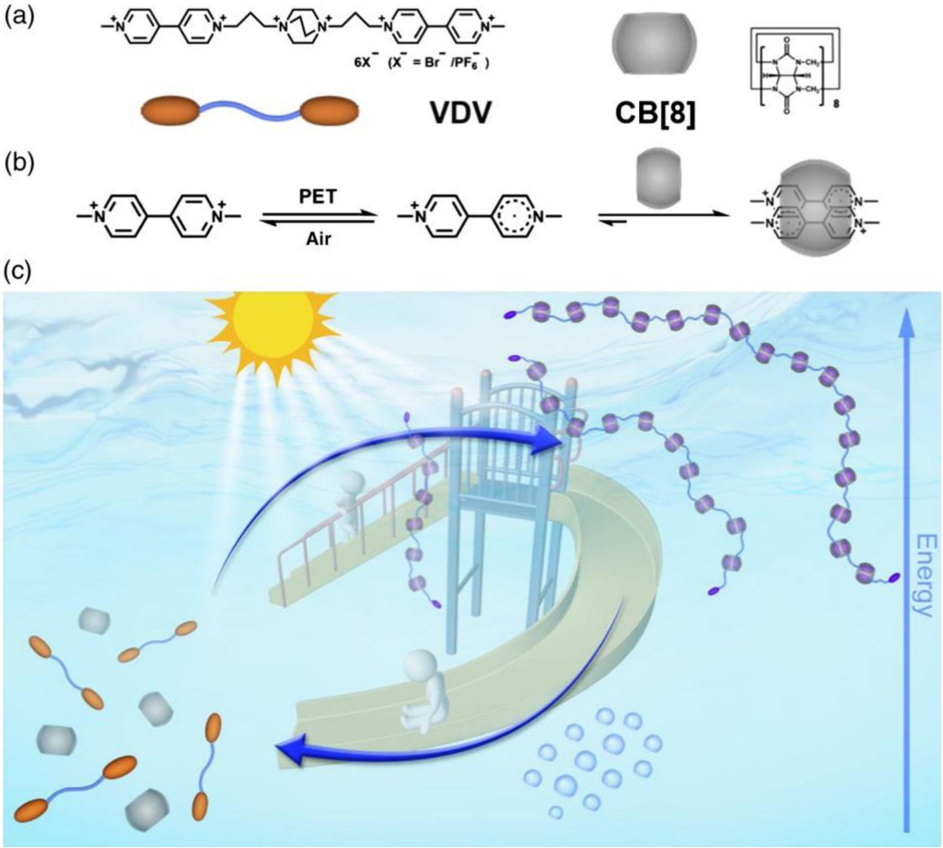


Essentially, all motion in living organisms emerges from the collective action of biological molecular machines transforming chemical energy, originally harvested from light, into ordered activity. As a man-made counterpart to nature's biomolecular machines, chemists have created artificial molecular machines that display controlled and even directional motion in response to light. However, to be of practical value, the motion of these light- fuelled molecular machines will have to be coupled to the rest of the world. Inspired by the complex functional movement seen in the plant and animal world, chemists have undertaken the challenge to harness molecular motion and, so, they have set artificial molecular motors and switches to work and perform useful mechanical action at the macroscopic level. Here, we review these recent developments. We show how modern research has embraced the full complexity of the molecular world by aiming at the design of autonomous, and sometimes adaptive, molecular systems that work continuously under the effect of illumination. We report evidence that molecular motion can be engineered into highly sophisticated movements and that, from a fundamental point of view, continuous movement can only emerge when man- made molecules cooperate, in space and time. Eventually, unravelling the rules of molecular motion will support the creation of molecular materials that produce work continuously under a constant input of energy.

Comment: From this review you could get some information about life-like motion based on light-responsive molecular machines. However, I think the content which only introduces light-responsive molecular machines is incompatible with such a comprehensive title, although they propose the reason that "all motion in living organisms emerges from the collective action of biological molecular machines transforming chemical energy, originally harvested from light, into ordered activity".

Paintable Room-Temperature Phosphorescent Liquid Formulations of Alkylated Bromonaphthalimide

Goudappagouda; Manthanath, A.; Wakchaure, V. C; Ranjeesh, K. C; Das, T.; Vanka, K.; Nakanishi, T.; Babu, S. S.* *Angew. Chem.* **2019**, *131*, 2306-2310.

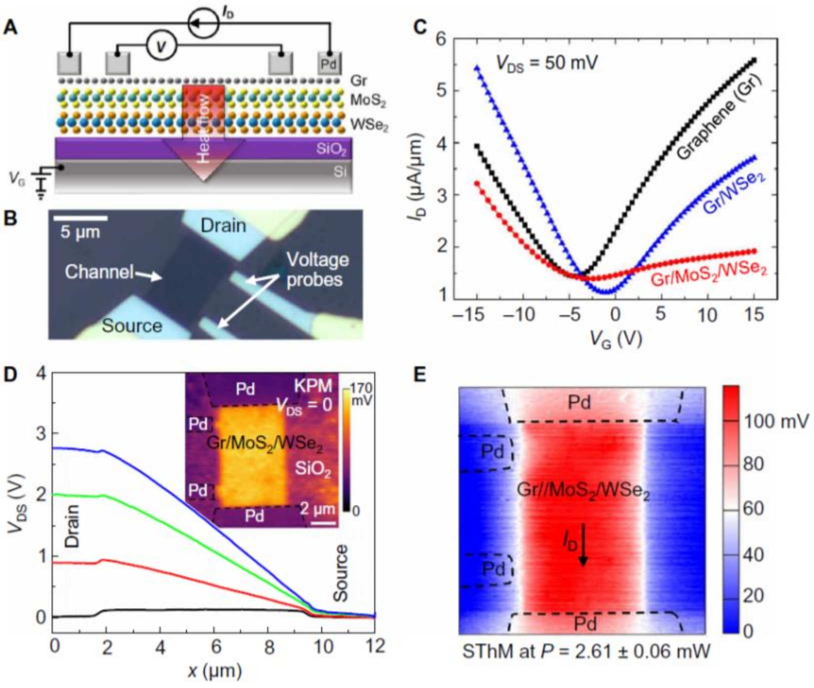


A new method of light-powered dissipative supramolecular polymerization is established, in which supramolecular polymerization is implemented in the far-from-equilibrium state. A bifunctional monomer containing two viologen moieties was designed. Upon inputting energy by light, the system was driven far from equilibrium, and the monomers were photoreduced and activated to form supramolecular polymers driven by 2:1 host–guest complexation of the viologen cation radical and cucurbit[8]uril. As the system returned to equilibrium, the supramolecular polymers depolymerized spontaneously by air oxidation. This method works in both linear and in cross-linked supramolecular polymerization. The strategy of light-powered dissipative supramolecular polymerization is anticipated to have potential in the fabrication of functional supramolecular materials, especially in creating novel "living" materials.

Comment: An interesting system which could implement the controllable supramolecular polymerization due to the light and air stimuli. Actually, triarylamine is similar to viologen, which is visible-light responsive and can form supramolecular polymers after irradiation by light. Maybe, we also could design such a system.

Ultrahigh thermal isolation across heterogeneously layered two-dimensional materials

Vaziri1, S.*; Yalon1, E.*; Muñoz Rojo, M.; Suryavanshi, S. V.; Zhang, H.; McClellan, C. J.; Bailey, C. S.; Smithe, K. K. H.; Gabourie, A. J.; Chen, V.; Deshmukh, S.; Bendersky, L.; Davydov, A. V.; Pop E. *Sci. Adv.* **2019**; 5, ASAP

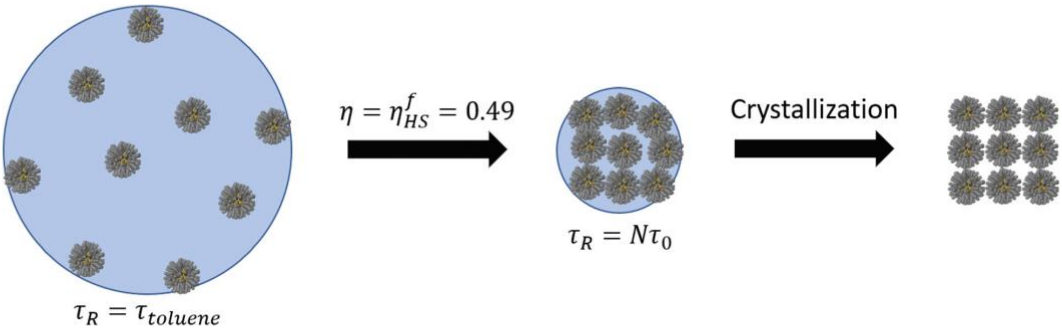


Heterogeneous integration of nanomaterials has enabled advanced electronics and photonics applications. However, similar progress has been challenging for thermal applications, in part due to shorter wavelengths of heat carriers (phonons) compared to electrons and photons. Here, we demonstrate unusually high thermal isolation across ultrathin heterostructures, achieved by layering atomically thin two-dimensional (2D) materials. We realize artificial stacks of monolayer graphene, MoS2, and WSe2 with thermal resistance greater than 100 times thicker SiO2 and effective thermal conductivity lower than air at room temperature. Using Raman thermometry, we simultaneously identify the thermal resistance between any 2D monolayers in the stack. Ultrahigh thermal isolation is achieved through the mismatch in mass density and phonon density of states between the 2D layers. These thermal metamaterials are an example in the emerging field of phononics and could find applications where ultrathin thermal insulation is desired, in thermal energy harvesting, or for routing heat in ultracompact geometries.

Comment: Not sure I understood everything behind the fact that a solid – way denser than air – is actually a much better isolator. I will need a few more articles to fully understand, but I really like this proof of concept.

Assembly by solvent evaporation: equilibrium structures and relaxation times

Waltmannn T.; Travesset A.* *Nanoscale,* **2019**, *11,* 18702

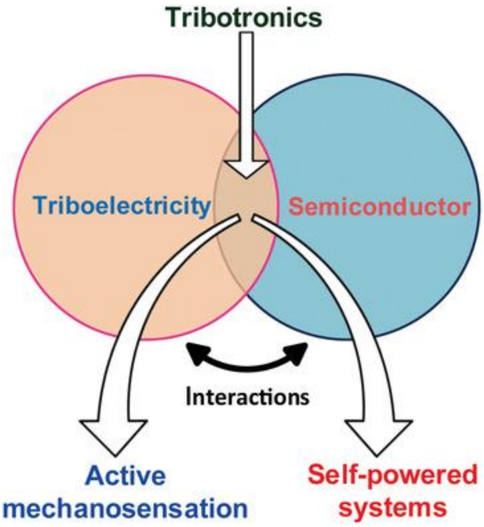


We present a study describing the dynamics and equilibrium of the assembly of nanostructures by solvent evaporation. We first consider N nanocrystals stabilized by capping ligands in a spherical droplet of liquid solvent coexisting with its gas and show that, as the liquid solvent evaporates slowly, NCs crystallize into clusters of high symmetry based on tetrahedral and octahedral units: tetrahedron (N = 4), octahedron (N = 6), icosahedron (N = 13), Archimedean truncated tetrahedron (N = 16) and Z20 (N = 21). We derive explicit formulas for the process and rigorously compute relaxation times, which drastically increase when the packing parameter reaches the hard-sphere liquid–solid transition ηf HS = 0.49. This result shows that contrary to what occurs in an evaporation of a single component system, the relaxation times are not determined by the diffusion constant of the vapor, but rather, are dominated by the residence time of solvent molecules trapped within the capping ligands. Our theory provides a number of predictions that enable the design of new structures while improving the control and quality of their assembly.

Comment: The authors describe here a multi-steps thermodynamic model to explain/predict assembly by solvent evaporation. This model is, however, only limited to nano crystals. It also lacks solvent diversity: Everything is made in toluene and they simulated only around 20 molecules: it needs to be further developed. Nevertheless, it can still be helpful to have an idea of the crystal formation upon solvent evaporation.

Tribotronics for Active Mechanosensation and Self-Powered Microsystems

Zhang, C.*; Bu, T.; Zhao, J.; Liu, G.; Yang, H.; Wang, Z. L.* *Adv. Funct. Mater.* **2019**, *29,* 1808114.

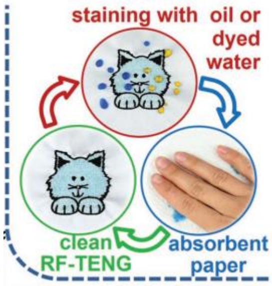


Tribotronics has attracted great attention as a new research field that encompasses the control and tuning of semiconductor transport by triboelectricity. Here, tribotronics is reviewed in terms of active mechanosensation and human–machine interfacing. As a fundamental unit, contact electrification field-effect transistors are analyzed, in which the triboelectric potential can be used to control electrical transport in semiconductors. Several tribotronic functional devices have been developed for active control and information sensing, which has demonstrated triboelectricity-controlled electronics and established active mechanosensation for the external environment. In addition, the universal triboelectric power management strategy and the triboelectric nanogenerator-based constant sources are also reviewed, in which triboelectricity can be managed by electronics in the reverse action. With the implantation of triboelectric power management modules, the harvested triboelectricity by various kinds of human kinetic and environmental mechanical energy can be effectively managed as a power supply for self-powered microsystems. In terms of the research prospects for interactions between triboelectricity and semiconductors, tribotronics is expected to demonstrate significant impact and potential applications in micro-electro-mechanical systems/nano-electro-mechanical systems (MEMS/NEMS), flexible electronics, robotics, wireless sensor network, and Internet of Things.

Comment: I have the feeling that I see more and more papers about triboelectronics, mainly for the design of flexible wearable electronic devices. If you do not really know a lot about this field, like I do, I recommend this review. While some physical aspects are not so easy to understand, it gives a decent overview of the advantages and challenges in this field.

Waterproof, Breathable, and Antibacterial Self-Powered E-Textiles Based on Omniphobic Triboelectric Nanogenerators

Sala de Medeiros, M.; Chanci, D.; Moreno, C.; Goswami, D.; Martinez, R. V.* *Adv. Funct. Mater.* **2019**, *29*, 1904350.

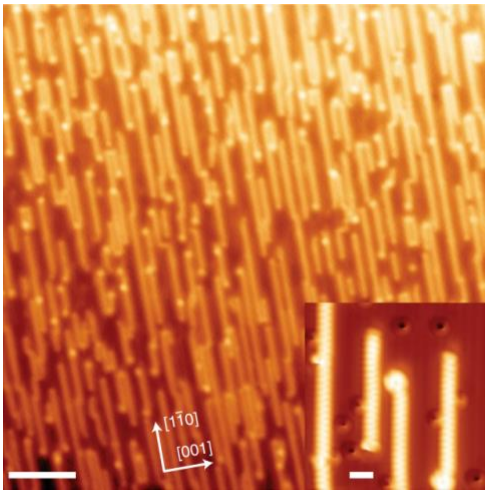


Multifunctional electronic textiles (e-textiles) incorporating miniaturized electronic devices will pave the way toward a new generation of wearable devices and human–machine interfaces. Unfortunately, the development of e-textiles is subject to critical challenges, such as battery dependence, breathability, satisfactory washability, and compatibility with mass production techniques. This work describes a simple and cost-effective method to transform conventional garments and textiles into waterproof, breathable, and antibacterial e-textiles for self-powered human–machine interfacing. Combining embroidery with the spray-based deposition of fluoroalkylated organosilanes and highly networked nanoflakes, omniphobic triboelectric nanogenerators (R_F-TENGs) can be incorporated into any fiber-based textile to power wearable devices using energy harvested from human motion. R_F-TENGs are thin, flexible, breathable (air permeability 90.5 mm s$_{-1}$), inexpensive to fabricate (<0.04$ cm$_{-2}$), and capable of producing a high power density (600 µW cm$_{-2}$). E-textiles based on R_F-TENGs repel water, stains, and bacterial growth, and show excellent stability under mechanical deformations and remarkable washing durability under standard machine-washing tests. Moreover, e-textiles based on R_F-TENGs are compatible with large-scale production processes and exhibit high sensitivity to touch, enabling the cost-effective manufacturing of wearable human–machine interfaces.

Comment: Speaking of which, this article is representative of wearable electronic devices. From a fundamental point of view, it is not new; from a functional point of view, though, it shows the on-going research to obtain optimal multifunctional e-textiles. We may have little triboelectric embroidered cats on our shirts soon.

On-Surface Synthesis and Characterization of Individual Polyacetylene Chains

Wang, S.; Sun, Q.; Gröning, O.; Widmer, R.; Pignedoli, C. A.; Cai, L.; Yu, X.; Yuan, B.; Li, C.; Ju, H.; Zhu, J.; Ruffieux, P.; Fasel, R.*; Xu, W.* *Nat. Chem.* **2019**, *11*, 924–930.

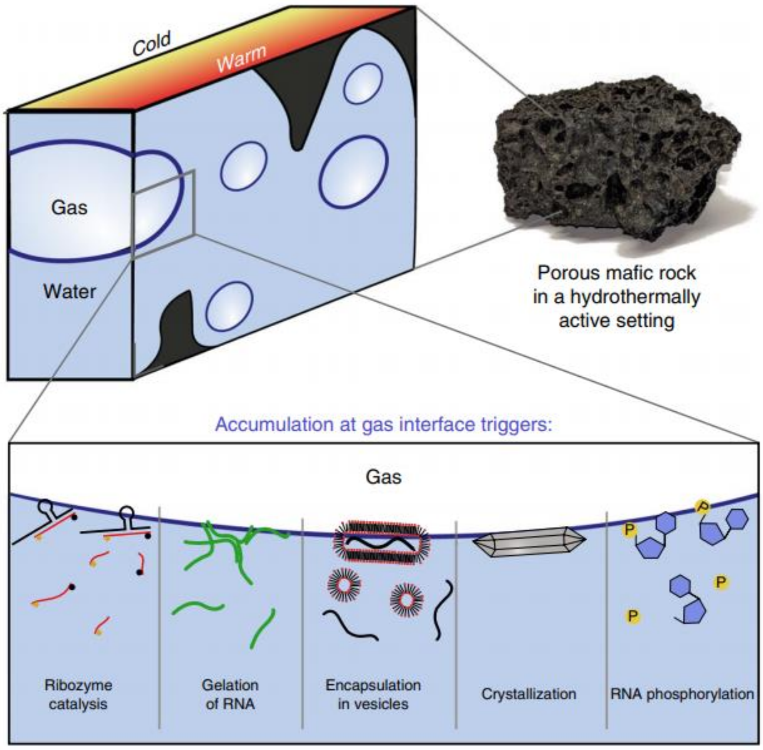


Polyacetylene (PA) comprises one-dimensional chains of *sp*$_2$-hybridized carbon atoms that may take a *cis* or *trans* configuration. Owing to its simple chemical structure and exceptional electronic properties, PA is an ideal system to understand the nature of charge transport in conducting polymers. Here, we report the on-surface synthesis of both *cis*- and *trans*-PA chains and their atomic-scale characterization. The structure of individual PA chains was imaged by non-contact atomic force microscopy, which confirmed the formation of PA by resolving single chemical bond units. Angle-resolved photoemission spectroscopy suggests a semiconductor-to-metal transition through doping-induced suppression of the Peierls bond alternation of trans-PA on Cu(110). Electronically decoupled *trans*-PAs exhibit a band gap of 2.4 eV following copper oxide intercalation. Our study provides a platform for studying individual PA chains in real and reciprocal space, which may be further extended to study the intrinsic properties of non-linear excitons in conducting polymers.

Comment: The use of crystalline surfaces to prepare ordered carbon structures, like carbon nanoribbons, has been applied here for the polymerization of polyacetylene. Side reactions were avoided with a proper control of the temperature and, more interestingly, a "curing" step at mild temperature caused *cis*- to *trans*- isomerizations in the backbone, hence producing straight polymer chains (this is the picture above). These results are quite impressive alone, but the authors further investigated the electronic properties of the polymers, observing either a semi-conducting or metallic behavior depending on the supporting surface.

Heated Gas Bubbles Enrich, Crystallize, Dry, Phosphorylate and Encapsulate Prebiotic Molecules

Morasch, M.; Liu, J.; Dirscherl, C. F.; Ianeselli, A.; Kühnlein, A.; Le Vay, K.; Schwintek, P.; Islam, S.; Corpinot, M. K.; Scheu, B.; Dingwell, D. B.; Schwille, P.; Mutschler, H.; Powner, M. W.; Mast, C. B.; Braun, D.* *Nat. Chem.* **2019**, *11*, 779–788.

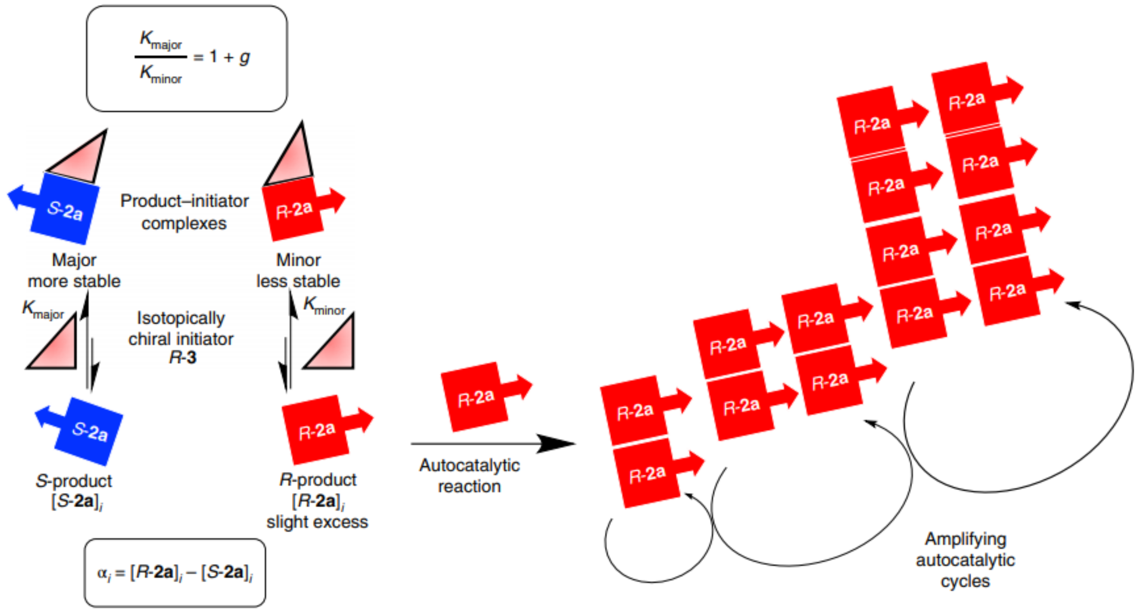


Non-equilibrium conditions must have been crucial for the assembly of the first informational polymers of early life, by supporting their formation and continuous enrichment in a long-lasting environment. Here, we explore how gas bubbles in water subjected to a thermal gradient, a likely scenario within crustal mafic rocks on the early Earth, drive a complex, continuous enrichment of prebiotic molecules. RNA precursors, monomers, active ribozymes, oligonucleotides and lipids are shown to (1) cycle between dry and wet states, enabling the central step of RNA phosphorylation, (2) accumulate at the gas–water interface to drastically increase ribozymatic activity, (3) condense into hydrogels, (4) form pure crystals and (5) encapsulate into protecting vesicle aggregates that subsequently undergo fission. These effects occur within less than 30 min. The findings unite, in one location, the physical conditions that were crucial for the chemical emergence of biopolymers. They suggest that heated microbubbles could have hosted the first cycles of molecular evolution.

Comment: So many commas in this title (and so many authors for this paper), which is quite understandable considering the amount of work. I do not know enough about prebiotic life to have a critical point of view on this paper, but I guess it may interest some of you.

Energy Threshold for Chiral Symmetry Breaking in Molecular Self-Replication

Hawbaker, N. A.; Blackmond, D. G.* *Nat. Chem.* **2019**, *11*, 957–962.

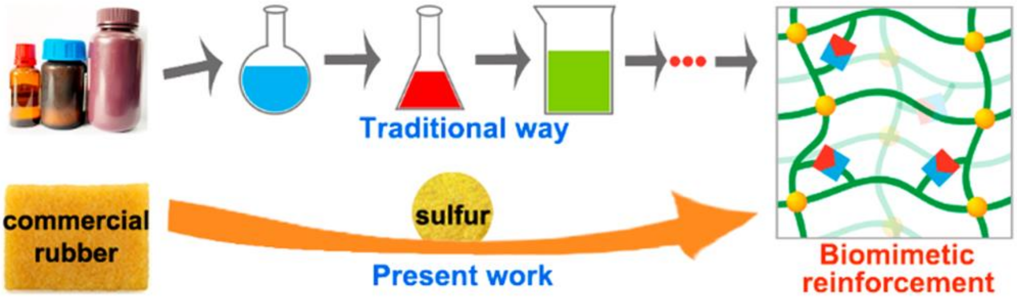


The homochirality of biological molecules (right-handed sugars and left-handed amino acids) is a signature of life. Extensive research has been devoted to understanding how enrichment of one enantiomer over the other might have emerged from a prebiotic world. Here, we use experimental data from the model Soai autocatalytic reaction system to evaluate the energy required for symmetry breaking and chiral amplification in molecular self-replication. One postulate for the source of the original imbalance is the tiny difference in energy between enantiomers due to parity violation in the weak force. We discuss the plausibility of parity violation energy difference coupled with asymmetric autocatalysis as a rationalization for absolute asymmetric synthesis and the origin of the homochirality of biological molecules. Our results allow us to identify the magnitude of the energy imbalance that gives rise to directed symmetry breaking and asymmetric amplification in this autocatalytic system.

Comment: Again, this work deals with the beginning of “life”, this time emphasizing how a preferential chirality may have emerged in biological systems.

Elastomer Reinforced with Innate Sulfur-Based Cross-Links as Ligands

Zhang,X.;Yu,S.; Tang,Z.;Guo,B.; *ACS Macro. Lett.* **2019**, 8, 1091−1095



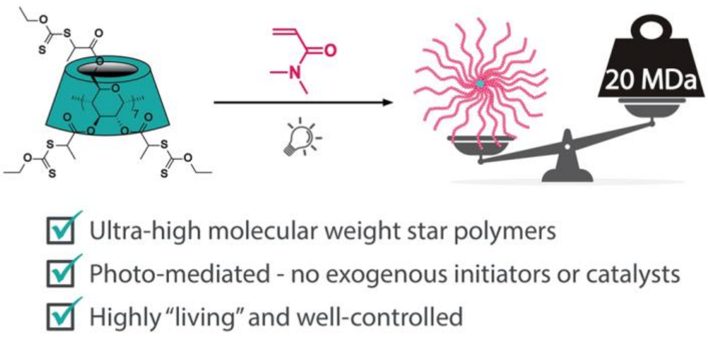
Although the incorporation of sacrificial bonds into an elastomer is an effective way to provide a combination of high strength and high fracture toughness, this method normally involves complicated chemical processes. The coordination between metal ions and polysulfides has been documented. However, the potential of polysulfide structures in vulcanizates as ligands has long been neglected. Using innate sulfur-based cross-links, we show how weak and nonpolar elastomers achieve significant reinforcement without modification of the backbone. By simply soaking vulcanizates into solutions containing metal ions, dual ions are simultaneously introduced into the vulcanizate to generate coordinations with different bond strengths, resulting in an unprecedented high modulus. Overall, this work presents a universal yet high-efficiency reinforcing strategy to prepare high-performance elastomers without additional chemical modifications, which should promote comprehensive research and industrial application of sacrificial bond strategies for elastomers.

Comment: This work presents a novel, generic, and high-efficiency method to prepare high-performance elastomers without any chemical modification. For the people who are working with polymers, you may gain some inspiration.

Highly Living Stars via Core-First Photo-RAFT Polymerization: Exploitation for Ultra-High Molecular Weight Star Synthesis

Allison-Logan, S.; Karimi, F.; Sun, Y.; G. McKenzie, T.; Nothling, M.; Bryant, G.; Qiao, G.;

ACS Macro Lett. **2019**, 8, 1291−1295



Star polymers are highly functional materials that display unique properties in comparison to linear polymers, making them valuable in a wide range of applications. Currently, ultra-high molecular weight (UHMW) star polymers synthesized using controlled radical polymerization are prone to termination reactions that have undesirable effects, such as star−star coupling. Herein, we report the synthesis of the largest star polymers to date using controlled radical techniques via xanthate-mediated photoreversible addition−fragmentation chain transfer (RAFT) polymerization using a core-first approach. Polymerization from xanthate-functionalized cores was highly living, enabling the synthesis of well-defined star polymers with molecular weights in excess of 20 MDa

Comment: The facile synthesis of well-defined UHMW star polymers may provide access to unique star-based polymeric materials that were previously unattainable. I think that we can learn a lot from this method and use for applications in the gel formation.

Construction of A Two-photon Fluorescent Probe for Ratiometric Imaging of Hypochlorous Acid in Alcohol-induced Liver Injury

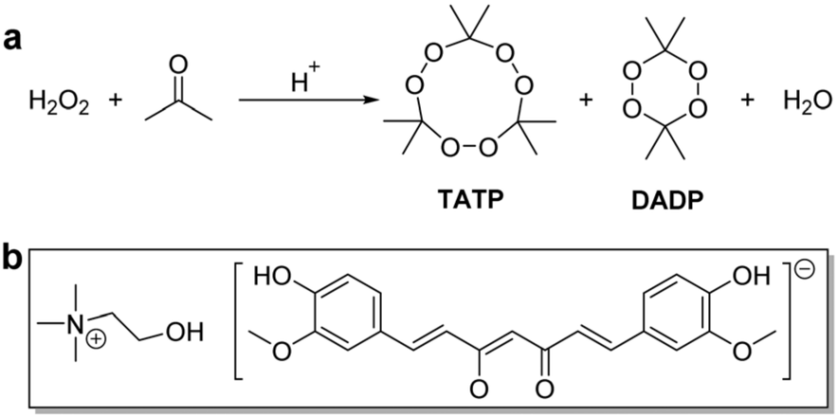
Lou, Y.; Wang, C.; Chi, S.; Li, S.; Mao, Z.;* Liu, Z. H.* *Chem Commum.* **2019**, *ASAP.*

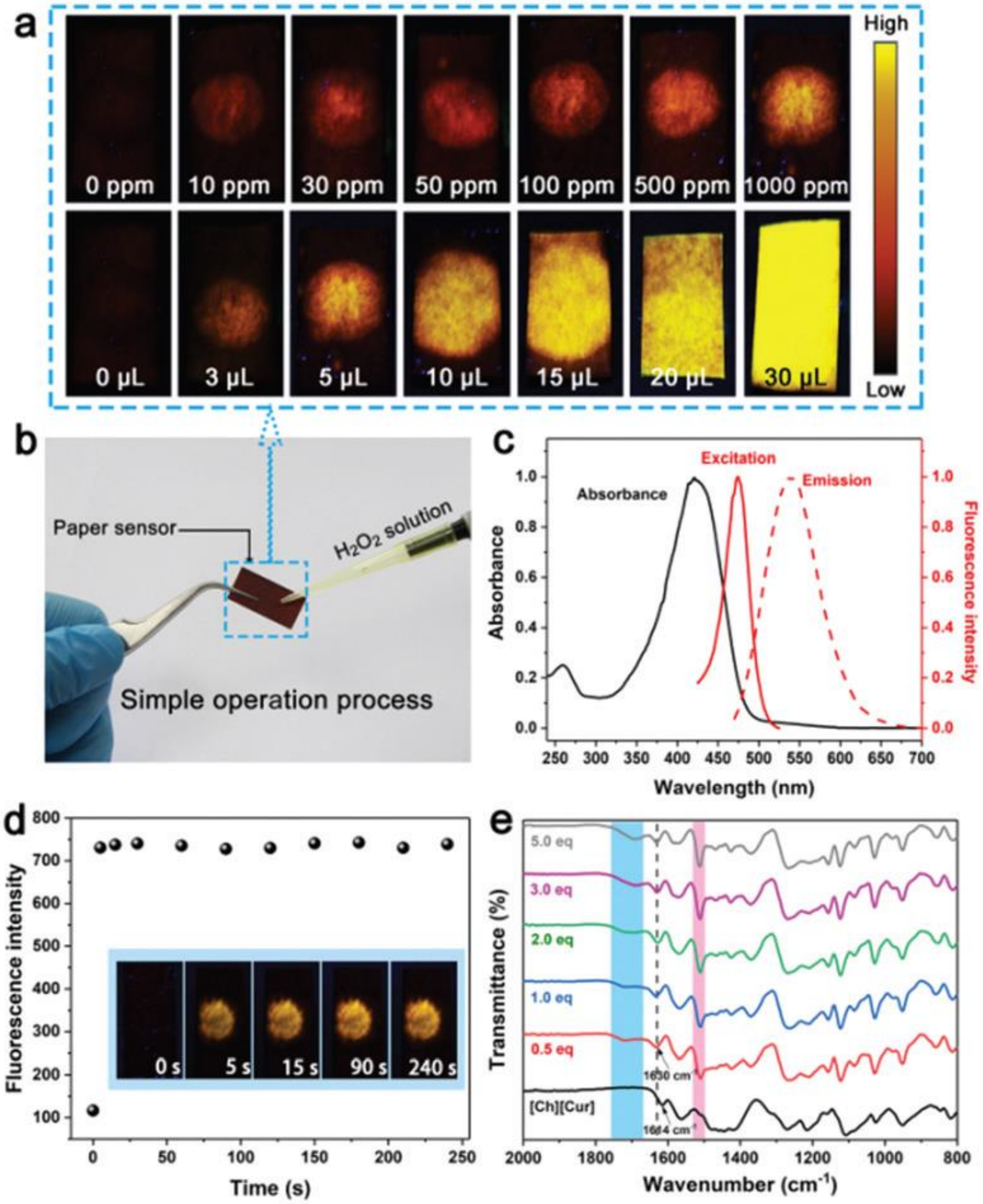
Alcohol-induced liver injury has been a terrible threat to human health and life. The relationship between HClO and the process is unclear. Thus, a ratiometric two-photon fluorescent probe for HClO was deliberately constructed and revealed the generation of HClO in the alcohol-induced liver injury process for the first time.

Comment: There are lots of group focusing on the fluorescence properties of TAA. This work take advantage of the two-photon absorption, caused by the oxidation of the thioether, to detect hypochlorous acid (HClO).

Handy Fluorescent Paper Device Based on A Curcumin Derivative for Ultrafast Detection of Peroxide-based Explosives

Zhu, Q. H.; Zhang, G. H.; Yuan, W. L.; Wang, S. L.; He, L.; Yong, F.; Tao, G. H.* *Chem Commum.* **2019**, *ASAP.*



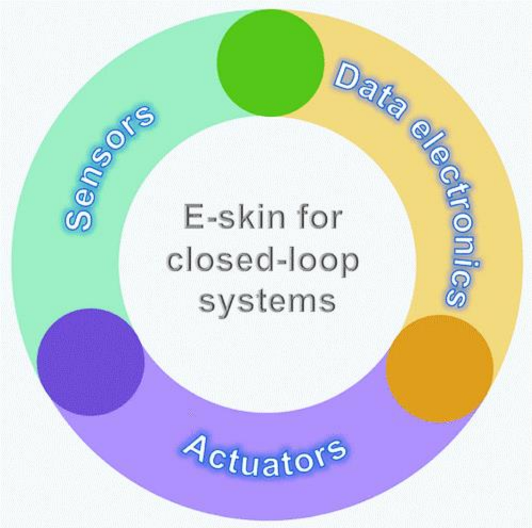


We report a handy, simple and inexpensive paper device for extremely sensitive detection of peroxide-based explosives. The sensing device fabricated using a curcumin derivative was capable of ultrafast sensing of triacetone triperoxide. The detection time was below 5 s. Moreover, the sensor retained full function under storage at ambient temperature for at least 120 days.

Comment: I just was attracted by the behavior of this ultrafast testing method paper. It is a good example of the application and combination of methodological research and real needs.

Electronic Skin for Closed-Loop Systems

Wang, C; Pan, C.; Wang, Z.* *ACS Nano*, **2019**, ASAP

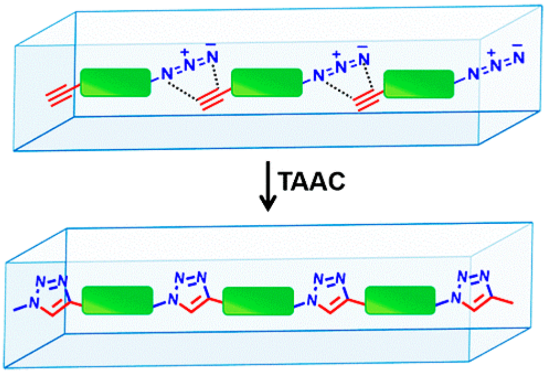


Electronic skin (e-skin) uses advanced electronics and sensor arrays to manufacture human-skin-like robotics skin. The creation of e-skin has been made possible due to various physics effects/mechanisms, innovative materials, structural designs, and advanced fabrication techniques. In this Perspective, we describe the current advances in and emerging uses of e-skin for closed-loop systems, with a view toward applications in smart robotics, Internet of Things, and human–machine interfaces.

Comment: A very interesting perspective article about the field of electronic skins. Here, the authors describe the different types of sensors used in electronic skins and briefly comment their functioning principles. Also, they mention the relevance of materials chemistry in the search for stretchable and self-healable materials containing dynamic covalent cross-linkages and hydrogen bonding among others. It seems that this is a very interdisciplinary research area that will be fundamental in the development of robots and in the construction of prosthesis for different body parts.

Topochemical Azide−Alkyne Cycloaddition Reaction

Hema, K.; Sureshan, K.* *Acc. Chem. Res.* **2019**, ASAP



Topochemical reactions are solid-state reactions that transpire under the strict control of molecular packing in the crystal lattice. Due to this lattice control, these reactions generate products in a regio-/stereospecific manner and in very high yields. In a broader sense, topochemical reactions mimic nature’s way of carrying out reactions in a confined environment of enzymes giving specific products. Apart from their remarkable specificity, topochemical reactions have many other interesting features that make these reactions more attractive than solution-phase reactions.

Solution-phase reactions necessitate the use of reactants, reagents, catalysts, and solvents and often give products along with varying amounts of byproducts, necessitating complex workup and chromatographic purification using various chemicals. These inevitable chemical wastes from solution-state reactions could be avoided by topochemical reactions, as they are solvent-free and catalyst-free and often do not require any chromatographic purification in view of their specificity and high yielding nature. Also the confinement offered by the crystal lattice gives products that are not possible by solution-phase reactions. Another interesting feature of topochemical reactions is the possibility of formation of products in an ordered (crystalline) form, which imparts interesting properties. Thus, topochemical reactions have control not only at the molecular level (regio-/stereospecificity) but also at the supramolecular level (packing). Many topochemical reactions happen in single-crystal-to-single-crystal (SCSC) fashion, and crystal structure analysis of such reactions often gives mechanistic insights and knowledge about the geometrical criteria required for the reaction. **Despite all these attractive features, reactions that can be done topochemically are limited. There is tremendous interest in the development of new categories of topochemical reactions and strategies to achieve reactivity in crystals.**

In this Account, we will summarize our attempts to develop topochemical azide–alkyne cycloaddition (TAAC) reactions. We have used hydrogen-bonding as the main noncovalent interaction for aligning azide-and-alkyne-substituted derivatives of various biomolecules in orientations suitable for their proximity-driven cycloaddition reaction in crystals. Overall, three major classes of biomolecules; carbohydrates, nucleosides, and peptides were successfully exploited for their TAAC reactions using conventional O–H···O, N–H···O, and N–H···N hydrogen bonds as supramolecular glues for controlling their assembly in crystals. The crystals of these monomers underwent TAAC reaction either spontaneously at room temperature or under heating yielding triazole-linked biopolymer mimics. The ordered packing of product molecules imparted special properties to the products formed. The legendary “cream of the crop” azide–alkyne click reaction has diverse applications in the areas of bioconjugation, material science, polymer synthesis, and so forth. Belonging to the same genre, TAAC is a novel metal-free approach for making the triazole-linked products employing the ordered crystal/gel as a reaction medium. In brief, our studies suggest that TAAC reaction can be implemented in diverse molecular categories and has high potential to develop into a field with practical applications.

Comment: Personally, I did not know about this topic, and I think it is a big review with a vast content about this topochemichal click reaction, presenting its impact in different fields of chemistry ranging from organic synthesis to biochemistry, and in different reaction enviroments like gels and crystals.