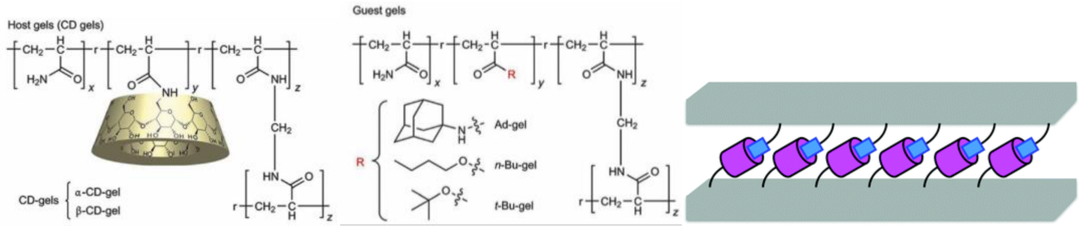
Adhesive Supramolecular Polymeric Materials Constructed from Macrocycle-Based Host–Guest Interactions

Ji, X.; Ahmed, M.; Long, L.*; Khashab, N. M.*; Huang, F.;* Sessler, J. L.* *Chem. Soc. Rev.* ***2019**, Advance Article*.

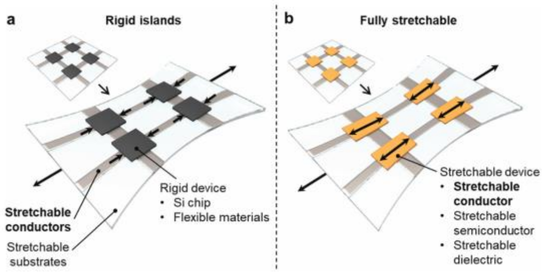


Nature uses the power of non-covalent interactions as the basis for many kinds of adhesion phenomena. Inspired by nature, scientists have prepared various synthetic adhesive materials that rely on a number of non-covalent interactions at the interfaces. Commonly used non-covalent interactions include **hydrogen bonding**, **π–π stacking**, **charge transfder interactions**, **electrostatic interactions**, **hydrophobic interactions**, **macrocycle-based host–guest interactions**, among others. Within this context, macrocycle-based host–guest interactions are of particular interest. Often they give rise to distinct properties, such as multiple combined noncovalent interactions and a diversity of stimuli-based responsiveness. In this tutorial review, we will **summarise recent advances** in **adhesive supramolecular polymeric materials** that rely primarily on **macrocycle-based host–guest interactions**. An overview of future challenges and a perspective of this sub-field are also provided.

Comment: This review may be of interest to anyone who wishes to familiarize themselves with macrocycle-based host-guest interactions. This paper is not comprehensive but is well explained and short enough to quickly understand the main aspects of this specific field.

Materials and Structural Designs of Stretchable Conductors

Matsuhisa, N.*; Chen, X.; Bao, Z.; Someya, T. *Chem. Soc. Rev.* ***2019**, Advance Article*

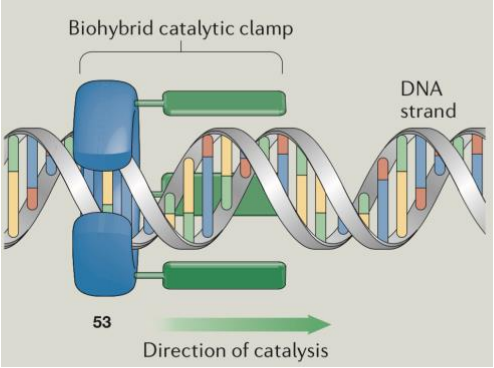


Stretchable conductors are essential building blocks for stretchable electronic devices used in next-generation wearables and soft robotics. Over 10 years of research in stretchable electronics has produced stretchable sensors, circuits, displays, and energy harvesters, mostly enabled by unique stretchable conductors. This review covers **recent advances in stretchable conductors**, which have been achieved by engineering their structures, materials, or both. **Advantages**, **mechanisms**, and **limitations** of the different classes of stretchable conductors are discussed to provide insight into which class of stretchable conductor is suitable for fabrication of various stretchable electronic devices. The significantly improved electronic performance and wide variety of stretchable conductors are creating a new paradigm in stretchable electronics.

Comment: This second review offers a complete coverage of a theme which does not exactly concern our group. However, I found it really useful to have an insight of the field of stretchable conductors and its main limitations. Besides, this paper does not only present the description of the different strategies applied to obtain stretchable conductive materials but also an overview of the main examples of its applications. I definitely recommend this article.

Molecular Machines for Catalysis

van Dijk, L.; Tilby, M. J.; Szpera, R.; Smith, O. A.; Bunce, H. A. P.; Fletcher, S. P. *Nat. Rev. Chem.* **2018**, *2*, 0117.

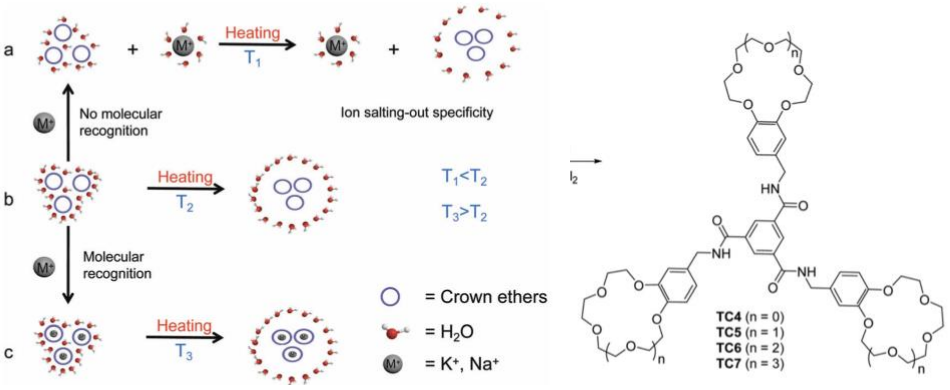


The past few decades have seen tremendous progress in the synthesis and operation of molecular systems capable of controlled mechanical movement. Here, **we review the use of molecular machines as catalysts for controlling chemical reactions**. We highlight the various catalyst designs with a focus on how mechanical motion is used to control catalysis with varying degrees of success. This Review discusses the current challenges of designing effective catalysts, the scope and limitations of various systems and the future potential and aims for the field. Although it is difficult to predict which concepts will become most important, as much of the work is at the proof-of-concept level, it seems clear that molecular machines have the potential to substantially impact the field of catalysis.

Comment: As far as I can tell this is a comprehensive review on the uses of molecular machines – you could argue switches – to control chemical reactions. It is, probably, one of the most obvious practical applications of molecular machines and, as a consequence, a valuable arsenal in your thesis-defense preparation. Happy reading!

LCST Behavior Controlled by Size-Matching Selectivity from Low Molecular Weight Monomer Systems

Luo, Z.; Deng, Y.; Li, X.; Zhang, Q.; Wu, J.; Qi, Z.; Jin, L.; Dong, S. *New J. Chem.* **2019**, *43*, 6890–6896.

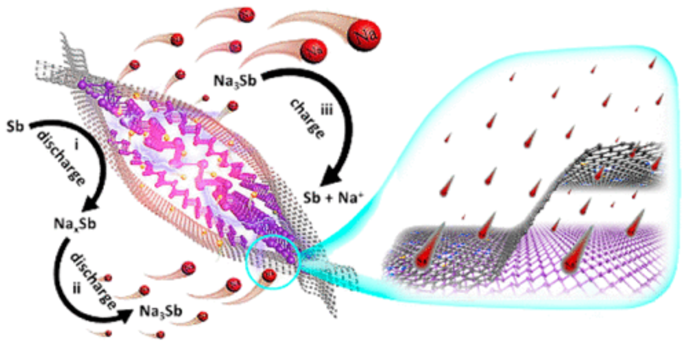


Despite increasing attention being focused on traditional polymer-based LCST systems, only a limited number of LCST systems induced by small molecules have been investigated. In this paper, we developed a series of new thermo-responsive small molecules with crown ether units as the thermo-sensitive cores. The diversity in the crown ether structures fully demonstrates the differences in water solubility and LCST properties. Due to the competition between the supramolecular recognition process induced by the size-matching selectivity and the salting-out effect caused by cation–water–crown ether solvation, controllable and programmable thermo-responsive properties are realized.

Comment: Somehow information got lost somewhere: If you read the paper you will notice that little to no mention is made of typical BTA aggregation. My first instinct was to imagine that they had miss it? But "how" was the question. The answer was more complex than that: They borrowed the molecular design from a paper (*Sci. Adv.* **2017**, *3*, eaao0900) that is (partially) authored by C. Schalley. In that paper, they discuss extensively the role on water in these systems and only quickly discuss triple hydrogen bonding (which is fair). Probably, that part and how important the basic structure might be for the system was deemed less important? Anyways, funny to read in any case.

Antimony Nanorod Encapsulated in Cross-Linked Carbon for High-Performance Sodium Ion Battery Anodes

Cui, C.; Xu, J.; Zhang, Y.; Wei, Z.; Mao, M.; Lian, X.; Wang, S.; Yang, C.; Fan, X.; Ma, J.*; Wang, C.* *Nano Lett.* **2019**, *19*, 538–544.

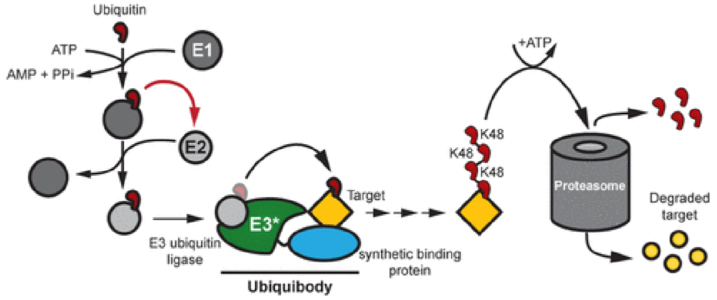


Antimony- (Sb) based materials have been considered as one of promising anodes for sodium ion batteries (SIBs) owing to their high theoretical capacities and appropriate sodium inserting potentials. So far, the reported energy density and cycling stability of the Sb-based anodes for SIBs are quite limited and need to be significantly improved. Here, we develop a novel Sb/C hybrid encapsulating the Sb nanorods into highly conductive N and S codoped carbon (Sb@(N, S–C)) frameworks. As an anode for SIBs, the Sb@(N, S–C) hybrid maintains high reversible capacities of 621.1 mAh g^{-1} at 100 mA g^{-1} after 150 cycles, and 390.8 mAh g^{-1} at 1 A g^{-1} after 1000 cycles. At higher current densities of 2, 5, and 10 A g^{-1}, the Sb@(N, S–C) hybrid also can display high reversible capacities of 534.4, 430.8, and 374.7 mAh g^{-1}, respectively. Such impressive sodium storage properties are mainly attributed to the unique cross-linked carbon networks providing highly conductive frameworks for fast transfer of ions and electrons, alleviating the volume expansion and preventing the agglomeration of Sb nanorods during the cycling.

Comment: Sodium batteries could be a suitable alternative to lithium in batteries. Sodium is easily available compared to lithium. However, there is still much development needed before we are there. Sb has shown remarkable properties with sodium but the volume changes with the sodium fluxes during the charge/discharge cycles make it quite a challenge. Here, the coating of Sb nanorods with a thin, doped, conductive carbon layer, helps stabilize the electrode and allows for the sodium fluxes.

Broad-Spectrum Proteome Editing with an Engineered Bacterial Ubiquitin Ligase Mimic

Ludwicki, M. B.; Li, J.; Stephens, E. A.; Roberts, R. W.; Koide, S.; Hammond, P. T.; DeLisa, M. P.* *ACS Cent. Sci.* **2019**, ASAP.

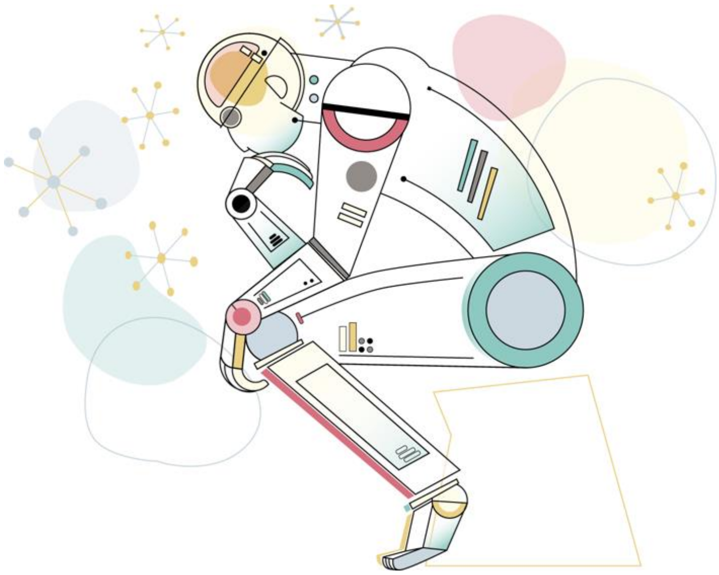


Manipulation of the ubiquitin-proteasome pathway to achieve targeted silencing of cellular proteins has emerged as a reliable and customizable strategy for remodeling the mammalian proteome. One such approach involves engineering bifunctional proteins called ubiquibodies that are comprised of a synthetic binding protein fused to an E3 ubiquitin ligase, thus enabling post-translational ubiquitination and degradation of a target protein independent of its function. Here, we have designed a panel of new ubiquibodies based on E3 ubiquitin ligase mimics from bacterial pathogens that are capable of effectively interfacing with the mammalian proteasomal degradation machinery for selective removal of proteins of interest. One of these, the *Shigella flexneri* effector protein IpaH9.8 fused to a fibronectin type III (FN3) monobody that specifically recognizes green fluorescent protein (GFP), was observed to potently eliminate GFP and its spectral derivatives as well as 15 different FP-tagged mammalian proteins that varied in size (27–179 kDa) and subcellular localization (cytoplasm, nucleus, membrane-associated, and transmembrane). To demonstrate therapeutically relevant delivery of ubiquibodies, we leveraged a bioinspired molecular assembly method whereby synthetic mRNA encoding the GFP-specific ubiquibody was coassembled with poly A binding proteins and packaged into nanosized complexes using biocompatible, structurally defined polypolypeptides bearing cationic amine side groups. The resulting nanoplexes delivered ubiquibody mRNA in a manner that caused efficient target depletion in cultured mammalian cells stably expressing GFP as well as in transgenic mice expressing GFP ubiquitously. Overall, our results suggest that IpaH9.8-based ubiquibodies are a highly modular proteome editing technology with the potential for pharmacologically modulating disease-causing proteins.

Comment: An interesting technology with incredible potential. The team also engineered a delivery method to create the proteins inside the cells. The major drawback is that this silencing happens post transcription compared to CRISPR that operates on DNA or RNA. However, it does mean that it can circumvent some of CRISPR's problems.

Machine Learning, Practically Speaking

Marx, V.* *Nat. Methods* **2019**, ASAP.



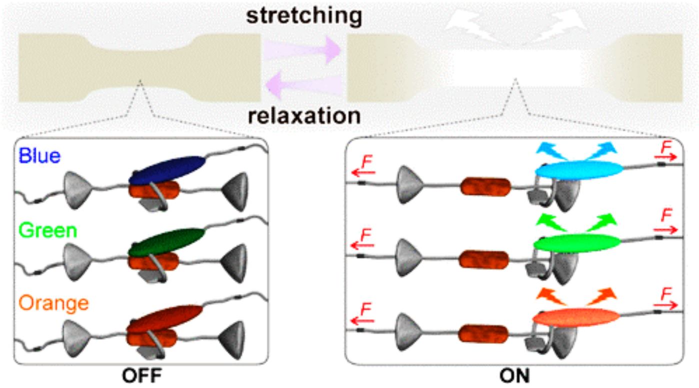
To apply machine learning, labs needn't have years of computational expertise, but they do need a cautious mind-set.

'Artificial intelligence' (AI) is hard to beat as an enigmatic term. Within the AI field, many projects involve machine learning (ML), in which a computer can learn iteratively from data and make predictions[1]. Basic ideas of ML architectures have been around for decades and have fallen in and out of favor, says Don Geman of Johns Hopkins University. What has changed of late is the availability of massive amounts of labeled data, such as faces, which can be used to train ML systems. Computing power has grown because of graphics-processing units. "Those two things allowed basically the same methodology to suddenly work far better than it had before and far better than anything else was working," he says.

Comment: As always with Nature methods, no abstract but just a sentence is given, so I included the first paragraph. Machine learning is a very powerful and promising technology that is beginning to appear in all the realms of science, it does not require a thorough understanding of it to be used and that may lead to dubious results. So here is a small recap of what this cryptic technology does, what it is good at, what it is not good at, and some of its limitations.

Rotaxane-Based Mechanophores Enable Polymers with Mechanically Switchable White Photoluminescence

Sagara, Y.; Karman, M.; Seki, A.; Mehboobali, P.; Tamaoki, N.; Weder, C.* *ACS Cent. Sci. ASAP*.

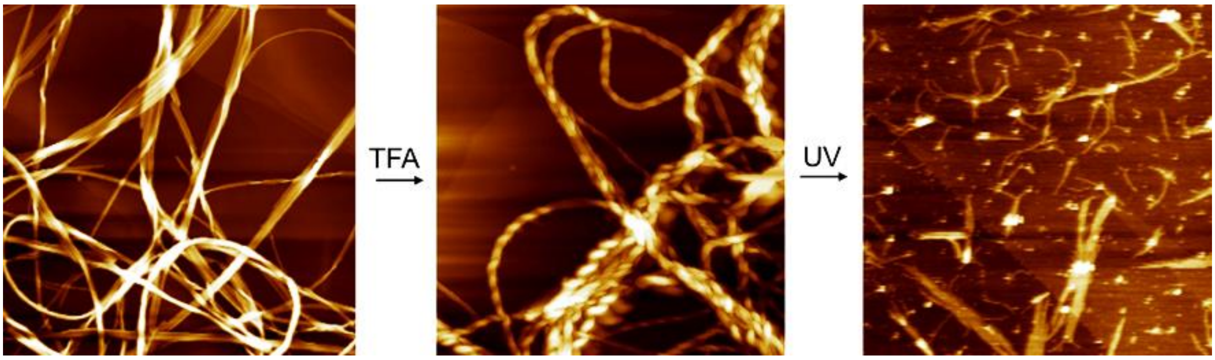


Three mechanoresponsive polyurethane elastomers whose blue, green, and orange photoluminescence can be reversibly turned on by mechanical force were prepared and combined to create a blend that exhibits deformation-induced white photoluminescence. The three polyurethanes contain rotaxane-based supramolecular mechanoluminophores based on π-extended pyrene, anthracene, or 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM) luminophores, respectively, and 1,4,5,8-naphthalenetetracarboxylic diimide as an electronically matched quencher. Each polymer shows instantly reversible, strain-dependent switching of its photoluminescence intensity when stretched and relaxed, as deformation leads to a spatial separation of the luminophore and quencher. The present study shows that the photoluminescence color can easily be tailored by variation of the luminophore and also by combining several mechanophores in one material and demonstrates that adaptability is a key advantage of supramolecular approaches to create mechanoresponsive polymers.

Comment: This article is really interesting since the authors show a supramolecular approach to mecanophores overcoming the principal disadvantages of these systems: high activation energy for the breaking of covalent bonds. In this case, the mecanophores do not require scission of the covalent bonds and the optical signal produced by a given polymer can be tuned in terms of the synthetic design. By the way, this paper is one of the most recent examples having polyurethane-embedded rotaxanes.

Mechanistic Insights into the Self-Assembly of an Acid-Sensitive Photoresponsive Supramolecular Polymer

Kartha, K.; Allampally, N.; Yagai, S.; Albuquerque, R.; Fernandez, G.* *Chem. Eur. J. ASAP*.

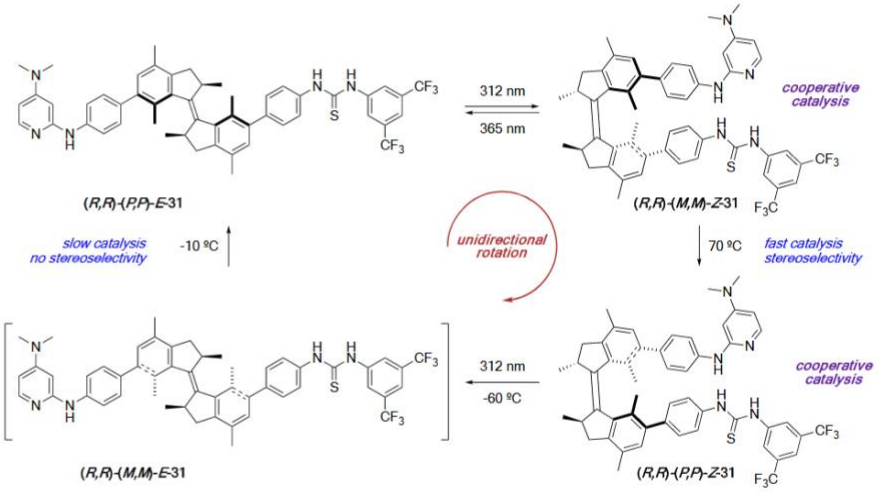


The supramolecular polymerization of an acid-sensitive pyridyl-based ligand (**L**$_1$) bearing a photoresponsive azobenzene moiety was elucidated by mechanistic studies. Addition of trifluoroacetic acid (TFA) led to the transformation of the antiparallel H-bonded fibers of $\mathbf{L_1}$ in methylcyclohexane into superhelical braid-like fibers stabilized by H-bonding of parallel-stacked monomer units. Interestingly, $\mathbf{L_1}$ dimers held together by unconventional pyridine–TFA N···H···O bridges represent the main structural elements of the assembly. UV-light irradiation caused a strain-driven disassembly and subsequent aggregate reconstruction, which ultimately led to short fibers. The results allowed to understand the mechanism of mutual influence of acid and light stimuli on supramolecular polymerization processes, thus opening up new possibilities to design advanced stimuli-triggered supramolecular systems.

Comment: In this paper, the authors tested the acid-sensitive properties of the pyridyl group of an azo ligand demonstrating that the addition of TFA on the self-assembly of a photoresponsive compound results in unconventional pyridine–TFA N···H···O bridges that drive the self-assembly process. Also, the findings about the relationship between acid and light on supramolecular polymerization processes is intriguing.

Photoswitchable Catalysis Based on the Isomerisation of Double Bonds

Dorel, R.; Feringa, B. L.* *Chem. Commun.* **2019**.

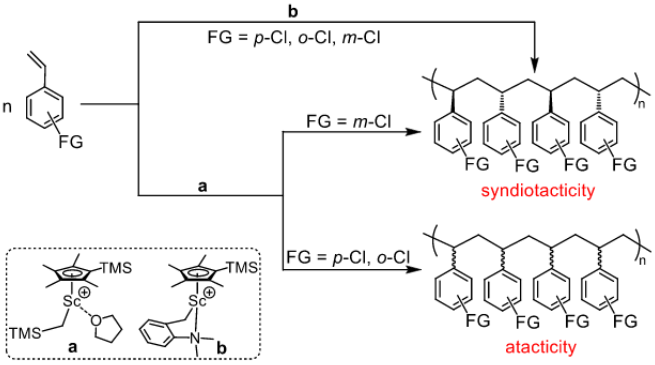


Photoswitchable catalysis is a young but rapidly evolving field that offers great potential for non-invasive dynamic control of both activity and selectivity in catalysis. Within this context, the E/Z photoisomerisation of double bonds in molecular switches and motors is one of the most popular tools to control the catalytic activity essentially due to its reversible nature, the large concomitant geometrical changes, and the high tunability of such photochromic entities. This Feature Article summarises the key developments accomplished over the past years through the incorporation of photoswitchable double bonds into catalytically competent molecules and shows some perspectives on the remaining challenges and possibilities arising from this, yet still somehow immature, exciting area of research.

Comment: This article presents a review on the field of photoswitchable catalysis. The review describes the recent advances and paves the way for the development of future applicable light-responsive catalysts. Maybe it is a good idea to compare this review to the one published ca. 6 months earlier (*Nat. Rev. Chem.* **2018**, *2*, 0117.)

“C−H•••π Interaction” Regulates Stereoselectivity in Olefin Polymerization

Zhao, Y.; Luo, G.*; Kang, X.; Guo, F.; Zhu, X.; Zheng, R.; Hou, Z.; Luo, Y.* *Chem. Commun.* **2019**, ASAP.



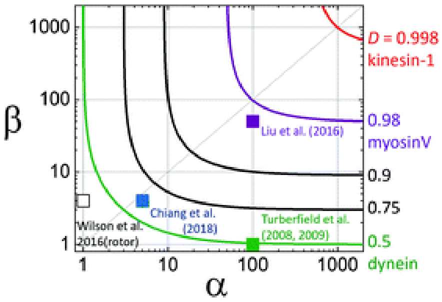
Scheme 1 Polymerization of Various ClSt by Cationic Species **a** and **b**.

DFT calculations disclosed that the stereoselectivity of Sc-catalysed polymerization of halogenated styrenes could be co-regulated via C−H···π interactions between a coordinating THF and the phenyl ring of monomer. Such a regulation mechanism was theoretically confirmed by further calculating the polymerization of various monomers, where the stereoselectivity could even shift from syndiotacticity to isotacticity.

Comment: This article is based almost exclusively on DFT calculations. I reckon that this study may be a little far from our skills and interests, but it provides a better understanding of the supramolecular interaction mechanisms involved in stereo-controlled polymerization of polynaphthalene.

Track-Walking Molecular Motors: A New Generation Beyond Bridge-Burning Designs

Wang, Z.;* Hou, R.; Loh, I. Y. *Nanoscale*, **2019**, *Advance Article*.

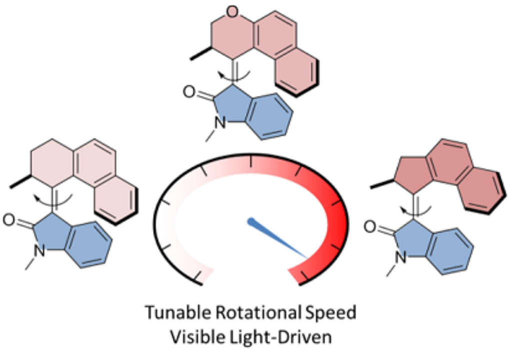


Track-walking molecular motors are the core bottom-up mechanism for nanometre-resolved translational movements – a fundamental technological capability at the root of numerous applications ranging from nanoscale assembly lines and chemical synthesis to molecular robots and shape-changing materials. Over the last 10 years, artificial molecular walkers (or nanowalkers) have evolved from the 1st generation of bridge-burning designs to the 2nd generation capable of truly sustainable movements. Invention of non-bridge-burning nanowalkers was slow at first, but has picked up speed since 2012, and is now close to breaking major barriers for wide-spread development. Here we review the 2nd generation of artificial nanowalkers, which are mostly made of DNA molecules and draw energy from light illumination or from chemical fuels for entirely autonomous operation. They are typically symmetric dimeric motors walking on entirely periodic tracks, yet the motors possess an inherent direction for large-scale amplification of the action of many motor copies. These translational motors encompass the function of rotational molecular motors on circular or linear tracks, and may involve molecular shuttles as 'engine' motifs. Some rules of thumb are provided to help readers design similar motors from DNA or other molecular building blocks. Opportunities and challenges for future development are discussed, especially in the areas of molecular robotics and active materials based on the advanced motors.

Comment: A review for those who are interested in learning about molecular motion mechanisms. Here they focus on the progress of the translational molecular motors beyond bridge-burning designs. The illustrated examples are mostly systems made of DNA and are powered by light from outside, or by chemical fuels via a motor's autonomous operation.

Visible-Light-Driven Tunable Molecular Motors Based on Oxindole

Roke, D.; Sen, M.; Danowski, W.; Wezenberg, S. J.*; Feringa, B. L.* *J. Am. Chem. Soc.* **2019**, *141*, 7622.

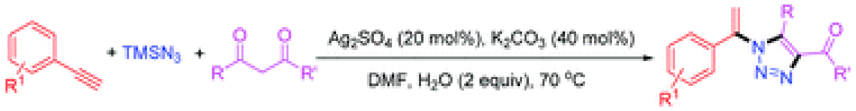


Molecular rotary motors based on oxindole which can be driven by visible light are presented. This novel class of motors can be easily synthesized via a Knoevenagel condensation, and the choice of different upper halves allows for the facile tuning of their rotational speed. The four-step rotational cycle was explored using DFT calculations, and the expected photochemical and thermal isomerization behavior was confirmed by NMR, UV/vis, and CD spectroscopy. These oxindole motors offer attractive prospects for functional materials responsive to light.

Comment: This new type of molecular motor reported by Feringa's group is interesting, because it can use visible light (455 nm) to drive the motion which is relevant to me and Joakim's project. The synthesis also seems pretty simple which is also very convenient.

Silver-Mediated Three-Component Cycloaddition Reaction for Direct Synthesis of 1-N-Vinylsubstituted 1,2,3-Triazoles

Chen, J.; Liang, T.; Zhao, H.; Lin, C.; Chen, L.; Zhang, M.* *Org. Biomol. Chem.* **2019**, *Advanced Article.*

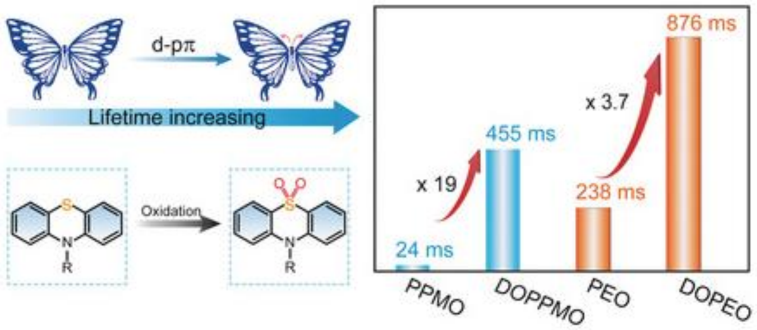


Herein, we report direct synthesis of 1-*N*-vinyl-1,2,3-triazoles *via* silver-mediated three-component cycloaddition reaction of phenylacetylenes, trimethylsilylazide, and 1,3-dicarbonyl compounds. The synthetic protocol proceeds with operational simplicity, good substrate and functional group compatibility, and easily available feedstocks, and without the need for pre-installation of vinylazide precursors, and offers a practical method for the efficient elaboration of triazole derivatives.

Comment: This is an interesting article describing an easy and simple direct synthesis of 1-N-vinyl-1,2,3-triazoles. It avoids the preparation of the vinyl organoazide derivatives, generally unstable compounds, by preparing it in situ in a silver-mediated three component cycloaddition reaction of phenyacetylenes, trimethylsilylazide, and 1,3-dicarbonyl compounds.

Utilizing d-pπ Bond for Ultralong Organic Phosphorescence

Tian, S.; Ma, H.; Wang, X.; Lv, A.; Shi, H.; Geng, Y.; Li, J.; Liang, F.; Su, Z.-M.; An, Z.; Huang, W.* *Angew. Chem. Int. Ed.* **2019**, 58, 6645.

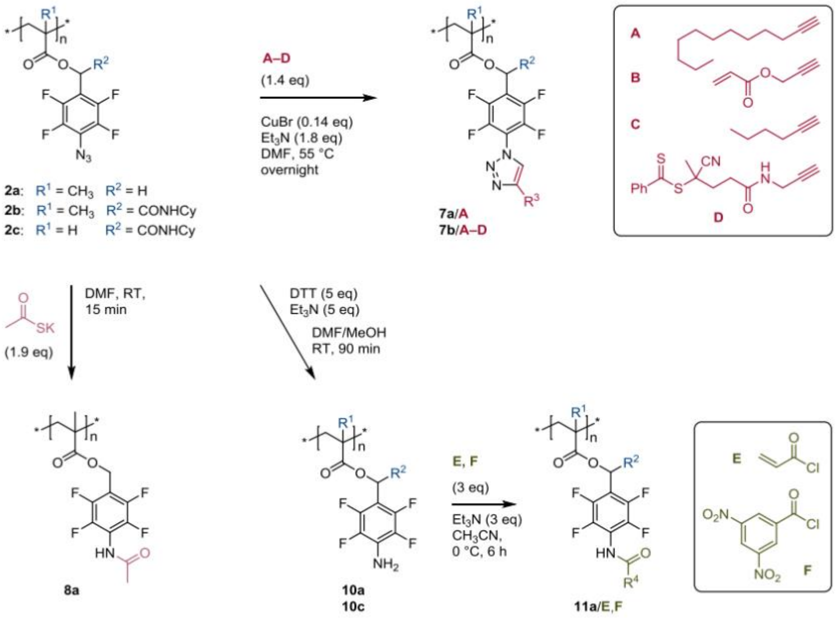


Developing pure organic materials with ultralong lifetimes is attractive but challenging. Here we report a concise chemical approach to regulate the electronic configuration for phosphorescent enhancement. After introduction of d-pπ bonds in phenothiazine model, up to 19 times phosphorescence lifetime enhancement was observed for DOPPMO, compared with the reference PPMO. A record phosphorescence lifetime of up to 876 ms was obtained in phenothiazine phosphors. Theoretical calculations and single crystal analysis reveal that the d-pπ bond not only reduces the (n, π*) proportion of T1, but also frames rigid molecular environment with multiple intermolecular interactions, thus enabling long-lived phosphorescence. This finding will take a giant step forward in prolonging phosphorescence lifetime and extending the scope of phosphorescent materials.

Comment: Creating phosphorescent materials without heavy metals is an interesting challenge. This paper describes a relatively simple chemical method to produce a remarkably long phosphorescent lifetime for an organic molecule.

Azide–*para*-Fluoro Substitution on Polymers: Multipurpose Precursors for Efficient Sequential Postpolymerization Modification

Noy, J.-M.; Li, Y.; Smolan, W.; Roth, P. J.* *Macromolecules* **2019**, *52*, 3083–3091.

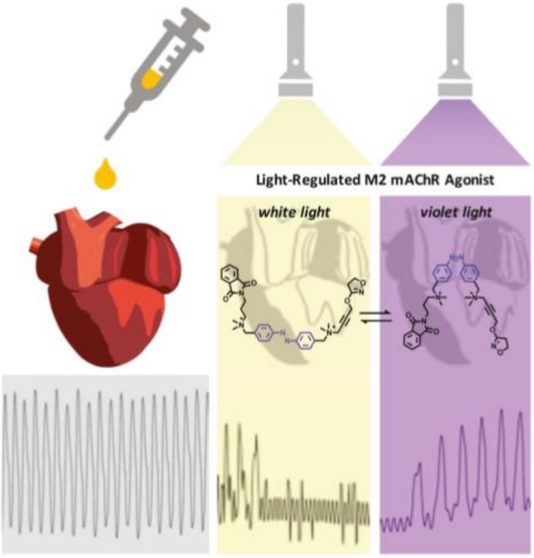


The **2,3,4,5,6-pentafluorobenzyl group** has become a popular reactive functionality in polymer chemistry because of its high susceptibility to *para*-fluoro substitution with thiols. Herein, it is demonstrated postpolymerization that the ***para*-fluoride can be substituted using sodium azide** and that the resulting 4-azido-2,3,5,6-tetrafluorobenzyl-functional polymers are versatile precursors for a multitude of onward modifications with click-like efficiencies. Quantitative azide–*para*-fluoro substitution was found for poly(2,3,4,5,6-pentafluorobenzyl methacrylate) and the related Passerini ester–amide (meth)acrylic (co)polymers when heated in DMF with sodium azide to 80 °C for 60–90 min. Conversely, the azidation of poly(2,3,4,5,6-pentafluorostyrene) under similar conditions resulted in ~90% substitution efficiency. Azide-functional (co-)polymers were thermally stable below 100 °C and were subsequently modified with (i) four different alkynes (CuBr, triethylamine, DMF, 55 °C, overnight) to **give 1,4-substituted 1,2,3-triazoles in >95% conversions**; (ii) potassium thioacetate (DMF, RT, 15 min) with **quantitative amidation to the acetanilide derivative**; and (iii) DL-dithiothreitol (methanol/DMF, RT, 90 min), resulting in **complete reduction of the azides to primary amines**, which were subsequently acylated with two different acyl chlorides. Products were characterized by ^{1}H NMR, ^{19}F NMR, Fourier transform infrared spectroscopies, and size exclusion chromatography. Given their adaptability, perfluorophenylazides have huge potential as multipurpose intermediates in polymer and materials chemistry.

Comment: Accessing new multifunctional polymeric materials requires new synthetic methodologies to functionalize macromolecules. The authors present the introduction of azide moieties by post-polymerization substitution of the *p*-fluoride of 2,3,4,5,6-pentafluorobenzyl groups with sodium azide, and the subsequent functionalizations, by either “click” coupling, amidation or reduction, which proceeded with good yields after optimization. Unfortunately, **the substitution with sodium azide worked quantitatively only for one of the tested polymers**, which will probably limit the potential application of this approach.

Optical Control of Cardiac Function with a Photoswitchable Muscarinic Agonist

Riefolo, F.; Matera, C.; Garrido-Charles A.; Gomilla, A. M. J.; Sortino, R.; Agnetta, L.; Claro E.; Masgrau R.; Holzgrabe, U.; Batlle M.; Decker, M.; Guasch, E.; Gorostiza, P.* *J. Am. Chem. Soc.*, **2019**, *141*, 7628–7636.

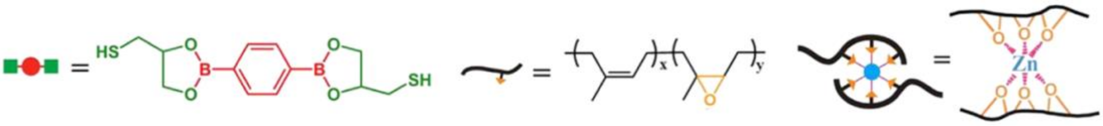


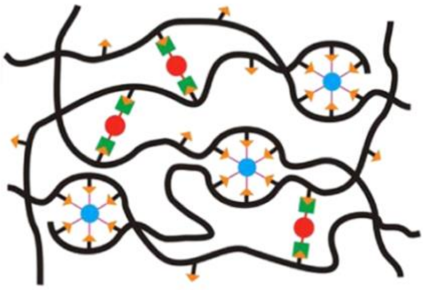
Light-triggered reversible modulation of physiological functions offers the promise of enabling on-demand spatiotemporally controlled therapeutic interventions. Optogenetics has been successfully implemented in the heart, but significant barriers to its use in the clinic remain, such as the need for genetic transfection. Herein, we present a method to modulate cardiac function with light through a photoswitchable compound and without genetic manipulation. The molecule, named PAI, was designed by introduction of a photoswitch into the molecular structure of an M2 mAChR agonist. In vitro assays revealed that PAI enables light-dependent activation of M2 mAChRs. To validate the method, we show that PAI photoisomers display different cardiac effects in a mammalian animal model, and demonstrate reversible, real-time photocontrol of cardiac function in translucent wildtype tadpoles. PAI can also effectively activate M2 receptors using two-photon excitation with near-infrared light, which overcomes the scattering and low penetration of short-wavelength illumination, and offers new opportunities for intravital imaging and control of cardiac function.

Comment: The proposed method still requires optimization (cis to trans isomerization efficacy, control of the cardiac rhythm…) but I am curious to see it applied to mammalians, which should be doable with two-photon NIR light. This is definitely, in my opinion, an interesting read for our group as this is a –very simple– molecular muscle of sorts.

Mechanically Robust, Self-Healable, and Reprocessable Elastomers Enabled by Dynamic Dual Cross-Links

Chen, Y.; Tang, Z.*; Liu, Y.; Wu, S.; Guo, B.* *Macromolecules* **2019**, *ASAP.*



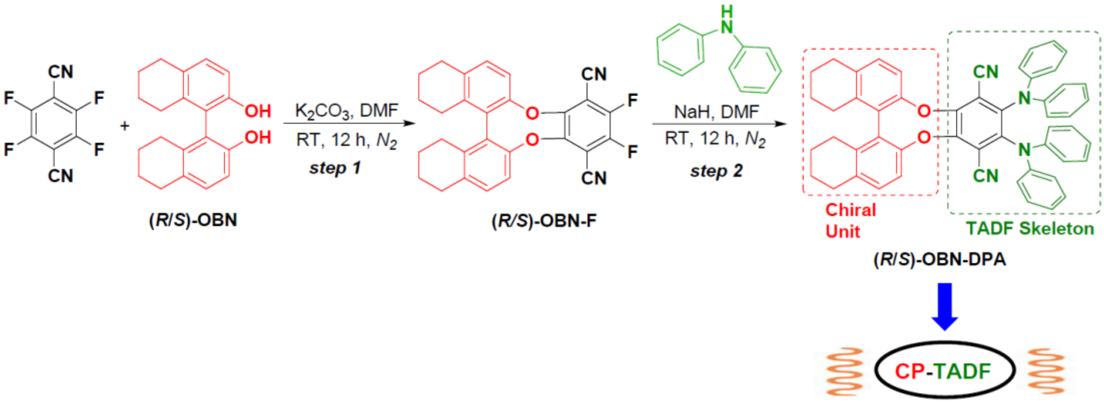


Covalent cross-linking of rubbers is essential for obtaining high resilience and environmental resistance but prevents healing and recycling. **Integrating dynamic covalent bonds into cross-linked rubbers can resolve the trade-off between permanent cross-linking and plasticity.** The state-of-the-art elastomer-based dynamic covalent networks require either intricate molecular makeup or present poor mechanical properties. In this work, we demonstrate a simple way to prepare **mechanically robust yet healable and recyclable elastomeric vitrimers** by engineering **dynamic dual cross-links of boronic esters and coordination bonds** into a commercial rubber. Specifically, epoxidized natural rubber is covalently cross-linked with a boronic ester cross-linker carrying dithiol through chemical reaction between epoxy and thiol groups. The covalently cross-linked networks are able to alter the topologies through boronic ester transesterifications, thereby conferring them with healing ability and reprocessability. In particular, the mechanical properties can be remarkably enhanced by introducing **sacrificial metal–ligand coordination** bonds into the networks without compromising the healing ability or reprocessability.

Comment: Considering that our team is working on self-healable and recyclable polyurethanes, this paper is of prime interest for the people working on this project. The design presented in this article is based on epoxidized polybutadiene rubber crosslinked with difunctional boronic esters, conferring the self-healing properties to the material. The loading with Zn^{2+} ions increases the mechanical properties of the resulting elastomer. **My main concern here is, however, about the zinc ions: do they stay in the material or will they pollute the environment when the rubber is used?**

Non-Doped and Doped Circularly Polarized Organic Light-Emitting Diodes with High Performances Based on Chiral Octahydro-binaphthyl Delayed Fluorescence Luminophores

Wu, Z. G.; Yan, Z. P.; Luo, X. F.; Yuan, L.; Liang, W. Q.; Wang, Y.; Zheng, W. X.; Zeng, Y. X.* *J. Mater. Chem. C* **2019**, *ASAP.*

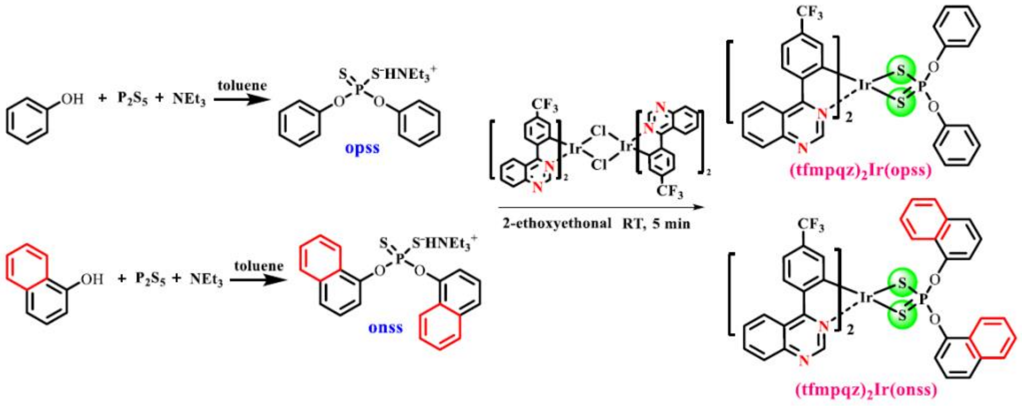


Circularly polarized organic light-emitting diodes (CP-OLEDs) are of great value for facilitating the development of the next generation of display technologies, especially for implementing real 3D display. However, most CP-OLEDs have insufficient efficiency and serious efficiency roll-off. In this study, a pair of octahydro-binaphthyl (**OBN**)-based chiral emitting enantiomers, **(R/S)-OBN-DPA**, were synthesized by ingeniously merging chiral source and luminophore skeleton of cyan and diphenylamine groups. The chirality–acceptor–donor (C–A–D) type enantiomers concurrently demonstrate a high photoluminescence quantum yield of 84.67%, and intense circularly polarized photoluminescence with dissymmetry factors ($|g_{PL}|$) around 2.0×10^{-3} in the films. The non-doped and doped CP-OLEDs achieve markedly circularly polarized electroluminescence signals with $|g_{EL}|$ up to 2.9×10^{-3}, high brightness over 25000 cd cm^{-2}, high efficiency with maximum external quantum efficiency (EQE_{max}) of 12.4%, and negligible efficiency roll-off with EQE of 11.5% at the practical luminance of 1000 cd m^{-2}, which are the best performances among the reported CP-devices to date.

Comment: The authors provide a feasible pathway towards the development of effective CPL materials, especially based on Small Organic Molecules (SOMs), and their corresponding CP-OLEDs with simultaneously high efficiency and intense CPE in the same device.

Rapid room temperature synthesis of red iridium(III) complexes with Ir-S-P-S structures for efficient OLEDs

Su, N.; Yang, H.; Shen, C.-Z.; Yan, Z.-P.; Chen, Z.-X.; Zheng, Y.-X.* *J. Mater. Chem. C* **2019**, ASAP.

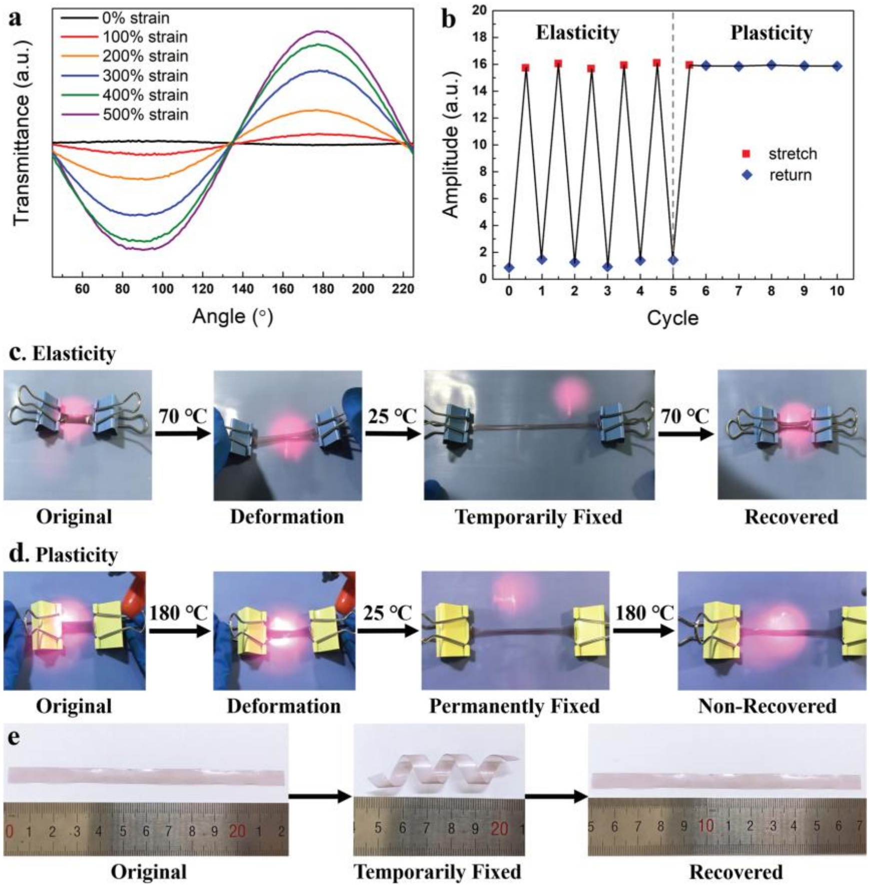


Due to the strong coordination ability between sulfur and iridium atoms, the O,O-diphenyl S-hydrogen phosphorodithioate acid (opss) and O,O-di(naphthalen-1-yl) S-hydrogen phosphorodithioate acid (onss) were applied as ancillary ligands in two red iridium(III) complexes. Both complexes (tfmpqz)$_2$Ir(opss) and (tfmpqz)$_2$Ir(onss) with Ir-S-P-S four membered ring structures were obtained rapidly at room temperature in 5 min with high yields, in which 4-(4-(trifluoromethyl)phenyl)-quinazoline (tfmpqz) was used as main ligand, and the calculated Gibbs free energy changes of both complexes formation reactions further prove that they are exothermic and thermodynamically beneficial processes. Both Ir(III) complexes show identical PL emissions at 600 nm with high phosphorescence quantum yields of 0.68 and 0.79, respectively. Using the two complexes as dopants, the organic light emitting devices with the structure of ITO/ HATCN (hexaazatriphenylenehexacabonitrile, 5 nm)/ TAPC ((bis(4-(N,N-ditolylamino)phenyl)cyclohexane, 30 nm)/ (tfmpqz)$_2$Ir(opss) or (tfmpqz)$_2$Ir(onss): 26DCzppy (2,6-bis-(3-(carbazol-9-yl)phenyl)pyridine) (12 wt%, 10 nm)/ TmPyPB (1,3,5-tri((3-pyridyl)-phen-3-yl)benzene, 30 nm)/ LiF (1 nm)/ Al (100 nm) achieve good performances. Especially, due to the larger conjugated degree of $(tfmpqz)_2Ir(onss)$ complex, its device exhibits better device performances with a maximum luminance of 52 030 cd m^{-2}, a maximum current efficiency of 57.98 cd A^{-1}, a maximum power efficiency of 44.40 lm W^{-1} and a maximum external quantum efficiency of 24.90%.

Comment: The synthesis of Ir complexes for phosphorescent devices require normally long reaction times and high temperatures which strongly increase the time and cost, and reduce the productivity. Here, the authors develop new ligands which could be used to rapidly synthesize Ir(III) complexes at room temperature.

Self-Healing of Polarizing Films via the Synergy Between Gold Nanorods and Vitrimer

Zhao, G.; Zhou, Y.; Wang, J.; Wu, Z.; Wang, H.* and Chen, H.* Adv. Mater. ***2019***, 31, *1900363*

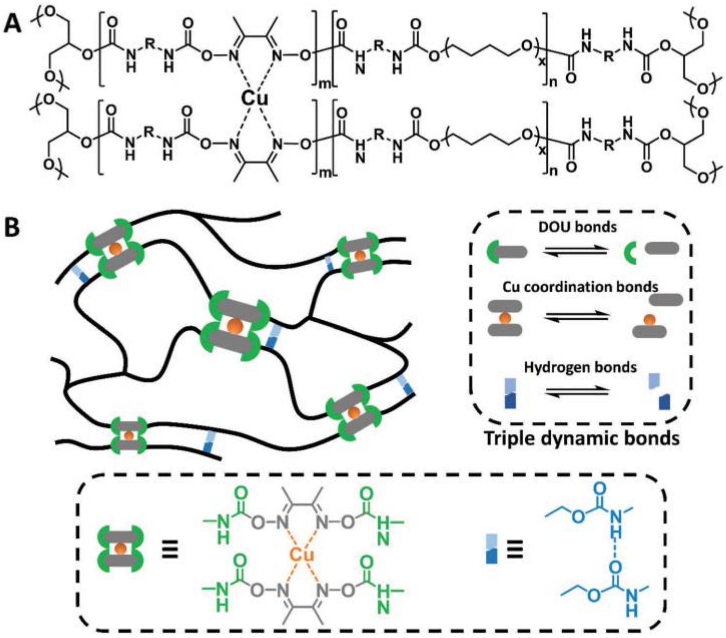


Conventional self-healing is about the recovery of shape and mechanical properties. In contrast, recovery of functional properties is still a great challenge, especially for optical functional materials, as the known self-healing methods are incompatible with optical properties. By utilizing the synergistic effect between Au nanorods and vitrimer, the alignment of Au nanorods can be achieved in the crosslinked polymer. **The optical properties** of the resulting polarizing film, such as light transmittance and polarization degree, **can be fully recovered** without an external repair agent. With simple laser irradiation to induce the photothermal effect of Au nanorods, the shape-memory effect of vitrimer returns the Au nanorods to their initial orientation, and the plasticity achieves in situ self-healing of the cutting area. The self-healing of polarizing film provides a new research direction and reference for the application of self-healing systems in functional materials.

Comment: The presented results go one step further in the self-healing ability of polymers. For once, the mechanical properties are absolutely not mentioned, only the optical properties are studied. Here, Au nanorods are properly aligned by stretching.

A Highly Efficient Self-Healing Elastomer with Unprecedented Mechanical Properties

Zhang, L.; Liu, Z.; Wu, X.; Guan, Q.; Chen, S.; Sun, L.; Guo, Y.; Wang, S.; Song, J.; Meade Jeffries, E.; He, C.; Qing, F.L.; Bao, X.; and You, Z.* *Adv. Mater.* **2019**, *31*, 1901402



It is highly desirable, although very challenging, to develop self-healable materials exhibiting both high efficiency in self-healing and excellent mechanical properties at ambient conditions. Herein, a novel Cu(II)–dimethylglyoxime–urethane-complex-based polyurethane elastomer (Cu–DOU–CPU) with synergetic triple dynamic bonds is developed. Cu–DOU–CPU demonstrates **the highest reported mechanical performance for self-healing elastomers at room temperature**, with a tensile strength and toughness up to 14.8 MPa and 87.0 MJ m−3, respectively. Meanwhile, the Cu–DOU–CPU spontaneously self-heals at room temperature with an instant recovered tensile strength of 1.84 MPa and a continuously increased strength up to 13.8 MPa, surpassing the original strength of all other counterparts. Density functional theory calculations reveal that the coordination of Cu(II) plays a critical role in accelerating the reversible dissociation of dimethylglyoxime–urethane, which is important to the excellent performance of the self-healing elastomer. Application of this technology is demonstrated by a self-healable and stretchable circuit constructed from Cu–DOU–CPU.

Comment: Here, the authors report a multi-dynamic self-healable polyurethane based elastomer. Dimethylglyoxime moieties are particularly interesting because of their double dynamicity: As covalent dynamic and coordination bonds. Pretty close to the PolyU^2 project…