## Synthetic Organic Chemistry Driven by Artificial Intelligence

de Almeida, A. F.; Moreira, R.; Rodrigues, T.\* Nat. Rev. Chem. 2019, 3, 589-604.



Synthetic organic chemistry underpins several areas of chemistry, including drug discovery, chemical biology, materials science and engineering. However, the execution of complex chemical syntheses in itself requires expert knowledge, usually acquired over many years of study and handson laboratory practice. The development of technologies with potential to streamline and automate chemical synthesis is a half- century-old endeavour yet to be fulfilled. Renewed interest in **artificial intelligence (AI)**, driven by improved computing power, data availability and algorithms, is overturning the limited success previously obtained. **In this Review**, we discuss the **recent impact of AI on different tasks of synthetic chemistry** and **dissect selected examples** from the literature. By examining the underlying concepts, we aim to **demystify AI** for bench chemists in order that they may embrace it as a tool rather than fear it as a competitor, spur future research by pinpointing the gaps in knowledge and delineate how chemical AI will run in the era of digital chemistry.

**Comment**: To be honest, this review is a little bit too technical on many aspects for non-chemoinformaticians, thus it may be necessary to re-read a few times the same paragraph before completely understand it. However, in despite of those difficulties, the reader **will** get a better understanding of the functioning principle of artificial intelligence systems.

#### **Dissipative Supramolecular Polymerization Powered by Light**

Yin, Z.; Song, G.; Jiao, Y.; Zheng, P.; Xu, J.\*; Zhang, X. CCS Chem. 2019, 1, 335-342.



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 polymerized 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**: The system discussed in this paper is cleverly designed. It can only remind us of nature's out-of-equilibrium polymers such as microtubules. In the end, one could argue that the number of cycles (UV-Air) is quite limited (25% loss in degree of polymerization in three cycles) but the authors should be granted the likeliness of that their method being improved in the future. To conclude, this paper is, in my humble opinion, worth reading and the progress should be followed as well.

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#### Artificial Phototropism for Omnidirectional Tracking and Harvesting of Light

Qian, X.; Zhao, Y.; Alsaid, Y.; Wang, X.; Hua, M.; Galy, T.; Gopalakrishna, H.; Yang, Y.; Cui, J.; Liu, N.; He, X.\* *Nat. Nanotechnol.* **2019**, *14*, 1048–1055.



Many living organisms track light sources and halt their movement when alignment is achieved. This phenomenon, known as phototropism, occurs, for example, when plants self-orient to face the sun throughout the day. Although many artificial smart materials exhibit non-directional, nastic behaviour in response to an external stimulus, no synthetic material can intrinsically detect and accurately track the direction of the stimulus, that is, exhibit tropistic behaviour. Here we report an artificial phototropic system based on nanostructured stimuli-responsive polymers that can aim and align to the incident light direction in the three-dimensions over a broad temperature range. Such adaptive reconfiguration is realized through a built-in feedback loop rooted in the photothermal and mechanical properties of the material. This system is termed a sunflower-like biomimetic omnidirectional tracker (SunBOT). We show that an array of SunBOTs can, in principle, be used in solar vapour generation devices, as it achieves up to a 400% solar energy-harvesting enhancement over non-tropistic materials at oblique illumination angles. The principle behind our SunBOTs is universal and can be extended to many responsive materials and a broad range of stimuli.

**Comment:** Light-sensitive materials are widely studied and, hence, it is surprising to notice that nobody thought of the system presented in this paper before. The concept is really simple: a 'stem' bends towards the light source because of an anisotropic contraction of the material along its thickness. While the authors proved that it can be applied to many systems with different morphologies, I still think that achieving the best response results in a delicate balance between thickness and the absorption of the material.

#### Cyclodextrin polymer networks decorated with subnanometer metal nanoparticles for high-performance low-temperature catalysis

Huang, T.; Sheng, G.; Manchanda, P.; Emwas, A.; Lai, Z.; Nunes, S.; Peinemann, K.; *Sci. Adv.* **2019**, *5*, eaax6976



The synthesis of support materials with suitable coordination sites and confined structures for the controlled growth of ultrasmall metal nanoparticles is of great importance in heterogeneous catalysis. Here, by rational design of a cross-linked ß-cyclodextrin polymer network (CPN), various metal nanoparticles (palladium, silver, platinum, gold, and rhodium) of subnanometer size (<1 nm) and narrow size distribution are formed via a mild and facile procedure. The presence of the metal

coordination sites and the network structure are key to the successful synthesis and stabilization of the ultrasmall metal nanoparticles. The as-prepared CPN, loaded with palladium nanoparticles, is used as a heterogeneous catalyst and shows outstanding catalytic performance in the hydrogenation of nitro compounds and Suzuki-Miyaura coupling reaction under mild conditions. The CPN support works synergistically with the metal nanoparticles, achieving high catalytic activity and selectivity. In addition, the catalytic activity of the formed catalyst is controllable.

**Comment**: The paper mentiones that the cyclodextrin-triazole network could be loaded with large amounts of metal ions. If this system is combined with some photo-responsive units and formed novel CPN, maybe the system comporting both CPNs will show a tunable catalytic properties.

#### A mutually stabilized host-guest pair

Zhang, C.; Wang, H.; Zhong, J.; Lei, Y.; Du, R.; Zhang, Y.; Shen, L.; Jiao, T.; Zhu, Y.; Zhu, H.; Li, H.; Li, H.; *Sci. Adv.* **2019**, *5*, eaax6707



By using click chemistry, a hexacationic cage was synthesized. The cage contains two triscationic -electron-deficient trispyridiniumtriazine (TPZ<sub>3+</sub>) platforms that are bridged in a face-to-face manner by three ethylene-triazole-ethylene linkers. A diversity of  $\Box$  -electron-rich guests can be recognized within the pocket of the cage, driven by host-guest-interactions. The cage cavity acts as a protecting group, preventing an anthracene guest from undergoing Diels-Alder reaction. Under ultraviolet (UV) light, the pyridinium C–N bonds in TPZ<sub>3+</sub> platforms are polarized and weakened, resulting in the occurrence of cage decomposition via -elimination. Guest recognition could help to prevent this UV-stimulated cage decomposition by suppressing the excitation of the TPZ<sub>3+</sub> units.

**Comment**: The main interesting point of this article is that the host-guest complex will stay stable with the presence of the guest molecule, otherwise -elimination will occurs. This providing an new method to use small molecular components to block the reaction pathways in large reaction systems.

#### **Origin of Lithium Whisker Formation and Growth under Stress**

He, Y.; Ren, X.; Xu, Y.; Engelhard, M. H.; Li, X.; Xiao, J.; Liu, J.; Zhang, J.-G.; Xu, W.\*; Wang, C.\* *Nat. Nanotechnol.* **2019**, *14*, 1042–1047.



Lithium metal has the lowest standard electrochemical redox potential and very high theoretical specific capacity, making it the ultimate anode material for rechargeable batteries. However, its application in batteries has been impeded by the formation of Li whiskers, which consume the electrolyte, deplete active Li and may lead to short-circuit of the battery. Tackling these issues successfully is dependent on acquiring sufficient understanding of the formation mechanisms and growth of Li whiskers under the mechanical constraints of a separator. Here, by coupling an atomic force microscopy cantilever into a solid open-cell set-up in environmental transmission electron microscopy, we directly capture the nucleation and growth behaviour of Li whiskers under elastic constraint. We show that Li deposition is initiated by a sluggish nucleation of a single crystalline Li particle, with no preferential growth directions. Remarkably, we find that retarded surface transport of Li plays a decisive role in the subsequent deposition morphology. We then explore the validity of these findings in practical cells using a series of carbonate-poisoned ether-based electrolytes. Finally, we show that Li whiskers can yield, buckle, kink or stop growing under certain elastic constraints.

**Comment**: Lara presented a few weeks back the winners of the Nobel Prize in Chemistry, for the development of lithium-based batteries. You may also remember that a main limitation is the formation of whiskers, which can cause short-circuit. Here, the authors investigated the growth mechanism of these whiskers by AFM. This work represents a necessary step to further understand how to avoid these objects in real-life batteries.

# Multiresponsive and Self-Healing Hydrogel via Formation of Polymer-Nanogel Interfacial Dynamic Benzoxaborole Esters at Physiological pH

Chen, Y. \*; Wang, W.; Wu, D.; Zeng, H.; Hall, D. G.; Narian, R.\* <u>ACS Appl. Mater. Interfaces</u> 2019, DOI:10.1021/acsami.9b16139.



Nanocomposite hydrogels with multiresponsiveness and self-healing property are attracting extensive interest due to their enhanced performance for a wide range of applications. In this work, we have successfully developed novel hydrogels based on interfacial polymer-nanogel benzoxaborolate cross-linking at physiological pH. Temperature- sensitive nanogels (NG-Gal) containing galactose residues on the nanosurface were prepared and subsequently used as macrocross-linkers to form a hydrogel network through formation of dynamic adducts with benzoxaborole groups of a hydrophilic copolymer poly(DMA-st-MAABO). Benefiting from the low pKa value of benzoxaborole ( $\sim$ 7.2), hydrogels can be constructed rapidly at physiological pH, which is of great significance for biomedical applications. Changing the molar ratio between benzoxaborole and galactose was found to alter the mechanical properties of hydrogels as confirmed by rheological measurements. The dynamic nature of benzoxaborole esters endowed the hydrogel with moldability and self-healing ability after disruption. Moreover, the hydrogel showed multiresponsiveness toward pH, sugar, adenosine triphosphate (ATP), hydrogen peroxide (H2O2), and temperature. Therefore, the novel nanocomposite hydrogel we demonstrated here exhibits great potential for biomedical applications such as tissue engineering and controlled drug delivery.

**Comment**: This paper describes a novel nanocomposite hydrogel system, which is composed of two components. The gel is based on dynamic benzoxaborole ester bonds exhibiting a multiresponsive and self-healing properties.

#### Stereotactic Photodynamic Therapy Using a Two-Photon AIE Photosensitizer

He, X.; Situ, B.; Gao, M.; Guan, S.; He, B.; Ge, X.; Li, S.; Tao, M.; Zou, H.; Tang, B.\*; Zheng, L.\* *Small* **2019**, 1905080.





Two-photon photodynamic therapy (TP-PDT) is emerging as a powerful strategy for stereotactic targeting of diseased areas, but ideal photosensitizers (PSs) are currently lacking. This work reports a smart PS with aggregation induced emission (AIE) feature, namely DPASP, for TP-PDT with excellent performances. DPASP exhibits high affinity to mitochondria, superior photostability, large two-photon absorption cross section as well as efficient reactive oxygen species generation, enabling it to achieve photosensitization both in vitro and in vivo under two-photon excitation. Moreover, its capability of stereotactic ablation of targeted cells with high-precision is also successfully demonstrated. All these merits make DPASP a promising TP-PDT candidate for accurate ablation of abnormal tissues with minimal damages to surrounding areas in the treatment of various diseases.

**Comment**: This is an interesting example in which TAA-based AIE molecule acts as TP-PDT. But it could only inhibit the growth of a tumour rather than kill it.

## Development of a Split Esterase for Protein–Protein Interaction-Dependent Small-Molecule Activation

Jones, K. A.; Kentala, K.; Beck, M. W.; An, W.; Lippert, A. R.; Lewis, J. C.; Dickinson, B. C.\* <u>ACS Cent Sci. 2019</u>, 5, 1768-1776.



Split reporters based on fluorescent proteins and luciferases have emerged as valuable tools for measuring interactions in biological systems. Relatedly, biosensors that transduce measured input signals into outputs that influence the host system are key components of engineered gene circuits for synthetic biology applications. While small-molecule-based imaging agents are widely used in biological studies, and small-molecule-based drugs and chemical probes can target a range of biological processes, a general method for generating a target small molecule in a biological system based on a measured input signal is lacking. Here, we develop a proximity-dependent split esterase that selectively unmasks ester-protected small molecules in an interaction-dependent manner. Exploiting the versatility of an ester-protected small-molecule output, we demonstrate fluorescent, chemiluminescent, and pharmacological probe generation, each created by masking key alcohol functional groups on a target small molecule. We show that the split esterase system can be used in combination with ester-masked fluorescent or luminescent probes to measure protein-protein interactions and protein-protein interaction inhibitor engagement. We demonstrate that the esterase-based reporter system is compatible with other commonly used split reporter imaging systems for the simultaneous detection of multiple protein-protein interactions. Finally, we develop a system for selective small-molecule-dependent cell killing by unmasking a cytotoxic molecule using an inducible split esterase. Presaging utility in future synthetic biology-based therapeutic applications, we also show that the system can be used for intercellular cell killing via a bystander effect, where one activated cell unmasks a cytotoxic molecule and kills cells physically adjacent to the activated cells. Collectively, this work illustrates that the split esterase system is a valuable new addition to the split protein toolbox, with particularly exciting potential in synthetic biology applications.

**Comment:** The interactions between proteins and small molecules is always attractive.

#### The Chemistry of Protein Oxidation in Food

Hellwig, M.; Angew. Chem. Int. Ed., 2019, 58, 47



Oxidation is one of the deterioration reactions of proteins in food, the importance of which is comparable to others such as Maillard, lipation, or protein-phenol reactions. While research on protein oxidation has led to a precise understanding of the processes and consequences in physiological systems, knowledge about the specific effects of protein oxidation in food or the role of "oxidized" dietary protein for the human body is comparatively scarce. Food protein oxidation can occur during the whole processing axis, from primary production to intestinal digestion. The present review summarizes the current knowledge and mechanisms of food protein oxidation from a chemical, technological, and nutritional–physiological viewpoint and gives a comprehensive classification of the individual reactions. Different analytical approaches are compared, and the relationship between oxidation of food proteins and oxidative stress in vivo is critically evaluated.

**Comment**: This article is not directly related to the topics of the groups. Nevertheless, I linked this review for bringing general knowledge about daily life. I didn't expect the radicals to be so abundant and so important in the bio-chemistry.

# Mechanically interlocked materials. Rotaxanes and catenanes beyond the small molecule

Mena-Hernando, S.; Perez, E. M.\*; Chem. Soc. Rev., 2019, 48, 5016



A mechanical bond presents a combination of the best features of covalent and supramolecular chemistries (stability and structural integrity), plus a unique dynamic nature, that makes it a very interesting tool for materials chemistry. Here, we overview the chemistry of the mechanical bond applied to polymers, metal–organic frameworks (MOFs) and carbon nanotubes. We first describe synthetic strategies towards polycatenanes and polyrotaxanes, and highlight their potential impact in polymer chemistry, exemplified by their use to make stimuli-responsive gels and as binders in battery electrodes. We continue by showing how to include mechanically interlocked components in MOFs, and analyse the distinctive dynamic properties of the final constructs. Finally, we describe the strategies towards mechanically interlocked derivatives of single-walled carbon nanotubes (SWNTs) and discuss the potential of the mechanical bond to tackle some of the classic problems of SWNT chemistry.

**Comment:** A review summarizing the different architectures available with rotaxanes and catenanes. It's a good review to have an overview for non-specialists like me but it's not diving so much into details.

#### Bottom-Up Structural Proteomics: Cryoem of Protein Complexes Enriched From the Cellular Milieu

Ho, C. M.; Li, X.; Lai, M.; Terwilliger, T. C.; Beck, J. R.; Wohlschlegel, J.; Zhou, Z. H.\* *Nat. Methods*, **2019**, ASAP.



X-ray crystallography often requires non-native constructs involving mutations or truncations, and is challenged by membrane proteins and large multicomponent complexes. We present here a bottom-up endogenous structural proteomics approach whereby near-atomic-resolution cryo electron microscopy (cryoEM) maps are reconstructed ab initio from unidentified protein complexes enriched directly from the endogenous cellular milieu, followed by identification and atomic modeling of the proteins. The proteins in each complex are identified using cryoID, a program we developed to identify proteins in ab initio cryoEM maps. As a proof of principle, we applied this approach to the malaria-causing parasite Plasmodium falciparum, an organism that has resisted conventional structural-biology approaches, to obtain atomic models of multiple protein complexes implicated in intraerythrocytic survival of the parasite. Our approach is broadly applicable for determining structures of undiscovered protein complexes enriched directly from endogenous sources.

**Comment:** The development of identification of the interactions between proteins or protein with small molecules will be achieved soon.

# A facile way to obtain near-infrared room-temperature phosphorescent soft materials basedon Bodipy dyes

Zhang, T; Xiang, M.;\* Tian, H. Chem. Sci., 2019, ASAP



Research on pure organic room-temperature phosphorescent (RTP) materials has made great advances but near-infrared (NIR) RTP emitting materials are still rare. Novel amorphous acrylamide copolymers containing iodine substituted borondipyrromethene (Bodipy) were prepared to obtain strong absorption in the visible region and moderate RTP in the NIR region with much larger Stokes shift than the fluorescence emission of traditional Bodipy dyes. Expensive metals and crystallization were left out to avoid biotoxicity and strict preparation conditions. **Monoiodo and diiodo-Bodipy derivatives were both designed to study the substitution effect of iodine atoms**. Photophysical properties, phosphorescence quantum yield and lifetime were characterized. Gels with NIR RTP emission were facilely prepared with the incorporation of ureidopyrimidone (UPy) and *N*,*N*'-methylenebisacrylamide (MBAA). The mechanical properties of the gels were measured using a rheometer and the results showed that the gels displayed fast self-healing ability due to the strong quadruple hydrogen bonding between UPy moieties.

**Comment**: The authors were able to design and synthesize for the first time a pure organic, room-temperature phosphorescent materials emitting in the NIR region stable in presence of air. The radical copolymerization with acrylamide formed a rigid polymeric matrix of polyacrylamide that can protect the emitting molecules from the quenching effect of molecular oxygen that occurs in solution. Additionally, using Upy moieties as crosslinkers, the authors were able to form self-healable gels. This study contributes to the literature related to the design of smart materials exhibiting room temperature phosphorescence, which could be used as probes, sensors, among other fields.

# Plasmon Enhanced Up-Conversion Nanoparticles in Perovskite Solar Cells for Effective Utilization of near Infrared Light

Park, J.; Kim, K.; Jo, E.-J.; Kim, W.; Kim, H.; Lee, R.; Lee, J. Y.; Jo, J. Y.; Kim, M.-G.\*; Jung, G. Y.\* *Nanoscale* **2019**, ASAP.



As an alternative to silicon-based solar cells, **organic-inorganic hybrid perovskite solar cells** (PSCs) have attracted much attention and achieved a comparable **power conversion efficiency** (PCE) to silicon-based ones, although the perovskite materials can absorb only visible light. Hence, the challenge remains to enhance the PCE utilizing **near infrared** (NIR) light in the solar light spectrum. One of the easiest ways to utilize the NIR is to incorporate NIR active materials in PSCs such as **up-conversion nanoparticles** (UCNPs); however, such a strategy is not simple to adopt in PSCs due to the inherent vulnerability of perovskite materials towards moisture. In this work, we present **NIR-utilizing PSCs by locating UCNPs within the PSC structure by a simple dry transfer method**. A maximum PCE of 15.56% was obtained in the case of PSC having the UCNPs located between the hole transport layer (HTL) and gold (Au) top electrode, which is an 8.4% enhancement compared to the cell without the UCNPs. This enhancement came from the combined effects of NIR light utilization and the surface plasmon resonance (SPR) phenomenon originating from the Au top electrode, which was interfacing the UCNPs.

**Comment**: An interesting article which nicely explains the main challenges that remain to be tackled in the perovskite solar cells field and proposes a first approach to solve them. I think the system is quite ambitious. I however remain quite sceptic concerning its application in industry due to the cost of such particles.

#### Additive-Free Green Light-Induced Ligation Using BODIPY Triggers

Li, M.; Dove, A. P.; Truong, V. X.\* Angew. Chem. Int. Ed. 2019, ASAP



Photochemical ligation is important in biomaterials engineering for spatiotemporal control of biochemical processes. Such reactions however generally require activation by high energy UV or short wavelength blue light, which can limit their use as a consequence of the potential of these high energy light sources to damage living cells. Herein, we present an additive-free, biocompatible, chemical ligation triggered by mild visible light. BODIPY dyes with a pendant thioether attached at the meso-position undergo photolysis of the [C-S] bond under green light ( $\lambda = 530$  nm)

excitation, producing an ion pair intermediate that can react specifically with a propiolate group. The utility of this photochemical ligation in materials science is demonstrated by the fabrication of hydrogels with specific architectures, photo-immobilization of biomacromolecules, and live cell encapsulation within a hydrogel scaffold.

**Comment**: It demonstrates a green-light responsive photo-trigger which is based on BODIBY. Compared with other types of photo-triggers, the advantages of this work is that the intermediate is oxygen stable and could further react with a propiolate group. Unfortunately, in this paper they just tried propiolate group, and the reactivity of other alkyne groups is unclear.

# Stimuli-responsive Biomolecule-based Hydrogels and their Applications

Vázquez-González. M.; Willner, I.\* Angew. Chem. Int. Ed. 2019, ASAP.



Within the broad interest in developing stimuliresponsive hydrogels, the synthesis, characterization and applications of biomolecule-based stimuli-responsive hydrogels are of major interest. In this review, polysaccharides, oligosaccharides, nucleic acids, peptides and proteins are used as functional stimuli-responsive polymer scaffolds to yield hydrogels of controlled stiffness. Different physical or chemical triggers, such as heat, light, pH, ions, redox agents and more are used to structurally reconfigure the crosslinking units and control the stiffness of the hydrogels. By the integration of stimuli-responsive supramolecular complexes and stimuliresponsive biomolecular units as crosslinkers, hybrid hydrogels undergoing reversible triggered transitions across different stiffness states are demonstrated. Different applications of the stimuli-responsive biomolecule-based hydrogels are discussed, including their use as sensing matrices, the development of controlled drug-delivery systems, the design of shape-memory and self-healing materials and their use as mechanical devices. The assembly of stimuli-responsive biomoleculebased hydrogel films on surfaces is addressed and the control over the iontransport through hydrogel-film-modified pores, or the application of the stimuli-responsive hydrogel films to switch the resistivity and electrocatalytic properties of electrode/solution interfaces are discussed. Also, the coating of drug-loaded nanoparticles with stimuli-responsive hydrogels for controlled drug release is presented. The perspectives of stimuliresponsive biomolecule-based hydrogels are addressed by identifying future scientific challenges and applications of these "smart" materials.

**Comment**: I choose this review because it contains so many examples which are stimuliresponsive functional materials.

# Rough substrate Lubricant Nepenthes

Liquid Infused Surfaces with Anti-Icing Properties Wang, G.; Guo, Z\*. *Nanoscale* **2019**, ASAP.

Ice accretion on solid surfaces, a ubiquitous phenomenon that occurs in winter, brings much inconvenience to daily life and can even cause serious catastrophes. Icephobic surfaces, a passive way of processing surfaces to prevent surface destruction from ice accumulation, have attracted much attention from scientists because of their special ice-repellent properties, and many efforts have been made to rationally design durable icephobic coatings. This review is aimed at providing a brief and crucial overview of ice formation processes and feasible de-icing strategies. Here, the excellent anti-icing performance of liquid infused surfaces (LIS) inspired from Nepenthes is emphatically introduced. After a short introduction, the recent progresses in ice nucleation theory and ice adhesion decrease mechanism are comprehensively reviewed to gain a general understanding of the long freeze process and low ice adhesion on LIS. Subsequently, the anti-icing performance of LIS is systematically evaluated from four aspects regarding water repellence, condensation-frosting, long freeze process, and low ice adhesion. Finally, this review focuses on discussing the advantages and disadvantages of LIS and the potential measures to eliminate and alleviate these drawbacks.

**Comment**: This review is a nice surprise as it give us the oportunity to learn a lot concerning the formation of ice on surfaces and how to avoid it. I would recommend it for the sole purpose of expanding one's knowledge on such unusual topic.