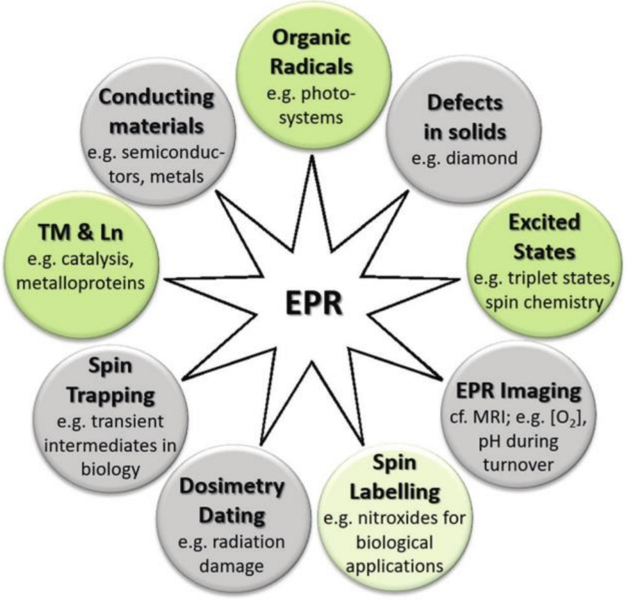
Principles and Applications of EPR Spectroscopy in the Chemical Sciences

Roessler, M. M.*; Salvadori, E.* *Chem. Soc. Rev.* **2018**, *47*, 2534.

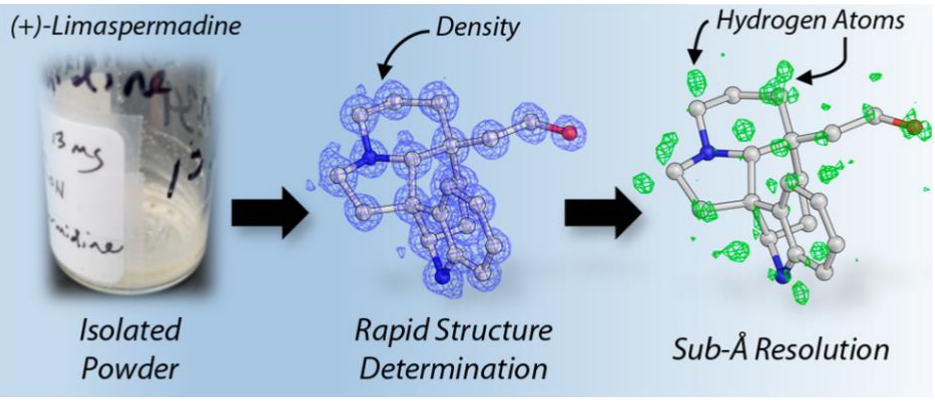


Electron spins permeate every aspect of science and influence numerous chemical processes: they underpin transition metal chemistry and biochemistry, mediate photosynthesis and photovoltaics and are paramount in the field of quantum information, to name but a few. Electron paramagnetic resonance (EPR) spectroscopy detects unpaired electrons and provides detailed information on structure and bonding of paramagnetic species. In this tutorial review, **aimed at non-specialists**, we provide a theoretical framework and examples to illustrate the vast scope of the technique in chemical research. Case studies were chosen to exemplify systematically the different interactions that characterize a paramagnetic centre and to **illustrate how EPR spectroscopy may be used to derive chemical information.**

Comment: I only learned about the existence of this review from Stephen Goldup during the ERC conference. You can thank him for the brilliant idea of limiting the (few and very basic for the expert community?) mathematical equations to boxes, while keeping the “easy” to understand information as the main text. Nevertheless, it remains complex enough as to require a clear mind and a bit of force of will to read it. Then again, it is the nature of EPR! Don’t expect it to be easy. But it might well be **one of the best options there is to approach the technique** for the point of view we care about: chemistry (sort of).

The CryoEM Method MicroED as a Powerful Tool for Small Molecule Structure Determination.

Jones, C. G.; Martynowycz, M. W.; Hattne, J.; Fulton, T. J.; Stoltz, B. M.*; Rodriguez, J. A.*; Nelson, H. M.*; Gonen, T.* *ACS Cent. Sci.* **2018**, *4*, 1587.

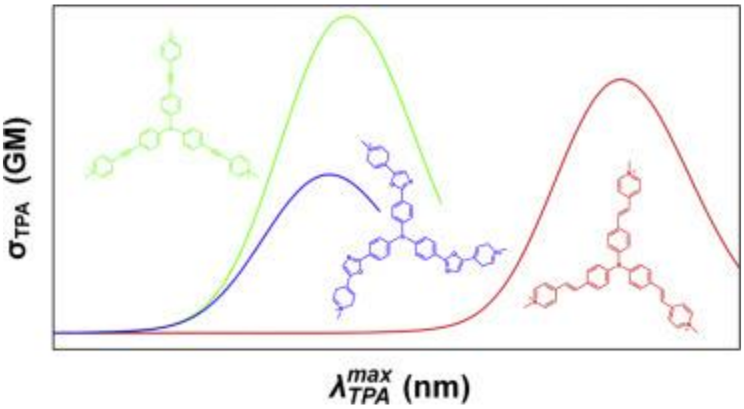


In the many scientific endeavors that are driven by organic chemistry, unambiguous identification of small molecules is of paramount importance. Over the past 50 years, NMR and other powerful spectroscopic techniques have been developed to address this challenge. While almost all of these techniques rely on inference of connectivity, the unambiguous determination of a small molecule's structure requires X-ray and/or neutron diffraction studies. In practice, however, X-ray crystallography is rarely applied in routine organic chemistry due to intrinsic limitations of both the analytes and the technique. Here we report the use of the electron cryo-microscopy (cryoEM) method microcrystal electron diffraction (MicroED) to provide routine and unambiguous structural determination of small organic molecules. **From simple powders, with minimal sample preparation, we could collect high-quality MicroED data from nanocrystals** (~100 nm, ~10-15 g) resulting in atomic resolution (<1 Å)

Comment: Someone fancies crystal structure characterization of their molecules in less than 30 minutes? Well, if you would have enough resources you could do this (within certain limits). I'm not necessarily unconvinced that this technology could be broadly applied in "the future". I guess the main reason hindering its development is that, to be fair, NMR is "good enough" so why go any further?

A theoretical study of a series of water-soluble triphenylamine photosensitizers for two-photon photodynamic therapy

Wang, X.; Yin, X.; Lai, X.-Y.; Liua1, Y.-T.* *Spectrochim. Acta A* **2018**, *203*, 229–235.

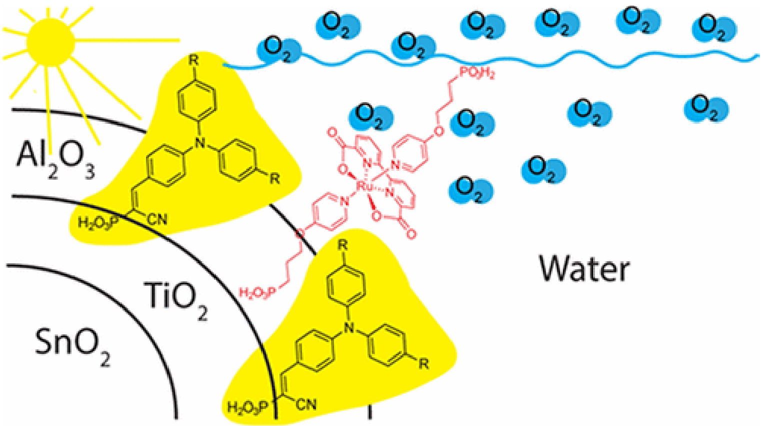


In this study, the therapeutic activity of a series of water-soluble triphenylamine (TP) photosensitizers (Ps) was explored by using theoretical simulations. The key photophysical parameters which determined the efficiency of Ps, such as absorption electronic spectra, singlet-triplet energy gaps and spin-orbit matrix elements were calculated at density functional theory and its time-dependent extension (DFT, TD-DFT). The calculated results showed that these TP photosensitizers possessed large two-photon absorption cross-section in the near infrared region (NIR), efficient intersystem crossing (ISC) transition from the first singlet excited state to the lowlying triplet excited states and sufficient energy for generating reactive oxygen species (ROS). These suitable features made these TP series holding great promise for applications in two-photon photodynamic therapy (PDT). These TP photosensitizers studied here in principle extended the application range of two-photon PDT in water solution.

Comment: I think this article is interesting because of several reasons: *i*) It highlights a use for TP molecules we do not mention often in our group; *ii*) They study how substituents on the TP core change the absorption spectra, energy states, inter system crossing etc.; *iii*) It shows how theoretical studies can pinpoint which (family of) molecules have potential and should be studied further in laboratory (circumventing the need to test all compounds in laboratory). However, as I am no expert in DFT calculations, I cannot guarantee the quality of the work.

Water Photo-Oxidation Initiated by Surface-Bound Organic Chromophores

Eberhart, M. S.; Wang, D.; Sampaio, R. N.; Marquard, S. L.; Shan, B.; Brennaman, M. K.; Meyer, G. J.; Dares, C.; Meyer, T. J.* *J. Am. Chem. Soc.* **2017**, *139*, 16248–16255.

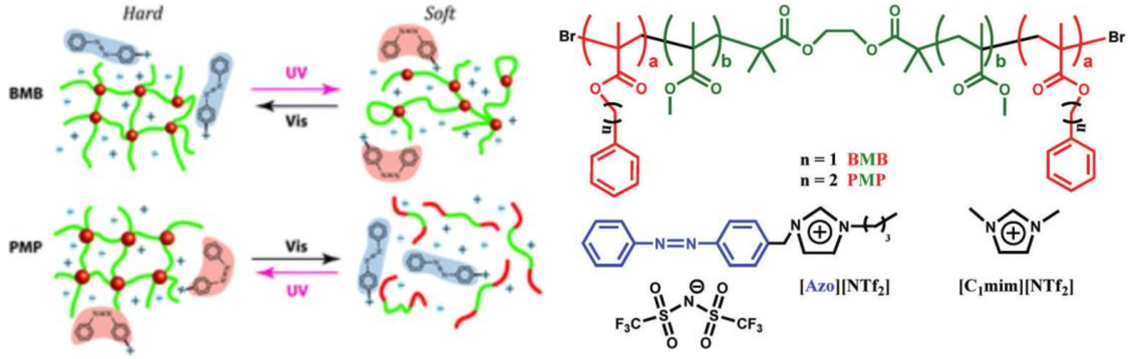


Organic chromophores can be synthesized by established methods and offer an opportunity to expand overall solar spectrum utilization for dye-sensitized photoelectrosynthesis cells. However, there are complications in the use of organic chromophores arising from the instability of their oxidized forms, the inability of their oxidized forms to activate a water oxidation catalyst, or the absence of a sufficiently reducing excited state for electron injection into appropriate semiconductors. Three new triarylamine donor–acceptor organic dyes have been investigated here for visible-light-driven water oxidation. They offer highly oxidizing potentials (>1 V vs NHE in aqueous solution) that are sufficient to drive a water oxidation catalyst and excited-state potentials (∼−1.2 V vs NHE) sufficient to inject into TiO_2. The oxidized form of one of the chromophores is sufficiently stable to exhibit reversible electrochemistry in aqueous solution. The chromophores also have favorable photophysics. Visible-light-driven oxygen production by an organic chromophore for up to 1 h of operation has been demonstrated with reasonable faradaic efficiencies for measured O_2 production. The properties of organic chromophores necessary for successfully driving water oxidation in a light-driven system are explored along with strategies for improving device performance.

Comment: Again, a function of triarylamine molecules (water splitting) that is not often mentioned in our group. Just to show some diversity in triarylamine applications.

Viscoelastic Change of Block Copolymer Ion Gels in a Photo-Switchable Azobenzene Ionic Liquid Triggered by Light

Watanabe, M.; Wang, C.; Hashimoto, K.; Tamate, R.; Kokubo, H.; Morishima, K.; Li, X.; Shibayama, M.; Lu, F.; Nakanishi, T.* *Chem. Commun.*, **2019**, Advance Article.

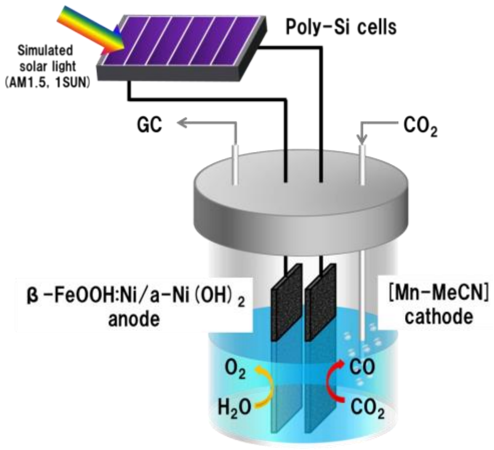


A **photo-switchable ionic liquid solvent** bearing an **azobenzene** moiety induced a **viscoelastic change** of block copolymer ion gels by light. ABA triblock copolymers having poly(phenethyl methacrylate) and poly(benzyl methacrylate) as A blocks exhibited opposite photo-induced rheological responses although they had only a tiny structural difference in the alkyl chain length.

Comment: I don't know if the structure described here can be classified as photo-responsive. Indeed, the polymer by itself doesn't interact with light, conversely, the ionic liquid used as a solvent does. I find the perspective of inducing photo-switchable properties to a material through the nature of the solvent is really intriguing. However, in my modest opinion, I believe it may be quite difficult to adapt those systems to any applicable materials. Besides, the authors have characterized their gel through various techniques that might be useful for those who would like to work with gels.

Solar-Driven CO_2 to CO Reduction Utilizing H_2O as an Electron Donor by Earth-Abundant Mn-Bipyridine Complex and Ni-Modified Fe-Oxyhydroxide Catalysts Activated in a Single-Compartment Reactor

Arai, T.; Sato, S.; Sekizawa, K.; Suzuki, T. M.; Morikawa, T.* *Chem. Commun.* **2019**, ASAP.

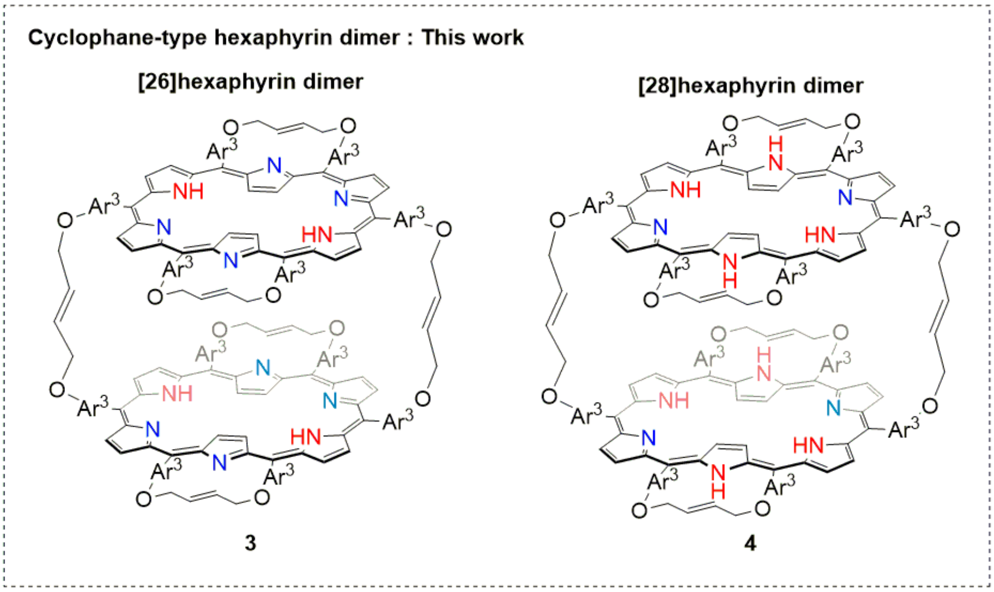


Photoelectrochemical CO_2 to CO reduction was demonstrated with **3.4% solar-to-chemical conversion** efficiency using **polycrystalline silicon photovoltaic cells** connected with earth-abundant catalysts: a manganese complex polymer for CO_2 reduction and iron oxyhydroxide modified with a nickel compound for water oxidation. The system operated around **neutral pH** in a **single-compartment reactor**.

Comment: This paper doesn't stand out by the originality of the work nor by its overall solar-to-chemical yield. However, it is interesting to see the increasing use of readily available metals in chemistry. The authors have made the choice of summing up all the major results in this field before describing their own work. It is quite enjoyable for someone (like me) who was completely ignorant in this domain.

Aromatic and Antiaromatic Cyclophane-type Hexaphyrin Dimers

Nakai A.; Yoneda T.; Ishida S.; Kato K. ; Osuka, A.* *Chem. Asian J.* **2018**, *Accepted Article*

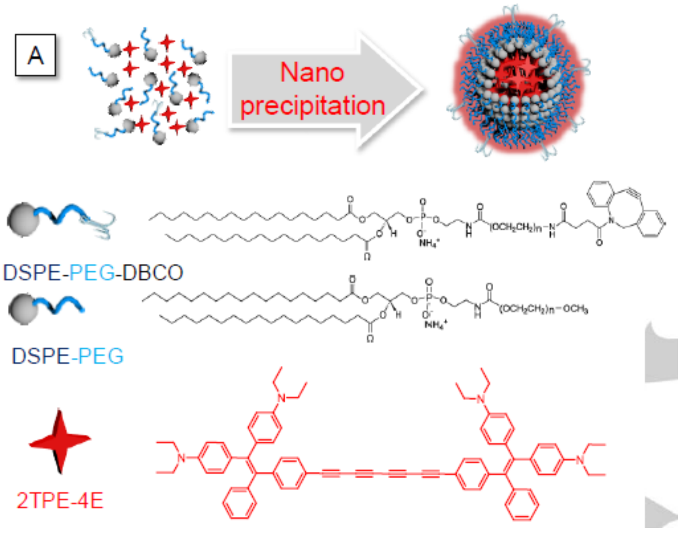


A peripherally strapped [28]hexaphyrin takes a rectangular conformation and exhibits antiaromatic character. A cyclophane-type dimer consisting of such [28]hexaphyrins was synthesized from hexakis(pentafluorophenyl) [26]hexaphyrin via S$_N$Ar reaction with allyl alcohol, one-pot intra- and intermolecular olefin metathesis under improved Hoveyda–Grubbs catalysis, and final reduction with $NaBH_4$. The cyclophane-type structures of [26]- and [28]hexaphyrin dimers have been revealed by X-ray analysis. Studies on the structural, optical, and electronic properties have led to a conclusion that there is no favorable electronic interaction between the two [28]hexaphyrin segments and thus **no indication of 3D aromaticity**.

Comment: I think it's quite interesting to design and synthesize such a dimer structure.

Bio-orthogonal AIE Dots Based on Polyyne-Bridged Red-emissive AIEgen for Tumor Metabolic Labeling and Targeted Imaging

Zhang, P.; Jiang, T.; Li, Y.; Zhao, Z.; Gong, P.; Cai, L.; Kwok, R. T. K.; Lam, J. W. Y.; Gu, X.*; Tang, B. Z.* *Chem. Asian J.* **2018**, *Accepted Article*

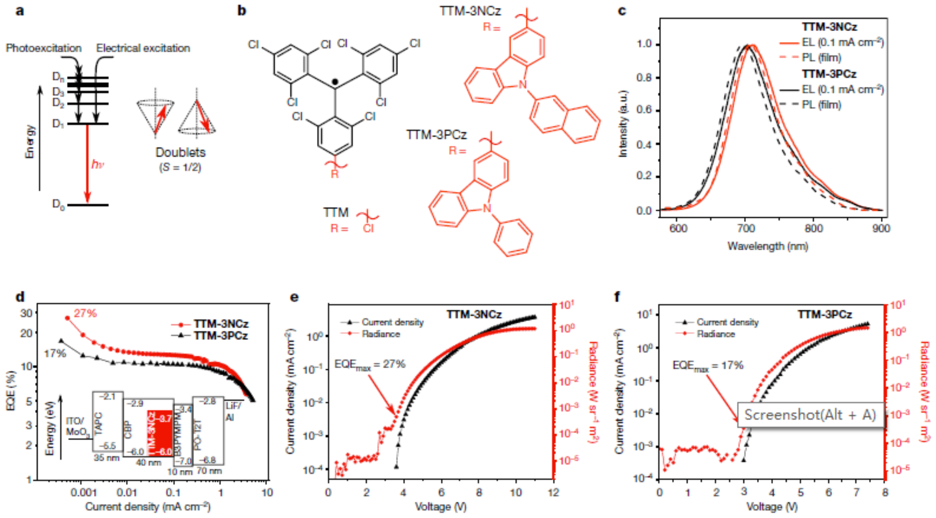


In this work, we aim to develop cancer cell-targeting AIE dots based on the polyyne-bridged red-emissive AIEgen, 2TPE-4E, through the combination of metabolic engineering and bio-orthogonal reactions. Azide groups on tumor were efficiently produced by intravenous injection of Ac4ManNAz and glycol-metabolic engineering. These bio-orthogonal azide groups could facilitate the specific targeting of DBCO-AIE dots to the tumor cells undergoing metal-free click reaction in vivo. The efficiency of this targeting strategy could be further improved along with the development of new bio-orthogonal chemical groups with higher reactivity and sufficient AIEgens could be delivered to tumor for diagnosis.

Comment: It's amazing that azide groups on the targeted cancer cell surface can dynamically and bio-orthogonally control the cancer cell-targeting ability of AIE dots.

Efficient Radical-based Light-emitting Diodes with Doublet Emission

Ai, X.; Evans, E. W.; Dong, S.; Gillett, A. J.; Guo, H.; Chen, Y.; Hele, T. J. H.; Friend, R. H.*; Li, F.*; *Nature* **2018**, *563*, 536–540.

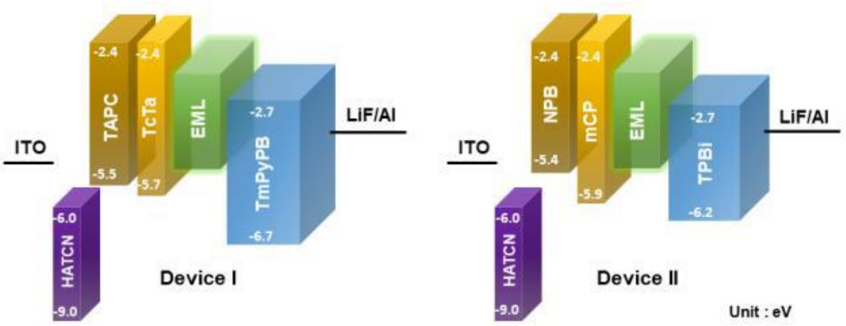


Organic light-emitting diodes (OLEDs)[1–5], quantum-dot-based LEDs[6–10], perovskite-based LEDs[11–13] and micro-LEDs[14,15] have been championed to fabricate lightweight and flexible units for next-generation displays and active lighting. Although there are already some high-end commercial products based on OLEDs, costs must decrease whilst maintaining high operational efficiencies for the technology to realise wider impact. **Here we demonstrate efficient action of radical-based OLEDs[16], whose emission originates from a spin doublet, rather than a singlet or triplet exciton.** While the emission process is still spin-allowed in these OLEDs, the efficiency limitations imposed by triplet excitons are circumvented for doublets. Using a luminescent radical emitter, we demonstrate an OLED with maximum external quantum efficiency of 27 per cent at a wavelength of 710 nanometres—the highest reported value for deep-red and infrared LEDs. For a standard closed-shell organic semiconductor, holes and electrons occupy the highest occupied and lowest unoccupied molecular orbitals (HOMOs and LUMOs), respectively, and recombine to form singlet or triplet excitons. Radical emitters have a singly occupied molecular orbital (SOMO) in the ground state, giving an overall spin-1/2 doublet. If—as expected on energetic grounds—both electrons and holes occupy this SOMO level, recombination returns the system to the ground state, giving no light emission. However, in our very efficient OLEDs, we achieve selective hole injection into the HOMO and electron injection to the SOMO to form the fluorescent doublet excited state with near-unity internal quantum efficiency.

Comment: It’s a nice work, but I know only little about the OLED. I think radical-based emission is quite interesting.

New Aggregation-Induced Delayed Fluorescence Luminogens for Efficient Organic Light-Emitting Diodes

Zeng, J.; Guo, J.; Liu, H.; Lam, J. W. Y.; Zhao, Z.*; Chen, S.*; Tang, B. Z.*; *Chem. Asian J.* **2018**, *Accepted Article*



Aggregation-induced delayed fluorescence (AIDF) can be regarded as a special case of aggregation-induced emission (AIE). Luminogens with AIDF can simultaneously emit strongly in solid state and fully utilize the singlet and triplet excitons in organic light-emitting diodes (OLEDs). In this work, two new AIDF luminogens, DMF-BP-DMAC and DPF-BP-DMAC, with an asymmetric D–A–D' structure, are designed and synthesized. The characteristics of both luminogens are systematically investigated, including single crystal structures, theoretical calculations, photophysical properties and thermal stabilities. Inspired by their AIDF nature, the green-emission non-doped OLEDs based on them are fabricated, which afford good electroluminescence performances, with low turn-on voltages of 2.8 V, high luminance of 52560 cd m^{-2}, high efficiencies of up to 14.4%, 42.3 cd A^{-1} and 30.2 lm W^{-1}, and very small efficiency rolloff. The results strongly indicate the bright future of non-doped OLEDs on the basis of robust AIDF luminogens..

Comment: Tang's group have applicated AIE in OLED, that's interesting.

Directing the reactivity of metal hydrides for selective CO_2 reduction

Ceballosa, B. M.; Yang, J. Y.* *Proc. Nat. Acad. Sci. USA.* **2018**, *115*,12686 - 12691.

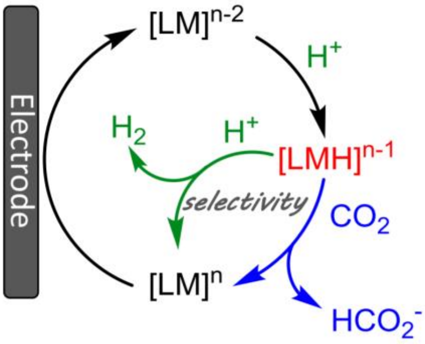


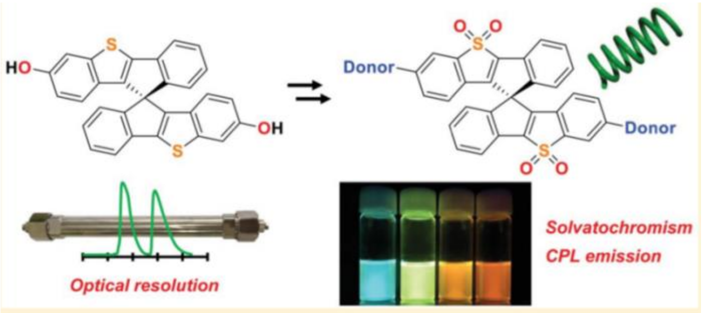
Fig. 1. Proposed catalytic cycles for H^+ and CO_2 reduction.

A critical challenge in electrocatalytic CO_2 reduction to renewable fuels is product selectivity. Desirable products of CO_2 reduction require proton equivalents, but key catalytic intermediates can also be competent for direct proton reduction to H_2. Understanding how to manage divergent reaction pathways at these shared intermediates is essential to achieving high selectivity. Both proton reduction to hydrogen and CO_2 reduction to formate generally proceed through a metal hydride intermediate. We apply thermodynamic relationships that describe the reactivity of metal hydrides with H^+ and CO_2 to generate a thermodynamic product diagram, which outlines the free energy of product formation as a function of proton activity and hydricity (ΔGH−), or hydride donor strength. The diagram outlines a region of metal hydricity and proton activity in which CO_2 reduction is favorable and H^+ reduction is suppressed. We apply our diagram to inform our selection of $[Pt(dmpe)_2](PF_6)_2$ as a potential catalyst, because the corresponding hydride $[HPt(dmpe)_2]$ + has the correct hydricity to access the region where selective CO_2 reduction is possible. We validate our choice experimentally; $[Pt(dmpe)_2](PF_6)_2$ is a highly selective electrocatalyst for CO_2 reduction to formate (>90% Faradaic efficiency) at an overpotential of less than 100 mV in acetonitrile with no evidence of catalyst degradation after electrolysis. Our report of a selective catalyst for CO_2 reduction illustrates how our thermodynamic diagrams can guide selective and efficient catalyst discovery.

Comment: In this paper, the authors use thermodynamic relationships to understand the reactivity of metal hydrides. They also applied their analysis to construct a diagram that defines catalyst parameters for achieving selective CO_2 reduction by targeting an appropriate hydricity.

[1]Benzothiophene-Fused Chiral Spiro Polycyclic Aromatic Compounds: Optical Resolution, Functionalization, and Optical Properties

Takase, K.; Noguchi, K.; Nakano, K.* *J. Org. Chem.* **2018**, *ASAP.*

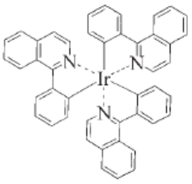


Spiro polycyclic aromatic compounds have been known as rigid chiral scaffolds. In order to extend their applications, an efficient preparation route to enantiopure derivatives is highly required. Here, we design 10,10-spirobi[indeno[1,2-b][1]benzothiophene]-7,7-diol to achieve efficient optical resolution. The compound was successfully synthesized and resolved by chiral HPLC on a semipreparative scale. The absolute configuration of its enantiopure isomer was determined through single-crystal X-ray structure analysis of its derivative. The compound was also transformed into its derivatives with donor−acceptor (D−A) type systems. The obtained chiral D−A type molecules exhibited remarkable solvent-dependence fluorescence and were found to be solvent-sensitive circularly polarized luminescent materials. These results clearly demonstrated the utility of 10,10-spirobi[indeno[1,2-b][1]benzothiophene]-7,7-diol as a versatile building block for chiral spiro polycyclic aromatic compounds.

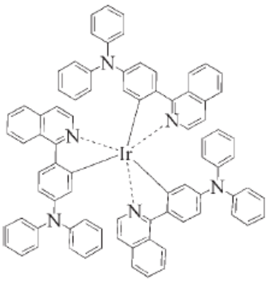
Comment: Just as the synthesis of the Feringa motor by our group, the introduction of hydroxy groups into chiral spiro polycyclic aromatic compounds in this paper should be a promising strategy for an efficient preparation of enantiopure isomers by chiral HPLC.

Triphenylamine-Dendronized Pure Red Iridium Phosphors with Superior OLED Efficiency/Color Purity Trade-Offs

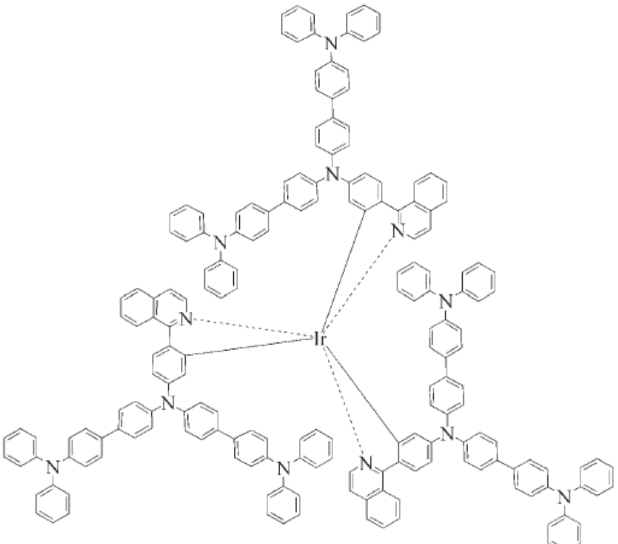
Zhou, G.; Wong, W. Y.; Yao, B.; Xie, Z.; Wang, L.* *Angew. Chem. Int. Ed.* **2007**, *46*, 1149–1151. (review special)



Ir–G0



Ir–G1



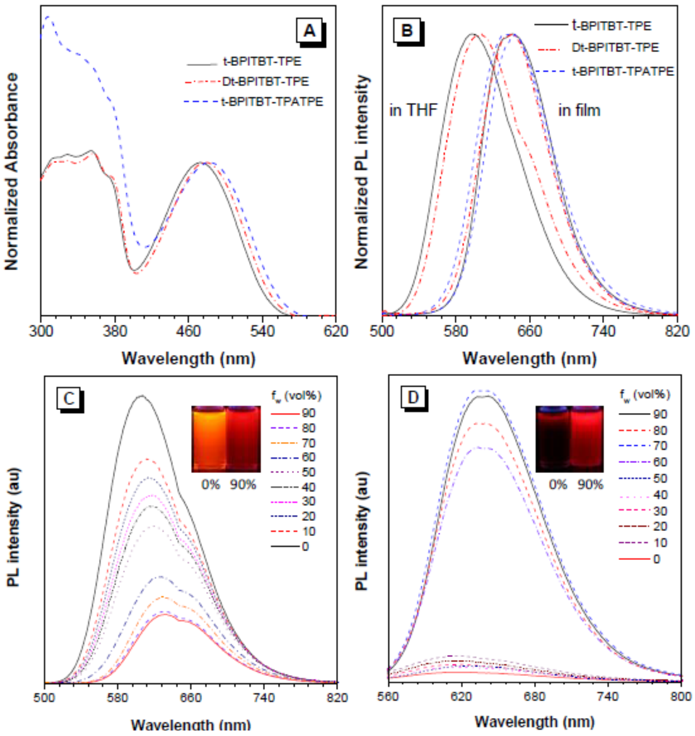
Ir–G2

As good as red: Highly efficient pure red OLEDs based on iridium electrophosphors functionalized with hole-transporting triphenylamine dendrons are prepared (see picture). These bifunctional dendrimers give a peak efficiency of 11.7 % with an excellent color quality and offer an attractive avenue for the development of metal phosphors with the optimized efficiency/color purity trade-offs required for pure red-emitting devices. OLED=organic light-emitting diode.

Comment: In this paper are reported some of the highest light emitting metallodendrimers reported for solution-processed devices; triarylamines strike again!!

Efficient Red AIEgens Based on Tetraphenylethene: Synthesis, Structure, Photoluminescence and Electroluminescence

Li, Y.; Wang, W.; Zhuang, Z.; Wang, Z.; Lin, G.; Shen, P.; Chen, S.; Zhao, Z.; Tang, B. Z.* *J. Mater. Chem. C*, **2018**, *6*, 5900–5907.

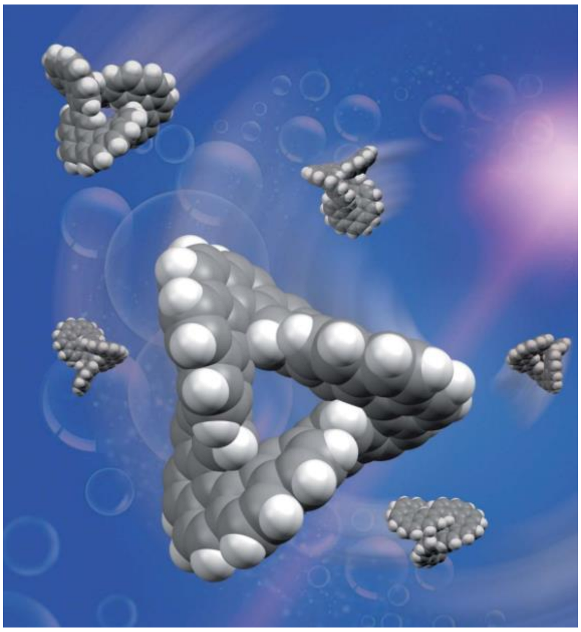


Red emitters are very important for the colour display and white lighting devices. However, efficient remitters are relatively rare because they often suffer from aggregation-caused quenching problem. In this work, a series of robust red molecules consisting of tetraphenylethene, benzo-2,1,3-thiadiazole, phenanthro[9,10-d]imidazole and triphenylamine moieties are synthesized and fully characterized. The photophysical property, transient fluorescence decay, thermal stability, and electrochemical behaviors and electronic structures are thoroughly investigated. The results show that these molecules have high thermal and electrochemical stabilities. They show aggregation-induced emission (AIE) property and emit strong red fluorescence in the aggregated state, which can be well modulated by functional groups. Nondoped OLEDs are fabricated by using these red molecules as light-emitting layers, offering red electroluminescence at 650 nm (CIE$_{x,y}$ = 0.665, 0.334) and high luminance and external quantum efficiency of up to 6277 cd m^{-2} and 2.17%, respectively. Moreover, a solution-processed red OLED with good performance is also achieved. This work not only present efficient red emitters for nondoped OLEDs, but also provide useful structure-property relationship insights for further development of efficient red luminescent materials

Comment: In this work they present a series of efficient red emitters with a framework composed by TPE, benzo-2,1,3-thiadiazole, and phenanthro[9,10-d]imidazole, and the *tert*-butyl and diphenylamine moieties are further introduced to modulate the intermolecular interactions and electron donor-acceptor interaction strength.

Cyclic Tris-[5]Helicenes with Single and Triple Twisted Möbius Topologies and Möbius Aromaticity

Naulet, G.; Sturm, L.; Robert, A.; Dechambenoit, P.; Röhricht, F.; Herges, R.; Bock, H.*; Durola, F.* *Chem. Sci.* **2018**, *9*, 8930–8936.

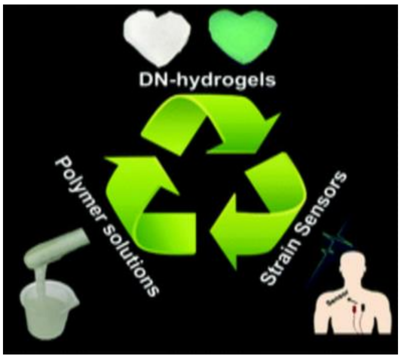


A number of singly (180°) twisted, largely single-stranded and thus conformationally rather fragile, Möbius molecules have been synthesized within the last 15 years, which are aromatic with 4n electrons, thus violating the Hückel rule. Annulenes with significantly higher twist (e.g. 540°) that retain a full cyclic conjugation path have been elusive, mainly because of the high strain and loss of orbital overlap. Recently, a topological strategy was devised to project the "twist" into "writhe", thus reducing the strain. However, orbital overlap was still severely reduced within the flexible building blocks. We now present a **single and a triple twisted annulene with fully conjugated peripheries**. They are unique in their pronounced band shape and conformational robustness as they are made up of three fully katacondensed [5]helicene fragments. The triple twisted molecule exhibits a strong diatropic ring current in the outer periphery, even though the π system includes 4n electrons. The diatropic current is counterbalanced by a paratropic current in the σ system, resulting in no net manifestation of macrocyclic aromaticity. The key step of the synthesis of both Möbius compounds is a Perkin condensation of complementary bifunctional bismaleates leading to a flexible macrocycle containing alternating benzene and biphenyl fragments. Subsequent photocyclization yields a separable mixture of rigid diastereomeric tris-helicene macrocycles of the above topologies.

Comment: The Hückel rule for aromaticity is dependent on the topology of the molecule; that is why Möbius molecules are aromatic with 4n π electrons. The fundamental aspect of this fact is rather interesting by itself, and is developed in this article, along with the synthesis of such a molecule. Also, the authors discuss the possible emerging applications of these compounds, so do not hesitate to read this paper, out of pure curiosity.

Recyclable, Stretchable and Conductive Double Network Hydrogels towards Flexible Strain Sensors

Lai, J.; Zhou, H.*; Wang, M.; Chen, Y.; Jin, Z.; Li, S.; Yang, J.; Jin, X.*; Liu, H.*; Zhao, W.
J. Mater. Chem. C **2018**, *6*, 13316–13324.

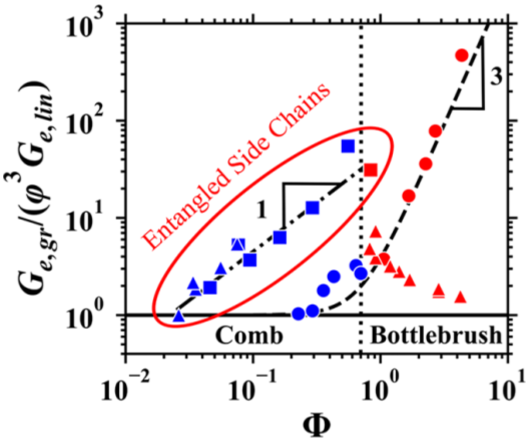


Stretchable and elastic double network (DN) hydrogels are increasingly investigated for flexible electronics but their recyclability is rarely considered. Herein, **recyclable, stretchable and conductive DN-hydrogels are explored and utilized in flexible resistive-type strain sensors**. Such DN-hydrogels are fully physically cross-linked and composed of a crystalline domain cross-linked poly(vinyl alcohol) (PVA) network and a Tb^{3+}-cross-linked poly(acrylic acid sodium) (PAANa–Tb^{3+}) network. Due to their unique structure, DN-hydrogels have excellent recyclability and flexibility, and they are also conductive and photoluminescent due to the presence of Tb^{3+}. Utilizing DN-hydrogels, flexible strain sensors are assembled and further applied to monitor large human motions, such as moving of two hands and bending of joints, as well as subtle physiological activities including moving of the bicipital muscle, swallowing and breathing. Overall, the present example not only helps to understand the toughening and strengthening mechanism of fully physically cross-linked DN-hydrogels, but also offers a clue to develop multifunctional hydrogels for recyclable flexible electronics.

Comment: Research on soft strain sensors is getting more and more common, obviously for their potential to be used in harmony with our bodies. The authors address here a problem that is seldom discussed in other articles: the recyclability of such “implants”.

Universality of the Entanglement Plateau Modulus of Comb and Bottlebrush Polymer Melts

Liang, H.; Morgan, B., J.; Xie, G.; Martinez, M. R.; Zhulina, E. B.; Matyjaszewski, K.; Sheiko, S. S.*; Dobrynin, A. V.* *Macromolecules* **2018**, *51*, 10028

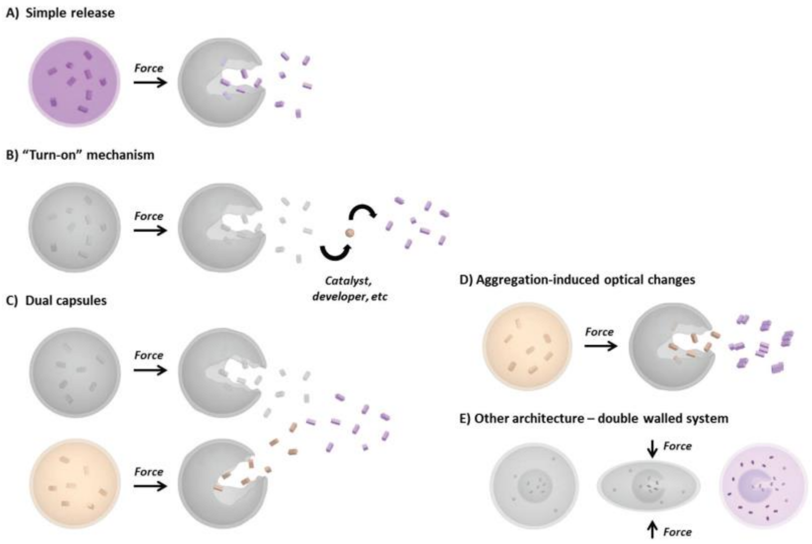


A combination of scaling analysis and rheological experiments was used to study correlations between the entanglement plateau modulus and grafting density of graft polymers in a melt. Using the crowding parameter Φ, which describes overlap of side chains belonging to neighboring macromolecules, we identified two classes of graft polymers—combs and bottlebrushes—that demonstrate distinct conformational and rheological behaviors. In comb systems, both the backbones and sparsely grafted side chains are coiled that allow side chains of neighboring macromolecules to overlap ($\Phi < 1$). In bottlebrush systems, steric repulsion between densely grafted side chains causes chain extension and inhibits side chain interpenetration ($\Phi \geq 1$). The ratio $G_{e,gr}/G_{e,lin} \cong \varphi^3(1 + (\Phi/0.7)^3)$ of the plateau modulus of a graft polymer melt, $G_{e,gr}$, to that of a melt of linear chains, $G_{e,lin}$, is a universal function of the crowding parameter $\Phi \cong \varphi^{-1} n_{sc}^{-1/2}$ and graft polymer composition $\varphi = n_g/(n_g + n_{sc})$, where n_{sc} and n_g are the degrees of polymerization of side chains and a spacer separating two consecutive side chains along the polymer backbone, respectively. This dependence of the plateau modulus is verified for poly(*n*-butyl acrylate) combs and other graft polymer systems reported in the literature. In a special case of graft polymers with long entangled side chains, the $G_{e,gr}/G_{e,lin}$ ratio is proportional to φ^2.

Comment: A bit of theory can't hurt. This paper explains in detail the talk given by Matyjaszewski about grafted polymers.

Microcapsule-Containing Self-Reporting Polymers

Calvino, C.; Weder, C.* *Small* **2018**, *14*, 1802489.

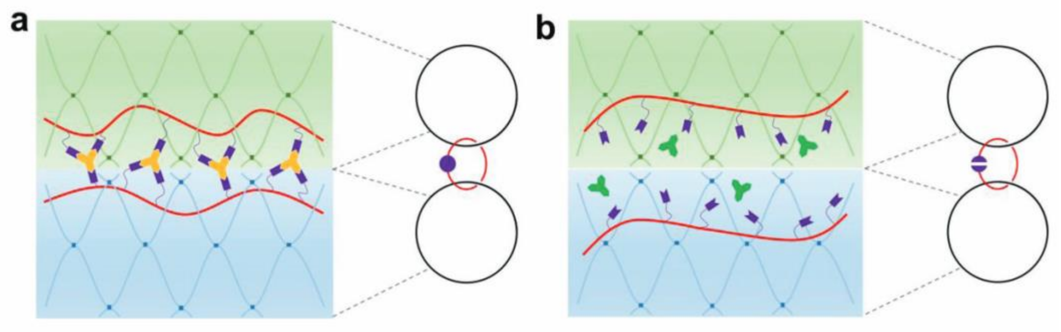


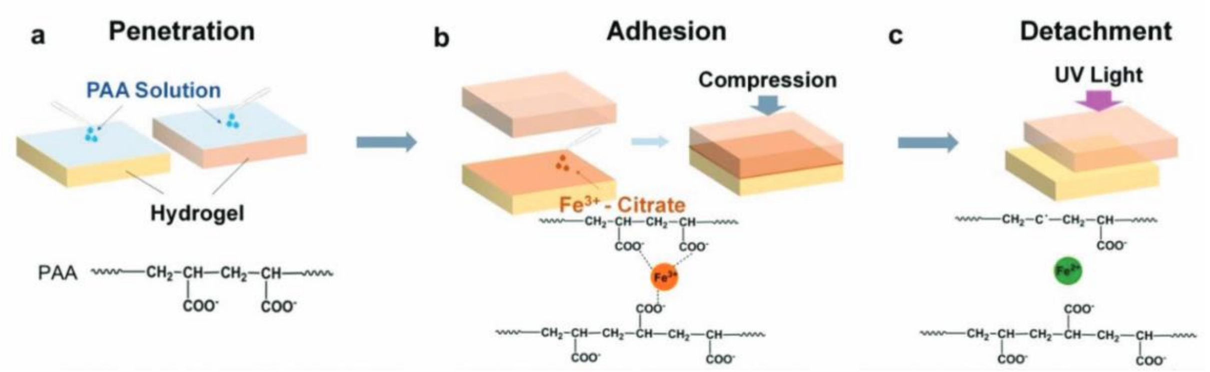
Self-reporting polymers, which can indicate damage or exposure to excessive stress with a clearly perceptible optical signal, are potentially useful for several technological applications, including stress-sensitive sensors that enable in situ monitoring of mechanical events and structural health monitoring systems. A versatile and simple concept to realize this function is the exploitation of microcapsules that are filled with solutions of dyes that are released and chemically or physically activated when the protective shell is damaged. Such microcapsules can readily be incorporated into polymers and the composites thus made can be processed into films, coatings, or other objects. Mechanochromic effects can be realized with different types of dyes and activation schemes. In this concept article, a selection of recent key studies is presented to provide an overview of the state of the field. Different architectures and operating principles and their advantages and drawbacks are reviewed. The parameters that influence the design of microcapsule-based mechanochromic systems are considered and unexplored chromophore systems that might be useful to design future self-reporting polymers are discussed. Finally, specific aspects of capsule design, fabrication, and integration into polymers are presented. Throughout the article, challenges and opportunities of the concept are highlighted and possible future directions are discussed.

Comment: A quite exhaustive review that reminds us that chemical techniques are available for stress mapping in bulk polymers.

Photodetachable Adhesion

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



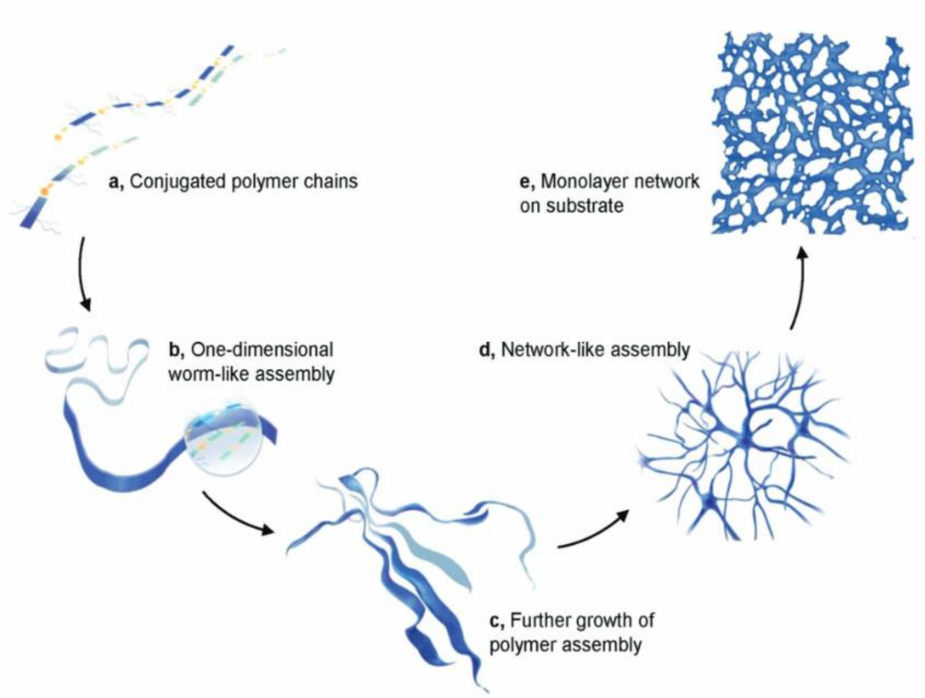


Peeling from strong adhesion is hard, and sometimes painful. Herein, an approach is described to achieve both strong adhesion and easy detachment. The latter is triggered, on-demand, through an exposure to light of a certain frequency range. The principle of photodetachable adhesion is first demonstrated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

Comment: It's a smart method for solving the peeling problem, which is hard for strong adhesion. The introduction of PAA and Fe^{3+} enables strong adhesion interaction, and the detached process also is executed efficiently due to the reduction of Fe^{3+} ions upon irradiation with UV light. Actually, I think that this entire process could be realized by the introduction of a photo or electrochemical responsive host-guest system.

Wafer-Scale Fabrication of High-Performance n-Type Polymer Monolayer Transistors Using a Multi-Level Self-Assembly Strategy

Yao, Z.; Zheng, Y.-Q; Li, Q.-Y.; Lei, T.*; Zhang, S.; Zou, L.; Liu, H.-Y.; Dou, J.-H.; Lu, Y.; Wang, J.-Y.; Gu, X.; Pei. J.* *Adv. Mater.* **2018**, 1806747.



Wafer-scale fabrication of high-performance uniform organic electronic materials is of great challenge and has rarely been realized before. Previous large-scale fabrication methods always lead to different layer thickness and thereby poor film and device uniformity. Herein, the first demonstration of 4 in. wafer-scale, uniform, and high-performance n-type polymer monolayer films is reported, enabled by controlling the multi-level self-assembly process of conjugated polymers in solution. Since the self-assembly process happened in solution, the uniform 2D polymer monolayers can be facilely deposited on various substrates, and theoretically without size limitations. Polymer monolayer transistors exhibit high electron mobilities of up to 1.88 $cm^2\ V^{-1}\ s^{-1}$, which is among the highest in n-type monolayer organic transistors. This method allows to easily fabricate n-type conjugated polymers with wafer-scale, high uniformity, low contact resistance, and excellent transistor performance (better than the traditional spin-coating method). This work provides an effective strategy to prepare large-scale and uniform 2D polymer monolayers, which could enable the application of conjugated polymers for wafer-scale sophisticated electronics.

Comment: Normally, we only focus on the self-assemblies of small organic molecules. This article demonstrates a growth process of conjugated polymers.