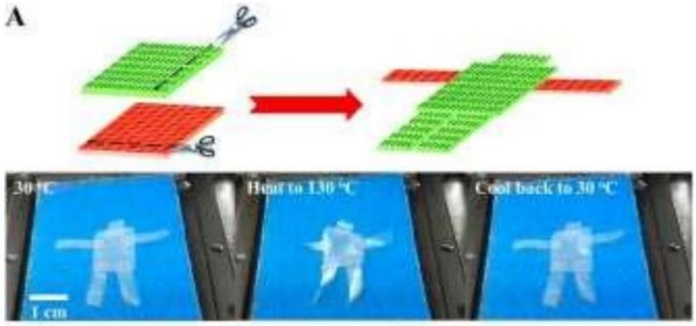
A Cut-and-Paste Strategy towards Liquid Crystal Elastomers with Complex Shape Morphing

Chen, L.; Wang, M.; Guo, L.-X.; Lin, B.-P.; Yang, H.* *J. Mater. Chem. C* **2018**, *6*, 8251–8257.

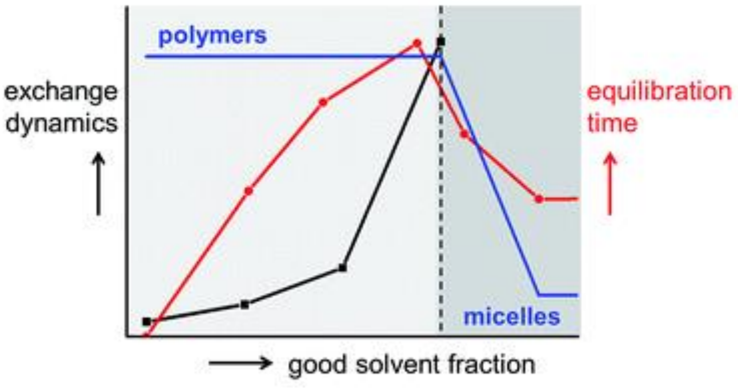


Nowadays, with the rapid progress in soft robotics and aerospace technology, novel soft actuator materials with reversible and complex shape morphing capabilities, such as helical curling, buckling, accordion-like folding, self-oscillating, waving and other three-dimensional motion modes, are highly desirable. In this manuscript, we report a new **cut-and-paste method** to construct liquid crystal elastomer actuators with complex shape morphing by combing dynamic covalent chemistry with the traditional surface-treated liquid crystal cell preparation strategy. In brief, we synthesize monodomain liquid crystal elastomer films with exchangeable disulfide crosslinkers through in-situ photopolymerization in anti-parallel surface-rubbed cells, cut the obtained uniaxial-aligned liquid crystal elastomer films into pieces and paste them together via dynamic disulfide exchange to form versatile shaped soft actuator materials.

Comment: The main point of this paper is about the processing of monodomain liquid crystalline films. By adjusting the direction of "cutting" and "pasting" different pieces of material together, complex shapes with a variety of bending modes can be obtained, in an **easier way than it would be to orient the different domains individually.**

Consequences of a Cosolvent on the Structure and Molecular Dynamics of Supramolecular Polymers in Water.

Lafleur, R. P. M.; Lou, X.; Pavan, G. M.; Palmans, A. R. A.; Meijer, E. W.* *Chem. Sci.* **2018**, *9*, 6199–6209.

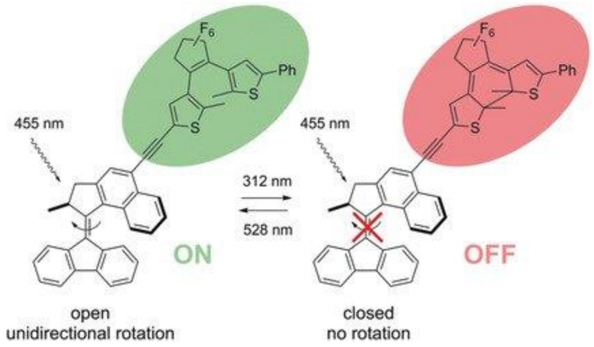


Polar cosolvents are commonly used to guide the self-assembly of amphiphiles in water. Here we investigate the influence of the cosolvent acetonitrile (ACN) on the structure and dynamics of a supramolecular polymer in water, which is based on the well-known benzene-1,3,5-tricarboxamide motif. Hydrogen/deuterium exchange mass spectroscopy measurements show that a gradual increase in the amount of ACN results in a gradual increase in the exchange dynamics of the monomers. In contrast, the morphology of the supramolecular polymers remains unchanged up to 15% of ACN, but then **an abrupt change occurs** and spherical aggregates are formed. Remarkably, this abrupt change coincides with the formation of micro-heterogeneity in the water–ACN mixtures. The results illustrate that in order to **completely characterize supramolecular polymers it is important to add time-resolved measurements that probe their dynamic behavior,** to the conventional techniques that are used to assess the morphology of the polymers. Subsequently we have used time-resolved measurements to investigate the influence of the concentration of ACN on the polymerization and depolymerization rates of the supramolecular polymers. Polymerization occurs within minutes when molecularly dissolved monomers are injected from ACN into water and is independent of the fraction of ACN up to 15%. In the depolymerization experiments—initiated by mixing equilibrated supramolecular polymers with dissolved monomers—the equilibration of the system takes multiple hours and does depend on the fraction of ACN. Interestingly, the longest equilibration time of the polymers is observed at a critical solvent composition of around 15% ACN. The differences in the timescales detected in the polymerization and depolymerization experiments are likely correlated to the non-covalent interactions involved, namely the hydrophobic effect and hydrogen-bonding interactions. We attribute the observed fast kinetics in the polymerization reactions to the hydrophobic effect, whereas the formation of intermolecular hydrogen bonds is the retarding factor in the equilibration of the polymers in the depolymerization experiments. Molecular dynamics simulations show that the latter is a likely explanation because ACN interferes with the hydrogen bonds and loosens the internal structure of the polymers. Our results highlight **the importance of the solution conditions during the non-covalent synthesis of supramolecular polymers,** as well as after equilibration of the polymers.

Comment: Is there something to add to this long abstract? This article provides a good characterization of the dynamics of supramolecular polymers, and is in the continuity of previous work from the Meijer's group.

Light-Gated Rotation in a Molecular Motor Functionalized with a Dithienylethene Switch

Roke, D.; Stuckhardt, C.; Danowski, W.; Wezenberg, S. J.*; Feringa, B. L.* *Angew. Chem. Int. Ed.* **2018**, *57*, 10515.

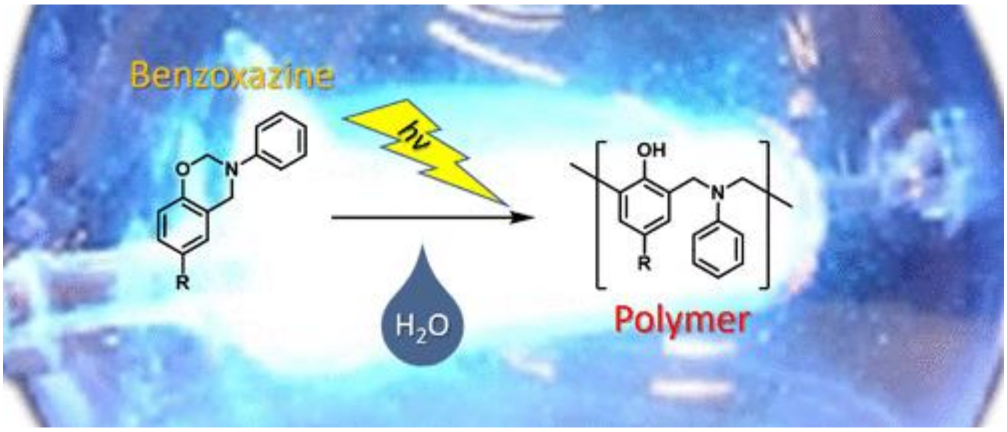


A multiphotochromic hybrid system is presented in which a light-driven overcrowded alkene-based molecular rotary motor is connected to a dithienylethene photoswitch. Ring closing of the dithienylethene moiety, using an irradiation wavelength different from the wavelength applied to operate the molecular motor, results in the inhibition of the rotary motion as is demonstrated by detailed ^{1}H NMR and UV/Vis experiments. For the first time, a light-gated molecular motor is thus obtained. Furthermore, the excitation wavelength of the molecular motor is red-shifted from the UV into the visible light region upon attachment of the dithienylethene switch.

Comment: Motor guys, take a look to this paper! Feringa succeed in creating a molecular motor working using visible light and having a light-gate by integrating a diarylethene on the overcrowded alkene structure.

Photochemical Polymerization of N-Phenyl Mono-1,3-benzoxazines in Aqueous Media

Salabert, J.; Maruyama, K.; Sebastián, R. M.*; Marquet, J. *Macromolecules* **2018**, *51*, 3672-3679.

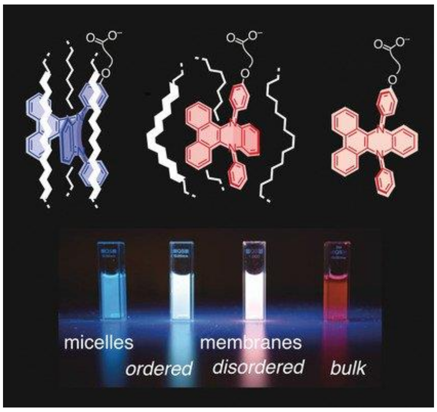


Some N-phenyl monosubstituted mono-1,3- benzoxazines can be polymerized under appropriate UV irradiation in aqueous solutions at room temperature. Photoinduced intramolecular electron transfer from the amine to the phenyl ring in aqueous media produces the mesolitic O−alkyl bond cleavage governed by “topologically controlled Coulombic interactions”. Irradiation of EWG-substituted benzoxazines produces opening of the oxazine ring as expected, but no propagation of the polymerization is observed probably due to the low nucleophilicity of the intermediate phenolic species. However, with more nucleophilic electron-donor substituted benzoxazines the photopolymerization proceeds smoothly, with excellent conversions and modest degrees of polymerization. The produced materials show a similar degree of polymerization to the observed in the non-cross-linked fraction when monobenzoxazines are polymerized under thermal conditions (>150 °C) but having a lower dispersity.

Comment: Rather than only presenting studies on the photopolymerization of different benzoxazine derivatives, two major points are of interest. First, the polymerization system itself and the associated studies: the authors present examples of a polymerization process close to be classified as green chemistry (*e.g.* no catalyst needed unlike previous examples, and in aqueous or semi-aqueous media) and with reasonable polydispersity. Then, it is really interesting to see the authors’ efforts delivered on their hypothesis of the mechanism.

White-Fluorescent Dual-Emission Mechanosensitive Membrane Probes that Function by Bending Rather than Twisting

Humeniuk, H. V.; Rosspeintner, A.; Licari, G.; Kilin, V.; Bonacina, L.; Vauthey, E.; Sakai, N.; Matile, S.* *Angew. Chem. Int. Ed.* **2018**, *57*, 10559.

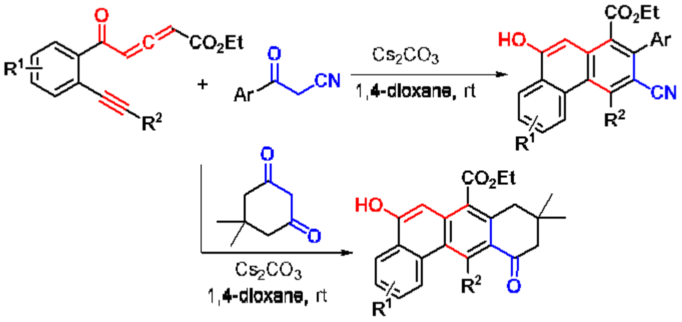


Bent N,N’-diphenyl-dihydrodibenzo[a,c]phenazine amphiphiles are introduced as mechanosensitive membrane probes that operate by an unprecedented mechanism, namely, unbending in the excited state as opposed to the previously reported untwisting in the ground and twisting in the excited state. Their dual emission from bent or “closed” and planarized or “open” excited states is shown to discriminate between micelles in water and monomers in solid-ordered (So), liquiddisordered (Ld) and bulk membranes. The dual-emission spectra cover enough of the visible range to produce vesicles that emit white light with ratiometrically encoded information. Strategies to improve the bent mechanophores with expanded p systems and auxochromes are reported, and compatibility with imaging of membrane domains in giant unilamellar vesicles by two-photon excitation fluorescence (TPEF) microscopy is demonstrated.

Comment: Interesting paper on mechanosensitive membranes probes with different shapes that operate with a fundamentally different mode of action. This system could be useful in biological research but also for us if we want prove that thanks to the molecular motor we succeed to displace a receptor (e.g. strepavidin) in a lipid bilayer.

Metal-Free Naphthannulation Reactions of Yne-Allenone Esters for Accessing Polycyclic Aromatic Hydrocarbons

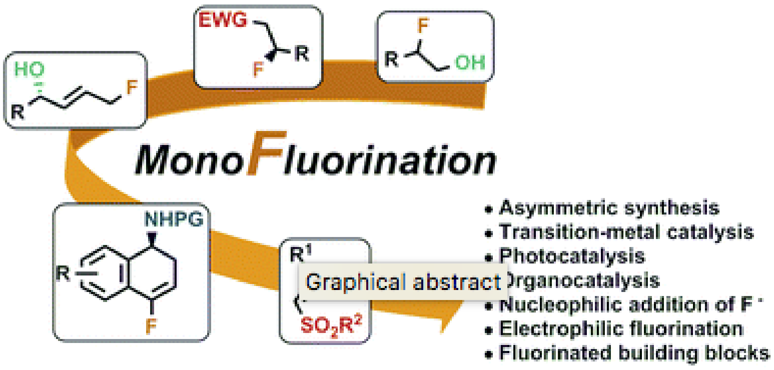
Sha, H. K.; Xu, T.; Liu, F.; Tang, B. Z.; Hao, W. J.*; Tu, S., J.*; Jiang, B.* *Chem. Commun.* **2018**, Advance Article.



The first **metal-free base-promoted naphthannulation reactions of yne-allenone esters** were established for the **direct assembly** of a **wide range of polycyclic aromatic hydrocarbons** with **generally good yields**. The naphthannulation reaction of yne-allenone esters with β-ketonitriles provided new phenanthrene-1-carboxylates *via* a base-mediated [2+2] cycloaddition/ring expansion sequence, whereas hitherto unreported tetracyclic tetrahydrotetraphene-7-carboxylates were obtained with good yield *via* a sequential double annulation cascade of yne-allenone esters with dimedone as a diphilic reagent.

Recent Advances in the Synthesis of Functionalised Monofluorinated Compounds

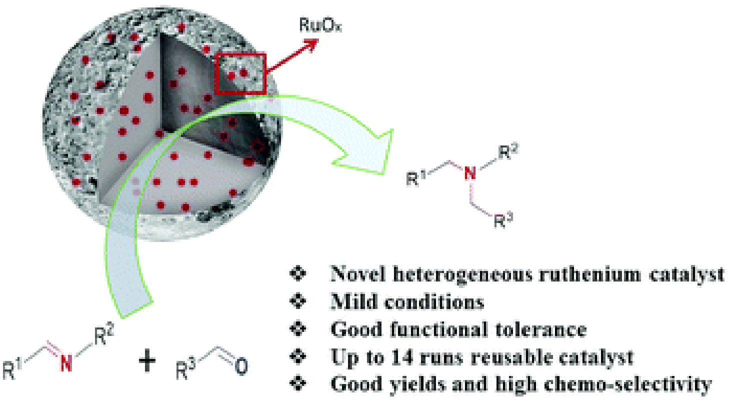
Fustero, S.*; Sedgwik, D., M.; Roman, R.; Barrio, P. *Chem.Commun.*, **2018**, Advance Article.



Over the past few years, we have tackled the synthesis of interesting **monofluorinated organic molecules**, such as: dihydronaphthalene derivatives, β-fluoro sulfones and related carbonyl compounds, fluorohydrins and allylic alcohols. Overall, a **wide range of modern synthetic techniques** are covered in this feature article including transition-metal, photo- and organocatalysis, nucleophilic and electrophilic fluorinations, chiral auxiliaries and enantioselective catalysis.

Ruthenium Nanoparticles Catalyzed Selective Reductive Amination of Imine with Aldehyde to Access Tertiary Amines

Li, B.*; Liu, S.; Lin, Q.; Shao, Y.*; Pen, S.; Li, Y. *Chem. Commun.*, **2018**, Advance Article.

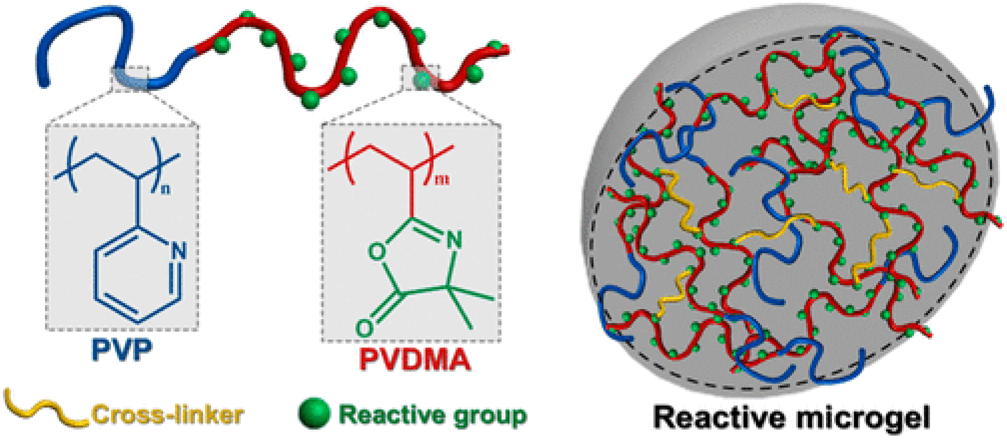


Reductive amination is one of the most frequently used transformations in organic synthesis. Herein, by developing a novel **ruthenium nanoparticles embedded within ordered mesoporous carbon catalyst** (Ru-OMC) and a new **hydrosilylation process** for the **synthesis of tertiary amines.** We present a direct reductive amination of imines (C=N bond) with aldehydes (C=O bond) using hydrosilane as reducing reagent under mild conditions. Moreover, the Ru-OMC catalytst can be reused up to 14 runs without noticeable losing activities.

Comment: These three articles may be useful for the elaboration of synthetic pathways. In the first one, the main approach is metal-free and allows the formation of functionalized Polycyclic Aromatic Hydrocarbons (PAHs). However, it is important to notice that the starting materials may also need to be synthesized. The second paper is similar to a small review dedicated to the formation of monofluorinated compounds, thus, allowing us to keep the different synthetic strategies in mind. The last one is dedicated to the reduction of imines using a heterogeneous Ruthenium catalyst. This article shows that the method can be applied to a relatively high number of aldehydes. However, it is relevant to mention that it only works with an aldehyde (i.e. is not reactive using ketones) and that the catalyst may require some specific equipment to be prepared (carbonization at 1000°C under N_2).

Versatile Synthesis of Amine-Reactive Microgels by Self-Assembly of Azlactone-Containing Block Copolymers

Wang, X.*; Davis, J. L.; Aden, B. M.; Lokitz, B. S.; Kilbey, S. M. II* *Macromolecules* **2018**, *51*, 3691-3701.

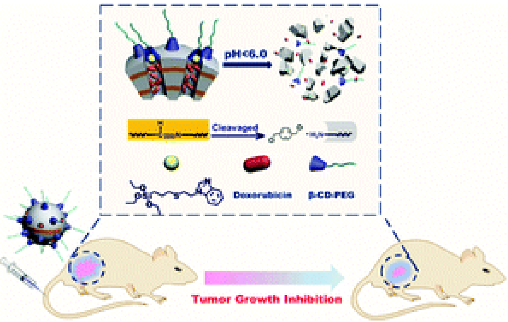


Relations between molecular design, chemical functionality, and stimulus-triggered response are important for a variety of applications of polymeric systems. Here, reactive amphiphilic block copolymers (BCPs) of poly(2-vinylpyridine)- block-poly(2-vinyl-4,4-dimethylazlactone) (PVP-b-PVDMA) were synthesized and assembled into microgels capable of incorporating functional amines. The composition of the PVP-b-PVDMA BCPs was varied to control the number of reactive sites in the spherical aggregates created by self-assembly of PVP-b-PVDMA BCPs in a 2-propanol/THF (v:v = 19:1) solvent mixture, which is selective for PVP. PVDMA and PVP segments were selectively cross-linked by 1,4-diaminobutane (DAB) or 1,4-diiodobutane (DIB) to fabricate core- and corona-cross-linked azlactone-containing microgels, respectively. Non-cross-linked aggregates of PVP-b-PVDMA and DIB-cross-linked microgels dissociate when exposed to THF, which is a good solvent for both blocks. However, the DAB-cross-linked BCP microgels swell in THF, suggesting the formation of a stable, three-dimensional network structure. Because of their ability to be reactively modified in ways that allows their stability or disassembly characteristics to be tailored, these azlactone-containing BCP microgels provide an attractive platform for applications in a wide range of fields, including catalysis, imaging, molecule separation, and guest loading for targeted delivery.

Comment: I am not really sure what to think about this paper. The information is so dense and the authors use so many acronyms that it is more than easy to get lost and I caught myself several times trying to remember what was the initial purpose of the work.

Schiff Base Interactions Tuned Mesoporous Organosilica Nanoplatforms with pH-Responsive Degradability for Efficient Anti-Cancer Drug Delivery *In Vivo*

Liu, L.; Kong, C.; Huo, M.; Liu, C.; Peng, L.; Zhao, T.; Wei, Y.; Qian, F.*; Yuan, J.* *Chem. Commun.* **2018**, Advance Article.

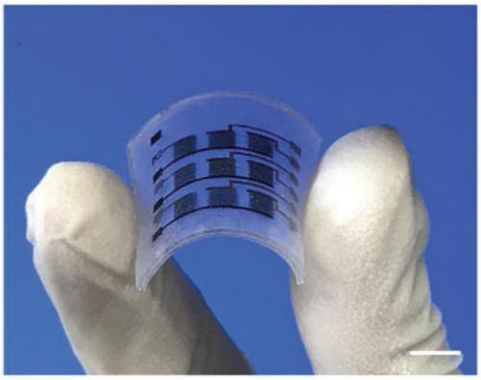


Chemically incorporating Schiff base interactions **into silicate frameworks** endows the obtained mesoporous organosilica based drug carriers **ultrafast pH-responsive degradability** and efficient anti-cancer **drug release kinetics**, resulting in enhanced cancer therapy.

Comment: This article is fascinating because it presents a clever approach to degrade silica structures (their degradation represents a major issue for *in vivo* applications). Even if it may not be related to our field of study, I think that the use of a Schiff base as a pH-sensitive trigger in some of our systems might be interesting.

Multiscale Hierarchical Design of a Flexible Piezoresistive Pressure Sensor with High Sensitivity and Wide Linearity Range

Shi, J.; Wang, L.; Dai, Z.; Zhao, L.; Du, M.; Li, H.*; Fang, Y.* *Small*, **2018**, *14*, 1800819.

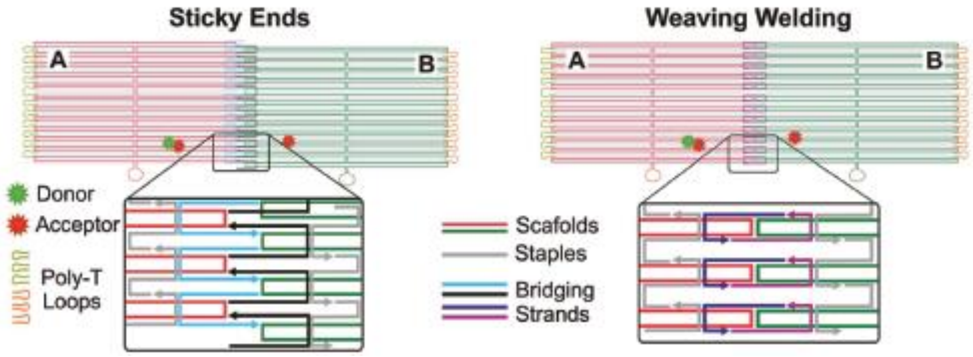


Flexible piezoresistive pressure sensors have been attracting wide attention for applications in health monitoring and human-machine interfaces because of their simple device structure and easy-readout signals. For practical applications, flexible pressure sensors with both high sensitivity and wide linearity range are highly desirable. Herein, a simple and low-cost method for the fabrication of a flexible piezoresistive pressure sensor with a hierarchical structure over large areas is presented. The piezoresistive pressure sensor consists of arrays of microscale papillae with nanoscale roughness produced by replicating the lotus leaf's surface and spray-coating of graphene ink. Finite element analysis (FEA) shows that the hierarchical structure governs the deformation behavior and pressure distribution at the contact interface, leading to a quick and steady increase in contact area with loads. As a result, the piezoresistive pressure sensor demonstrates a high sensitivity of 1.2 kPa−1 and a wide linearity range from 0 to 25 kPa. The flexible pressure sensor is applied for sensitive monitoring of small vibrations, including wrist pulse and acoustic waves. Moreover, a piezoresistive pressure sensor array is fabricated for mapping the spatial distribution of pressure. These results highlight the potential applications of the flexible piezoresistive pressure sensor for health monitoring and electronic skin.

Comment: Here they described the straightforward access to a flexible device with piezoresistive pressure sensor properties. The simplicity of the system and its high response and stability and major point of the paper. An impressive work from the authors.

Study of DNA Origami Dimerization and Dimer Dissociation Dynamics and of the Factors that Limit Dimerization

Liber, M.; Tomov, T. E.; Tsukanov, R.; Berger, Y.; Popov, M.; Khara, D. C.; Nir, E.* *Small*, **2018**, *14*, 1800218.

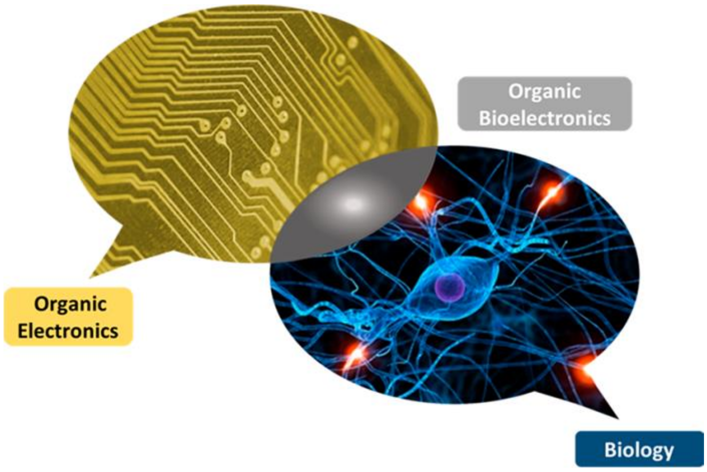


Organizing DNA origami building blocks into higher order structures is essential for fabrication of large structurally and functionally diverse devices and molecular machines. Unfortunately, the yields of origami building block attachment reactions are typically not sufficient to allow programed assembly of DNA devices made from more than a few origami building blocks. To investigate possible reasons for these low yields, a detailed single-molecule fluorescence study of the dynamics of rectangular origami dimerization and origami dimer dissociation reactions is conducted. Reactions kinetics and yields are investigated at different origami and ion concentrations, for different ion types, for different lengths of bridging strands, and for the "sticky end" and "weaving welding" attachment techniques. Dimerization yields are never higher than 86%, which is typical for such systems. Analysis of the dynamic data shows that the low yield cannot be explained by thermodynamic instability or structural imperfections of the origami constructs. Atomic force microscopy and gel electrophoresis evidence reveal self-dimerization of the origami monomers, likely via blunt-end interactions made possible by the presence of bridging strands. It is suggested that this mechanism is the major factor that inhibits correct dimerization and means to overcome it are discussed.

Comment: An interesting discussion on the specific dimerization of DNA origami and its limitations due to self-dimerization. Here it is pleasant to have well defined paragraphs, making the article easier to read. This one maybe lacks a bit of illustrations.

Conjugated Polymers in Bioelectronics

Inal, S.*; Rivnay, J.; Suiu, A.; Malliaras, G. G.; McCulloch, I. *Acc. Chem. Res.* **2018**, *51*, 1368-1376

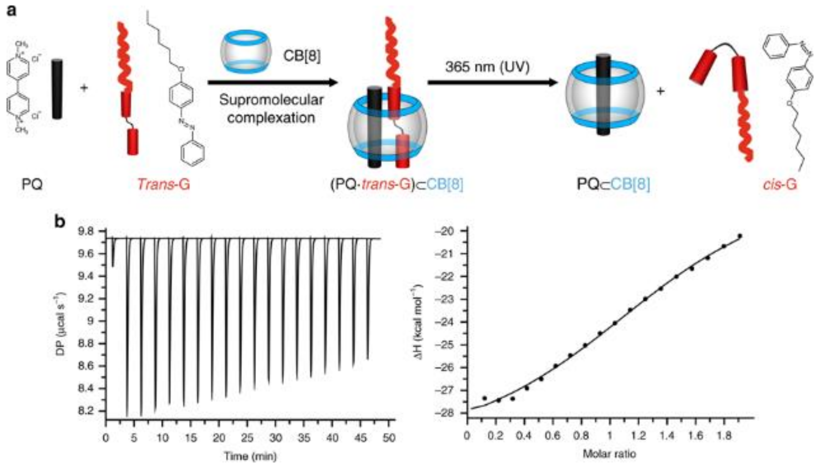


The emerging field of organic bioelectronics bridges the electronic world of organic-semiconductor-based devices with the soft, predominantly ionic world of biology. This crosstalk can occur in both directions. For example, a biochemical reaction may change the doping state of an organic material, generating an electronic readout. Conversely, an electronic signal from a device may stimulate a biological event. Cutting-edge research in this field results in the development of a broad variety of meaningful applications, from biosensors and drug delivery systems to health monitoring devices and brain−machine interfaces. Conjugated polymers share similarities in chemical “nature” with biological molecules and can be engineered on various forms, including hydrogels that have Young’s moduli similar to those of soft tissues and are ionically conducting. The structure of organic materials can be tuned through synthetic chemistry, and their biological properties can be controlled using a variety of functionalization strategies. Finally, organic electronic materials can be integrated with a variety of mechanical supports, giving rise to devices with form factors that enable integration with biological systems. While these developments are innovative and promising, it is important to note that the field is still in its infancy, with many unknowns and immense scope for exploration and highly collaborative research. The first part of this Account details the unique properties that render conjugated polymers excellent biointerfacing materials. We then offer an overview of the most common conjugated polymers that have been used as active layers in various organic bioelectronics devices, highlighting the importance of developing new materials. These materials are the most popular ethylenedioxythiophene derivatives as well as conjugated polyelectrolytes and ion-free organic semiconductors functionalized for the biological interface. We then discuss several applications and operation principles of state-of-the-art bioelectronics devices. These devices include electrodes applied to sense/trigger electrophysiological activity of cells as well as electrolyte-gated field-effect and electrochemical transistors used for sensing of biochemical markers. Another prime application example of conjugated polymers is cell actuators. External modulation of the redox state of the underlying conjugated polymer films controls the adhesion behavior and viability of cells. These smart surfaces can be also designed in the form of three-dimensional architectures because of the processability of conjugated polymers. As such, cell-loaded scaffolds based on electroactive polymers enable integrated sensing or stimulation within the engineered tissue itself. A last application example is organic neuromorphic devices, an alternative computing architecture that takes inspiration from biology and, in particular, from the way the brain works. Leveraging ion redistribution inside a conjugated polymer upon application of an electrical field and its coupling with electronic charges, conjugated polymers can be engineered to act as artificial neurons or synapses with complex, history-dependent behavior. We conclude this Account by highlighting main factors that need to be considered for the design of a conjugated polymer for applications in bioelectronics, although there can be various figures of merit given the broad range of applications, as emphasized in this Account.

Comment: Bioelectronics is an emerging field of research with great promise. I think that this account is written in a didactic manner; also non-specialists will understand. Therefore, a good read if you are interested in the subject.

A user-friendly herbicide derived from photo-responsive supramolecular vesicles

Gao, C.; Huang, Q.; Lan, Q.; Feng, Y.; Tang, F.; Hoi, M. P. M.; Zhang, J.; Lee, S. M. Y. *; Wang, R.* *Nat. Commun.* **2018**, *9*, 2967.

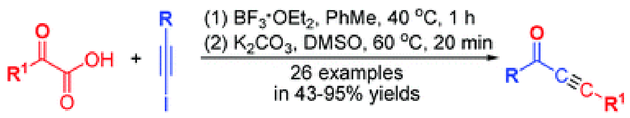


Paraquat, as one of the most widely used herbicides globally, is highly toxic to humans, and chronic exposure and acute ingestion leads to high morbidity and mortality rates. Here, we report user-friendly, photo-responsive paraquat-loaded supramolecular vesicles, prepared via one-pot self-assembly of amphiphilic, ternary host-guest complexes between cucurbit[8]uril, paraquat, and an azobenzene derivative. In this vesicle formulation, paraquat is only released upon UV or sunlight irradiation that converts the azobenzene derivative from its trans- to its cis- form, which in turn dissociates the ternary host-guest complexations and the vesicles. The cytotoxicity evaluation of this vesicle formulation of paraquat on in vitro cell models, in vivo zebrafish models, and mouse models demonstrates an enhanced safety profile. Additionally, the PQ-loaded vesicles' herbicidal activity against a model of invasive weed is nearly identical to that of free paraquat under natural sunlight. This study provides a safe yet effective herbicide formulation.

Comment: You might think this is another "new" story about CB-based host-guest vesicles with photo-controlled drug release again. But, actually, the authors found a new path to a safe herbicide formulation by looking at the paraquat-based host-guest self-assembled systems from the paraquat's original use as herbicide. The toxicity study of the assembled vesicles for in vitro cell models, in vivo zebrafish models, and mouse models showed an enhanced safety profile.

A General Two-Step One-Pot Synthesis of Ynones from *alpha*-keto Acids and 1-Iodoalkynes

Zeng, X.; Liu, C.; Yang, W.; Wang, X.; Wang, X.*; Hu, Y*. *Chem.Commun.* **2018**, Advance Article.



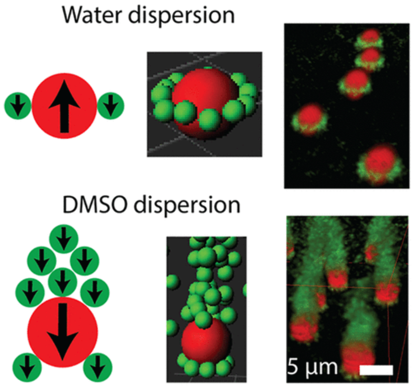
No hypervalent iodine(III) reagent is used.
Iodine-atom bonded to C(sp^2) remains intact.
α-Keto acids become a part of triple bond in ynones.

A **general two-step one-pot synthesis of ynones** was developed by a **cycloaddition of *alpha*-keto acids and 1-iodoalkynes** followed by a **ring-opening**. Its easy conditions and novel mechanism endowed it with two distinctive advantages: iodine-atom bonded to C(sp2) remained intact and *alpha*-keto acids became a part of triple bond in ynones.

Comment: This article presents an easy method to synthesize alkyne derivatives through a one-pot synthesis. Numerous examples are presented and with generally good yields. This approach may certainly be useful in the future for our team.

Electric Field Assembly of Colloidal Superstructures

Demirörs, A. F.*; Alison, L., *J. Phys. Chem. Lett.*, **2018**, 9, 4437–4443.

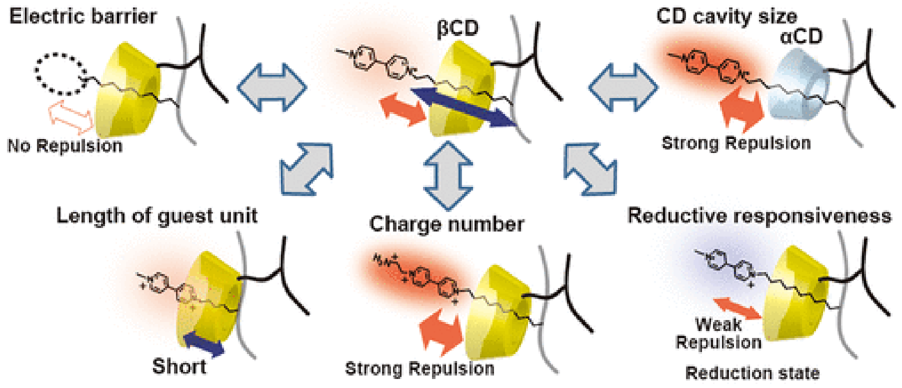


The assembly of materials from building blocks has been in the core of a wide range of applications from catalysis to photonics and electronics. External electric fields enable the interactions between building blocks to be controlled via induced dipoles. Dipolar interactions were used so far to obtain one-dimensional chains or three-dimensional non-close-packed lattices. However, complex colloidal assemblies and clusters of simple spherical particles are rare. Here we demonstrate a novel self-assembly approach enabling the formation of regular axially symmetric clusters, an array of colloidal assemblies as per design of posts, and hierarchical complex assemblies by using posts and dipolar interactions or combining them. Regulating the polarization of the particles from positive to negative allows us to control the interparticle interactions from attractive to repulsive at the poles or equator of the particles. Therefore, such particle–particle interactions enable switching between Saturn ring-like and candle-flame-like axially symmetric assemblies, which could potentially be exploited for display applications.

Comment: The technique described here provides a new way to construct complex assemblies of particles by manipulating them within electric fields. The method is good for programed assembly but could be combined with other orthogonal chemical or physical techniques to increase the complexity of the systems.

Mechanical Properties of Supramolecular Polymeric Materials Formed by Cyclodextrins as Host Molecules and Cationic Alkyl Guest Molecules on the Polymer Side Chain

Takashima, Y.*; Otani, K.; Kobayashi, Y.; Aramoto, H.; Nakahata, M.; Yamaguchi, H.; Harada, A.* *Macromolecules*, **2018**, *ASAP*

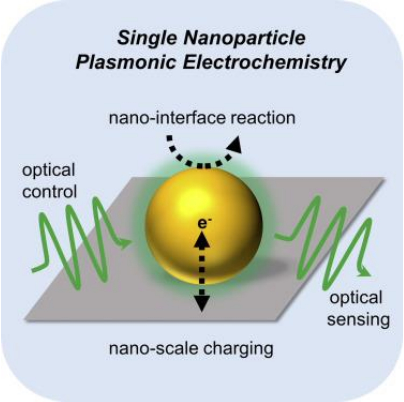


Supramolecular polymeric materials have received much attention in recent years due to the fabrication of supramolecular materials with mechanical properties and stimuli-responsive properties in response to polymeric designs based on noncovalent cross-linkers. Host−guest interactions are useful noncovalent interactions that can be employed to realize supramolecular materials. To understand the relationship between the mechanical properties of supramolecular polymeric materials based on host−guest interactions and the molecular structure of guest molecules on the polymer side chain, we prepared supramolecular hydrogels cross-linked by inclusion complexes between cyclodextrin (CD) and cationic alkyl guests on the polymer side chain. The mechanical properties were influenced by an electric barrier due to the cationic group, CD cavity size, length of the guest unit, charge number of the electric barrier, and reduction responsiveness. Although the introduction of an electric barrier to the end of the alkyl guest moiety increased the rupture stress, the rupture strain decreased due to the electric repulsion of the CD unit and the cationic group. The rupture stress of the αCD-cationic alkyl hydrogel was higher than that of the βCD-cationic alkyl hydrogel because electric repulsion between the αCD unit and the cationic group is higher than that of the βCD unit due to the relatively small cavity size of αCD. The fracture energy increased as the alkyl chain length or charge number of the cationic guest group increased. We demonstrated the change in the mechanical properties by reduction stimulus.

Comment: Part of the studies presented by Prof. Takashima when he visited the group are now published. It is worth reading if you liked his lecture.

Plasmonic Sensing and Control of Single-Nanoparticle Electrochemistry

Hoener, B. S.; Kirchner, S. R.; Heiderscheit, T. S.; Collins, S. S. E.; Chang, W.; Link, S.*; Landes, C. F.* *Chem* **2018**, *4*, 1560-1585

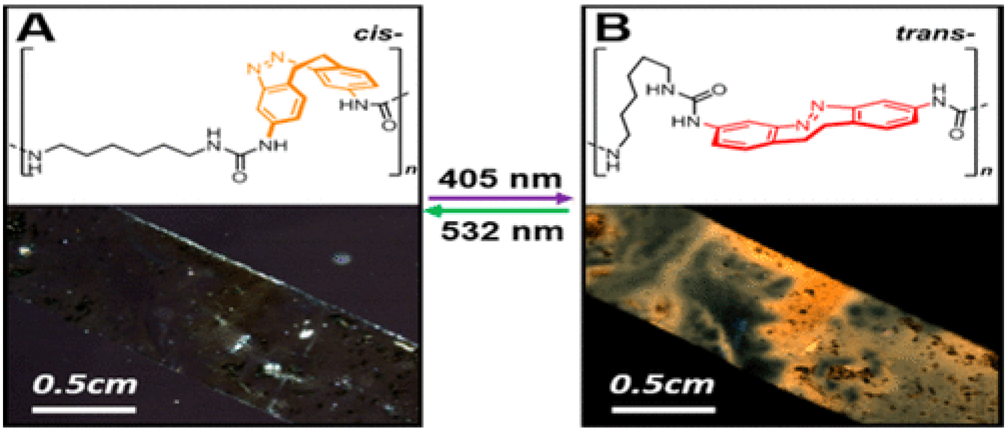


Plasmonic nanoparticles offer promise in photoelectrochemistry by enhancing the rate and selectivity of reactions and in sensing by responding optically to local reactions. Optical electrochemical measurements at the single-particle level are necessary for understanding and eventually controlling the role of plasmons in such complex environments. Recently, researchers have developed techniques to optically measure electrochemical reactions at the surface of single nanoparticles and individual aggregates, allowing for the high-throughput screening necessary to resolve subpopulations of active nanoparticle catalysts and identify active sites on aggregate structures. This review highlights single- nanoparticle and nanoparticle aggregate electrochemical techniques and how they can be used to isolate and elucidate the role of surface plasmons in enhancing catalyst activity and sensing electrochemical processes at the nanoscale.

Comment: In contrast with the Acc. Chem. Res. account on bioelectronics, this really is an in-depth review article, with an eye for details.

Concise Synthesis of Photoresponsive Polyureas Containing Bridged Azobenzenes as Visible-Light-Driven Actuators and Reversible Photopatterning

Li, S.; Han, G.; Zhang, W.* *Macromolecules*, **2018**, *51*, 4290-4297.



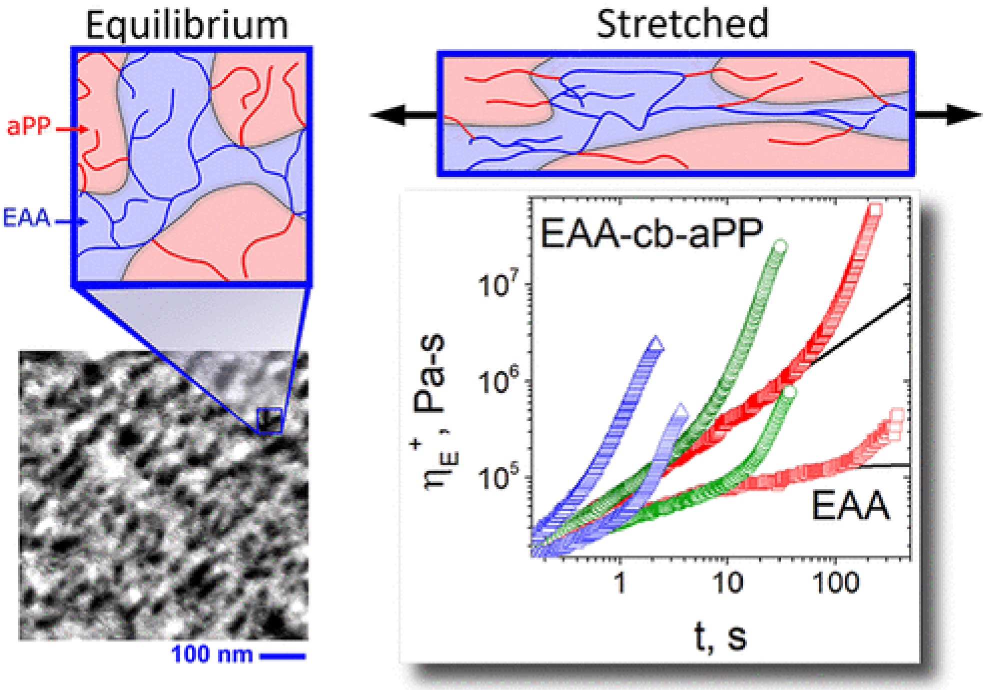
Linear photoresponsive polyurea of PbAzo containing bridged-azobenzene moieties in backbone was synthesized via polyaddition reaction between hexamethylene diisocyanate and cis-

3,3'-diamino ethylene-bridged azobenzene. The bridged-azobenzene moieties endow the PbAzo polyurea advantages of visible-light-driven isomerization and fast and powerful photoresponse. Under irradiation with 405 nm blue light, stable cis-PbAzo converts into metastable transPbAzo accompanying the amorphous-to-crystalline transition and the yellow-to-red color change via cis-to-trans isomerization. With further illumination with 532 nm green light, trans-to-cis isomerization reversibly takes place. This photoresponsive polyurea is used in photopatterning, in which patterns can be reversibly written or erased alternatively by 405 nm blue light and 532 nm green light or heating. Besides, the polyurea film can act as qualified visible-light-driven actuators. Under irradiation with 405 nm blue light, it initially bends away the light source with the bending angle above 110 deg in several seconds, and then it recovers to its initial state with no attenuation under irradiation with 532 nm green light. Our photoresponsive polyurea is different from photoresponsive polymers including planar azobenzene moieties, and this polyurea is expected to be promising for smart materials.

Comment: This changes a little bit from “conventional” polymers that contain azobenzenes. It could be interesting to further compare the effect of the bridged-design with conventional ones, first on the thermal relaxation and secondly on the macroscopic response efficiency, which might be the only discussion missing in the article.

Long-Chain Hyperbranched Comb Block Copolymers: Synthesis, Microstructure, Rheology, and Thermal Behavior

López-Barrón, C. R.*; Brant, P.; Shivokhin, M.; Lu, J.; Kang, S.; Throckmorton, J. A.; Mouton, T.; Pham, T.; Savage, R. C. *Macromolecules*, **2018**, *ASAP*

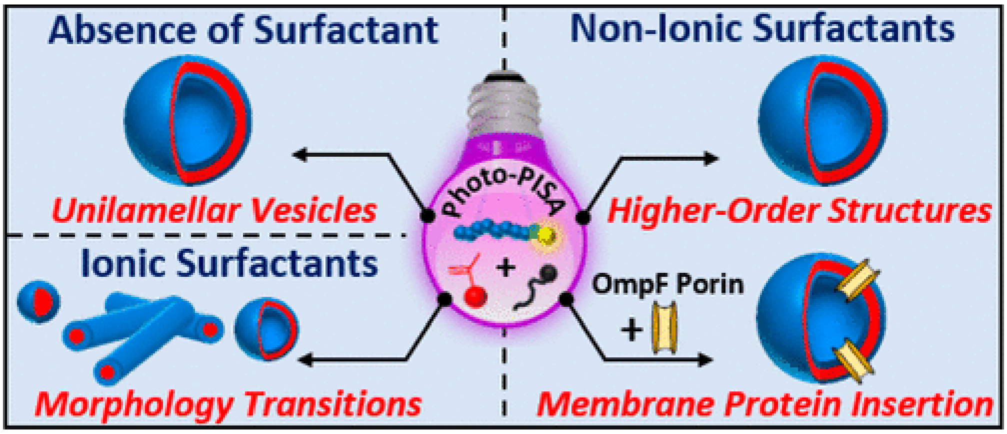


A series of poly(ethylene-co-acrylic acid)-cb-atactic polypropylene (EAA-cb-aPP) comb block copolymers were synthesized by grafting aPP-OH macromonomers onto a commercial EAA copolymer made by the high-pressure free radical process. The starting EAA copolymer contains 11 wt % of EAA units and has a significant amount of long chain branches. Therefore, the EAA-cb-aPP copolymers can be classified as hyperbranched. Room temperature atomic force microscopy and X-ray scattering measurements reveal strong, finely textured, phase segregation of the amorphous aPP and semicrystalline EAA domains, which persists in the melt state. The amorphous aPP side chains have an unexpected nucleating effect that facilitates crystallization of the EAA backbone, as evidenced by an increase in crystallization temperature. Moreover, phase segregation has a strong effect on both the linear and nonlinear viscoelastic response of the copolymers. Increases in both the branching density and branch chain length result in an improvement of melt strength as well as an increase in the extensional strain hardening (SH). We postulate that the SH enhancement may arise from the interfacial anchoring of the aPP side chains in the aPP homopolymer domains. This would produce additional resistance for the EAA backbone to stretch under uniaxial load due to an energetically unfavorable process of pulling the aPP arms into the EAA phase where they would face strong repulsions.

Comment: Question: is it because I am not well experienced in this field, or is this paper really difficult to read (figures everywhere cutting the text like nonsense, with some of them as ugly as possible [figure 1b in particular])? I would really like to have some feedbacks from our members with better knowledge in polymer science.

Photoinitiated Polymerization-Induced Self-Assembly in the Presence of Surfactants Enables Membrane Protein Incorporation into Vesicles

Varlas, S.; Blackman, L. D.; Findlay, H. E.; Reading, E.; Booth, P. J.; Gibson, M. I.; O’Reilly, R. K.* *Macromolecules*, **2018**, *ASAP*

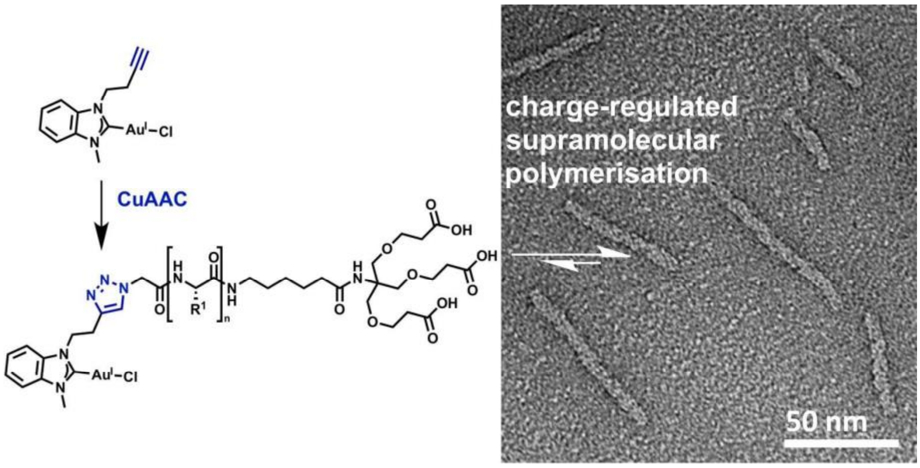


Photoinitiated polymerization-induced self-assembly (photo-PISA) is an efficient approach to predictably prepare polymeric nanostructures with a wide range of morphologies. Given that this process can be performed at high concentrations and under mild reaction conditions, it has the potential to have significant industrial scope. However, given that the majority of industrial (and more specifically biotechnological) formulations contain mixtures of polymers and surfactants, the effect of such surfactants on the PISA process is an important consideration. Thus, to expand the scope of the methodology, the effect of small molecule surfactants on the PISA process, specifically for the preparation of unilamellar vesicles, was investigated. Similar to aqueous photo-PISA findings in the absence of surfactant molecules, the originally targeted vesicular morphology was retained in the presence of varying concentrations of non-ionic surfactants, while a diverse set of lower-order morphologies was observed for ionic surfactants. Interestingly, a critical micelle concentration (CMC)-dependent behavior was detected in the case of zwitterionic detergents. Additionally, tunable size and membrane thickness of vesicles were observed by using different types and concentration of surfactants. Based on these findings, a functional channel-forming membrane protein (OmpF porin), stabilized in aqueous media by surfactant molecules, was able to be directly inserted into the membrane of vesicles during photo-PISA. Our study demonstrates the potential of photo-PISA for the direct formation of protein−polymer complexes and highlights how this method could be used to design biomimicking polymer/surfactant nanoreactors.

Comment: May be of interest for some of you I know are now working on self-assembly...?

A Clickable NHC-Au(I)-Complex for the Preparation of Stimulus-Responsive Metallopeptide Amphiphiles

Lewe, V.; Preuss, M.; Woznica, E. A.; Spitzer, D.; Otter, R.; Besenius, P.* *Chem. Commun.* **2018**, Advance Article.



We report the synthesis of an **alkyne functionalized NHC-Au(I)- complex** which is **conjugated with amphiphilic oligopeptides** using a copper(I) catalyzed cycloaddition. The resulting Au(I)- metalloamphiphiles are shown to self-assemble into charge-regulated stimulus-responsive supramolecular polymers in water *via* a weakly cooperative polymerization mechanism.

Comment: I found that the approach the authors used, in order to functionalize their Au nanoparticles, was very clever. It could be used with our motors in order to obtain another kind of polymer at the end.