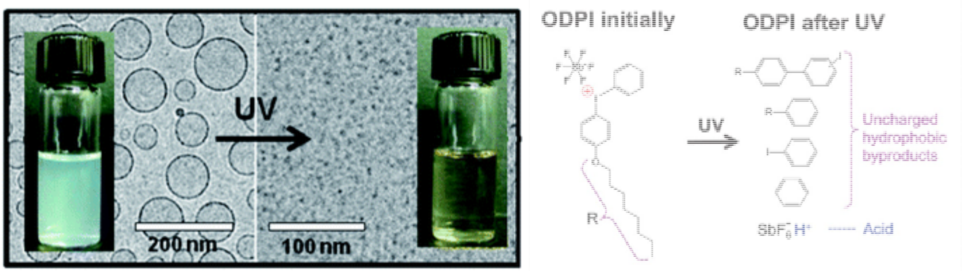
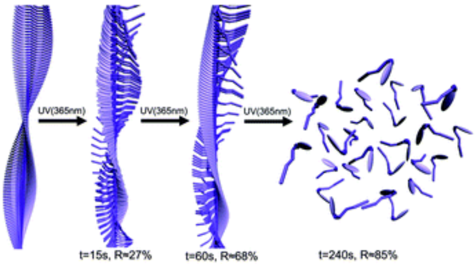
- Light-induced transformation of vesicles to micelles and vesicle-gels to sols
  Oh, H.; Javvaji, V.; Yaraghi, N. A.; Abezgauz, L.; Danino, D.; Raghavan, S. R. *Soft Matter* **2013**, *9,* 11576-11584.
  Abstract:



Vesicles are self-assembled nanocontainers that are used for the controlled release of cosmetics, drugs, and proteins. Researchers have been seeking to create photoresponsive vesicles that could enable the triggered release of encapsulated molecules with accurate spatial resolution. While several photoresponsive vesicle formulations have been reported, these systems are rather complex as they rely on special light-sensitive amphiphiles that require synthesis. In this study, we report a new class of photoresponsive vesicles based on two inexpensive and commercially available amphiphiles. Specifically, we employ p-octyloxydiphenyliodonium hexafluoroantimonate (ODPI), a cationic amphiphile that finds use as a photoinitiator, and a common anionic surfactant, sodium dodecylbenzenesulfonate (SDBS). Mixtures of ODPI and SDBS form “catanionic” vesicles at certain molar ratios due to ionic interactions between the cationic and anionic headgroups. When irradiated with ultraviolet (UV) light, ODPI loses its charge and, in turn, the vesicles are converted into micelles due to the loss of ionic interactions. In addition, a mixture of these photoresponsive vesicles and a hydrophobically modified biopolymer gives a photoresponsive vesicle-gel. The vesicle-gel is formed because hydrophobes on the polymer insert into vesicle bilayers and thus induce a three-dimensional network of vesicles connected by polymer chains. Upon UV irradiation, the network is disrupted because of the conversion of vesicles to micelles, with the polymer hydrophobes getting sequestered within the micelles. As a result, the gel is converted to a sol, which manifests as a 40 000-fold light-induced drop in sample viscosity.

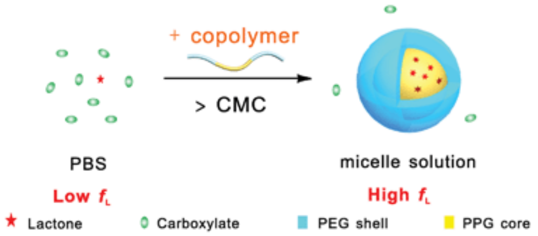
- Photo-responsive cholesterol-substituted diacetylenic organogels: morphology tuning, photo-switching and photo-polymerization
  Wang, J.; Yang, G.; Jiang, H.; Zou, G.; Zhang, Q. *Soft Matter* **2013**, *9,* 9785-9791.
  Abstract:



A novel cholesterol derivative organogelator (CAZODA) containing both azobenzene and diacetylenic units is synthesized. By using XRD, CD, TEM and SEM characterization, the gelation behavior, microscopic morphology and molecular packing structure in CAZODA assemblies are investigated in detail. It is found that the concentration of the CAZODA at the initial stage plays a crucial role in tuning the microstructure from helical fibers to spherulitic gel networks. Upon UV irradiation at 365

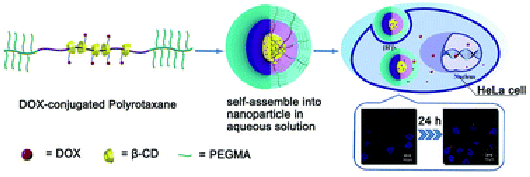
nm, the photoinduced transition of the helical packing structures for CAZODA assemblies has been demonstrated by CD characterization, and an explanation based on the co-assembly of both trans- and cis-form CAZODA has been proposed. In addition, upon irradiation at 254 nm for 3 h, the above organogel can be polymerized with concomitant color change from yellow to red. The polymerized gel exhibits enhanced stability upon thermo or photo-stimuli.

- Effects of amphiphilic block copolymers on the equilibrium lactone fractions of camptothecin analogues at different pHs
  Ci, T.; Chen, L.; Li, T.; Chang, G.; Yu, L.; Ding, j. *Biomater. Sci.* **2013**, *1*, 1235-1243.
  Abstract:



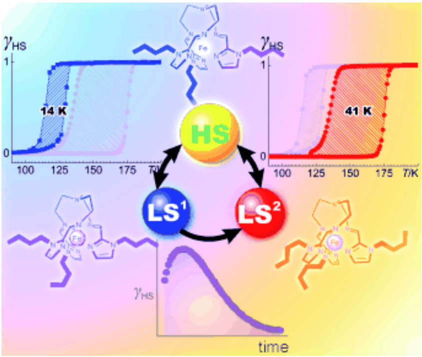
Camptothecin (CPT) and its analogues constitute one of the most important families of anticancer drugs. However, the CPT-family members have to confront the severe problem of hydrolysis from lactone form, the only form capable of antitumor efficacy, to the carboxylate form, leading to a significant decrease in therapy efficiency as well as severe side effects. Herein, two CPT analogues with different water solubilities, 10-hydrocamptothecin (HCPT) and topotecan (TPT), and four poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) (PEG–PPG–PEG, Pluronic) copolymers of varied hydrophilic–lipophilic balance (HLB) values, were examined with emphasis on the change of the equilibrium lactone fraction (f_{lactone}) of the drugs after addition of the copolymers. In all cases, f_{lactone} was enhanced. For weak water-soluble HCPT, the enhancement extent was significantly increased with decrease of the copolymer HLB, which is influenced by the block chain length for a given series of amphiphilic block copolymers. The effect was less significant for TPT, a more hydrophilic drug. The fluorescence experiments confirmed the assembly of the drugs into polymeric micelles. A series of pH titrations were also carried out, which quantified the shift of $pH_{1/2}$ (pH when$f_{\text{lactone}} = 0.5$) after addition of the copolymers. The optimal or most sensitive pH, pH_{opt}, which gave the maximum enhancement of f_{lactone} by the polymers, was found to depend upon the type of drug, the HLB value of copolymer, and also the polymer concentration. Hence, this work has indicated the universality of the enhancement effect of polymeric micelles on the equilibrium lactone fractions of CPT analogues, and meanwhile revealed the dependence of the enhancement extent upon the HLB values of the copolymer and hydrophilicity of the drug. The concept of optimal pH has also been put forward for the first time.

- A pH-sensitive nano drug delivery system of doxorubicin-conjugated amphiphilic polyrotaxane-based block copolymers
  Jiang, L.; Gao, Z.-M.; Ye, L.; Zhang, A.-Y.; Feng, Z.-G. *Biomater. Sci.* **2013**, *1*, 1282-1291.
  Abstract:



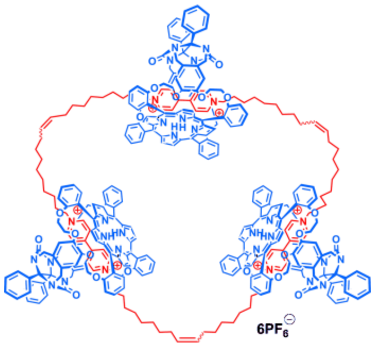
A pH-sensitive nano antitumor drug delivery system was prepared by conjugating doxorubicin (DOX) to amphiphilic polyrotaxane (PR)-based block copolymers through a pH-sensitive *cis*-aconityl moiety. The resulting polymer-drug conjugates were able to self-assemble into polymeric micelles in an aqueous solution with diameters varying from 297 nm to 178 nm after the conjugation as evidenced by DLS measurements. The pH-sensitive *cis*-aconityl linkage provided a controlled and sustained release of DOX over a period of more than 5 days in an acidic environment mimicking the tumor microenvironment, and a negligible amount of release in an environment with physiological pH. The nanoparticles had lower cytotoxicity than the free drug and can efficiently transfer and release the drug into HeLa cells. With these promising properties, the PR-based block copolymers have the potential to be carriers for the controlled release of antitumor drugs.

- Unprecedented Multi-Stable Spin Crossover Molecular Material with Two Thermal Memory Channels
  Seredyuk, M.; Muñoz, M. C.; Castro, M.; Romero-Morcillo, T.; Gaspar, A. B.; Real, J. A. *Chem. Eur. J.* **2013**, *19*, 6591–6596.
  <u>Abstract:</u>



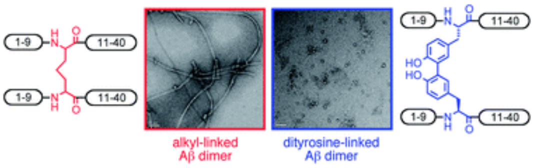
Two in one: A new iron(II) complex with short alkyl substituents exhibits an unprecedented bimodal behavior governed by the coexistence of three phases: two structurally different low-spin phases and one high-spin phase. The compound features two distinct well-separated strong cooperative spin-crossover transitions by varying the scan rate (see graphic).

- Interlocked Porphyrin Switches
  Coumans, R. G. E.; Elemans, J. A. A. W.; Rowan, A. E.; Nolte, R. J. M. *Chem. Eur. J.* **2013**, *19*, 7758–7770.
  <u>Abstract:</u>



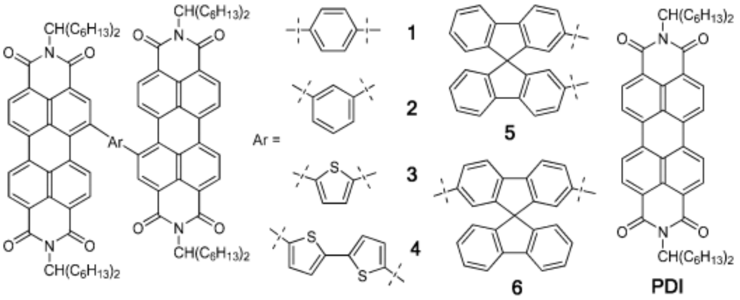
We describe the synthesis of a series of interlocked structures from porphyrin–glycoluril cage compounds and bis(olefin)-terminated viologens by an olefin-metathesis protocol. The length of the chain connecting the olefin substituents with the viologen has a marked effect on the products of the ring-closure reaction. Long chains give [2]- and [3]catenane structures, whereas short chains give a mixture of [3]-, [4]-, and [5]catenanes. For comparison several [2]rotaxane compounds were prepared. The interlocked catenane and rotaxane structures display switching behavior, which can be controlled by the addition of acid and base. The kinetic and thermodynamic parameters of the switching processes have been determined by NMR spectroscopy.

- Synthetic dityrosine-linked β-amyloid dimers form stable, soluble, neurotoxic oligomer
  Kok, W. M.; Cottam, J. M.; Ciccotosto, G. D.; Miles, L. A.; Karas, J. A.; Scanlon, D. B.; Roberts, B. R.; Parker, M. W.; Cappai, R.; Barnham, K. J.; Hutton, C. A. *Chem. Sci.* **2013**, *4,* 4449-4454.
  Abstract:



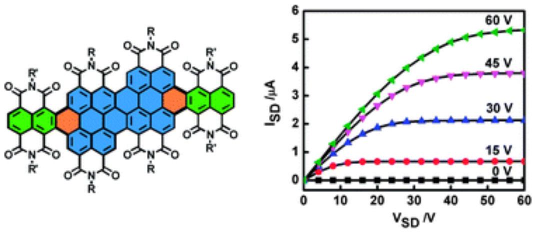
Substantial evidence suggests that soluble oligomers of Aβ are the neurotoxic form resulting in progression of Alzheimer's disease (AD). Tyrosine-10 has been identified as a pivotal residue in the neurotoxicity of Aβ species linked to the progression of AD. We describe the synthesis and characterization of dityrosine-linked Aβ dimers and demonstrate that, in contrast to other covalently linked Aβ dimers, dityrosine-linked Aβ dimers form discrete, stable, soluble aggregates. Furthermore, dityrosine-linked Aβ dimers display increased toxicity in a neuronal cell-line assay compared with the corresponding monomer, consistent with the hypothesis that dityrosine-linked Aβ dimers are implicated in the progression of AD.

- Towards rational design of organic electron acceptors for photovoltaics: a study based on perylenediimide derivatives
  Yan, Q.; Zhou, Y.; Zheng, Y.-Q.; Pei, J.; Zhao, D. *Chem. Sci.* **2013**, *4,* 4389-4394.
  Abstract:



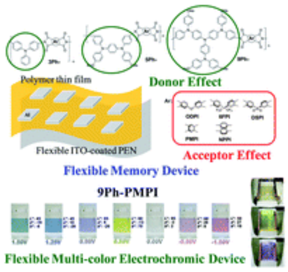
A series of PDI dimers featuring various arylene linkers are developed as electron acceptors in organic solar cells. Using P3HT as the donor, power conversion efficiency of up to 2.3 % is achieved with two PDI dimers having spirobifluorene linkers. The results indicate that such non-planar, three-dimensional structures effectively suppress self-aggregation and crystallization of the PDI units, which is favorable for their solar cell performance.

- High-performance electron-transporting hybrid rylenes with low threshold voltage
  Li, X.; Xiao, C.; Jiang, W.; Wang, Z. *J. Mater. Chem. C* **2013**, *1,* 7513–7518.
  Abstract:



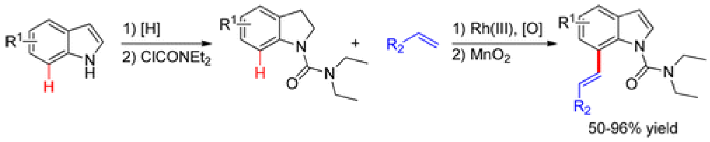
We present here a new family of hybrid rylene arrays (3a–d) by the combination of Stille coupling and C–H transformation via a facile one-pot synthesis. The π-expanded rylene diimides exhibit broadened and intensive optical absorption accompanied by higher electron affinity. The linear alkyl chain substituted NDI-diPDI-NDI (3b) revealed its electron transporting characteristics with good air stability and low threshold voltage.

- Novel programmable functional polyimides: preparation, mechanism of CT induced memory, and ambipolar electrochromic behavior
  Chen, C.-J.; Yen, H.-J.; Hua, Y.-C.; Liou, G.-S. *J. Mater. Chem. C* **2013**, *1,* 7623–7634.
  Abstract:



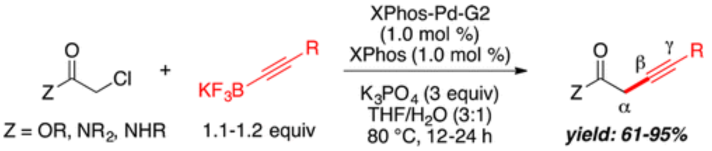
In this study, the new functional polyimides 9Ph-ODPI, 9Ph-DSPI, and 9Ph-PMPI consisting of electron-donating starburst triarylamine units and different dianhydrides were synthesized and used for memory device applications along with 9Ph-6FPI. To investigate the effects of donor moieties in polyimides on their memory behavior, the corresponding 3Ph- series polyimides (3Ph-PIs) and 5Ph-PIs were also discussed. With the intensity of electron donation increasing from 3Ph-PIs to 5Ph-PIs to 9Ph-PIs, the retention time of the memory device shows a systematic increase. The retention time of the memory device also increases with the increasing electron-withdrawing intensity of the dianhydrides. Furthermore, the in situ UV-vis absorption spectra of the memory devices during switching-ON were utilized as direct evidence to confirm the relationship between charge transfer (CT) complex stability and memory retention time. In electrochromic (EC) applications, the novel ambipolar 9Ph-PMPI exhibited a high contrast ratio and electroactive stability during EC operation with multiple colors at different applied potentials, due to its four oxidation and two reduction states. Finally, flexible colorful EC and volatile memory devices were fabricated for practical flexible electronics applications in the future.

- Rhodium(III)-Catalyzed Direct Regioselective Synthesis of 7-Substituted Indoles
  Song, Z.; Samanta, R.; Antonchick, A. P. *Org. Lett.* **2013**, *15*, 5662-5665.
  Abstract:



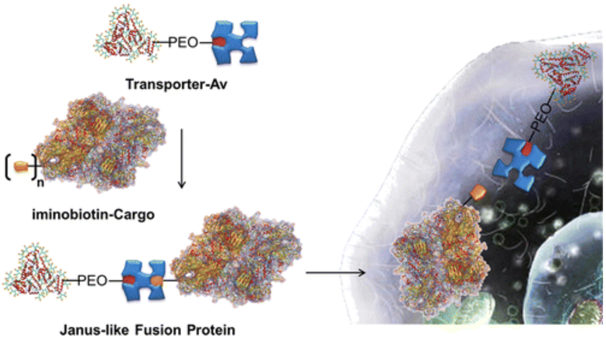
An efficient, atom-economic one-pot method was developed for the preparation of 7-substituted indoles via rhodium(III)-catalyzed oxidative crosscoupling. Regioselective olefination of indoline derivatives followed by one-pot subsequent oxidation provided the desired products in good to excellent yields.

- Pd-Catalyzed Alkynylation of 2-Chloroacetates and 2-Chloroacetamides with Potassium Alkynyltrifluoroborates
  Molander, G. A.; Traister, K. M. *Org. Lett.* **2013,** *15*, 5052-5055.
  Abstract:



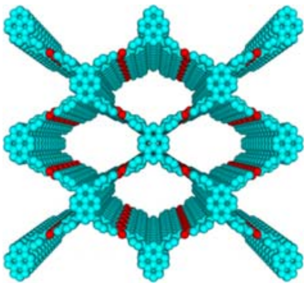
Pd-catalyzed direct C-H arylation of N-methyl-7-azaindole at the C-2 position by diverse arylboronic acids was achieved at room temperature. The method is general and was applied in chemoselective synthesis of multiarylated 7-azaindole derivatives bearing three different aryl groups at the 2, 3, and 5 positions.

- pH Responsive Janus-like Supramolecular Fusion Proteins for Functional Protein Delivery
  Kuan, S. L.; Ng, D. Y. W.; Wu, Y.; Förtsch, C.; Barth, H.; Doroshenko, M.; Koynov, K.; Meier, C.; Weil, T. *J. Am. Chem. Soc.* **2013**, *135*, 17254–17257.
  Abstract:



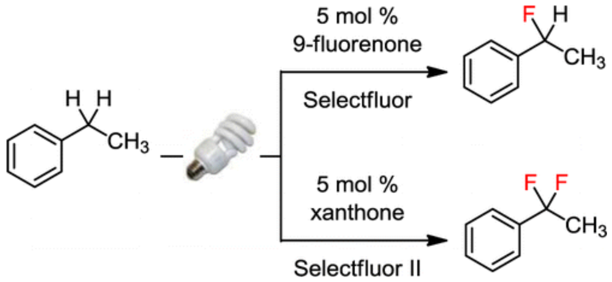
A facile, noncovalent solid-phase immobilization platform is described to assemble Janus-like supramolecular fusion proteins that are responsive to external stimuli. A chemically postmodified transporter protein, DHSA, is fused with (imino)biotinylated cargo proteins via an avidin adaptor with a high degree of spatial control. Notably, the derived heterofusion proteins are able to cross cellular membranes, dissociate at acidic pH due to the iminobiotin linker and preserve the enzymatic activity of the cargo proteins β-galactosidase and the enzymatic subunit of Clostridium botulinum C2 toxin. The mix-and-match strategy described herein opens unique opportunities to access macromolecular architectures of high structural definition and biological activity, thus complementing protein ligation and recombinant protein expression techniques.

- An Azine-Linked Covalent Organic Framework
  Dalapati, S.; Jin, S.; Gao, J.; Xu, Y.; Nagai, A.; Jiang, D. *J. Am. Chem. Soc.* **2013**, *135*, 17310–17313.
  Abstract:



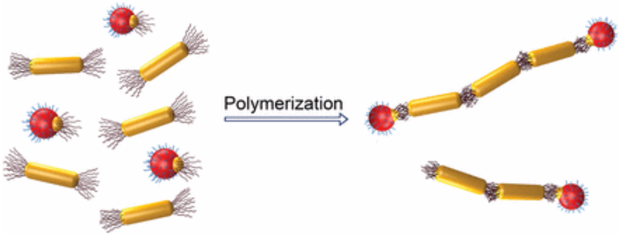
Condensation of hydrazine with 1,3,6,8-tetrakis(4-formylphenyl)pyrene under solvothermal conditions yields highly crystalline two-dimensional covalent organic frameworks. The pyrene units occupy the vertices and the diazabutadiene (−C═N−N═C−) linkers locate the edges of rohmbic-shaped polygon sheets, which further stack in an AA-stacking mode to constitute periodically ordered pyrene columns and one-dimensional microporous channels. The azine-linked frameworks feature permanent porosity with high surface area and exhibit outstanding chemical stability. By virtue of the pyrene columnar ordering, the azine-linked frameworks are highly luminescent, whereas the azine units serve as open docking sites for hydrogen-bonding interactions. These synergestic functions of the vertices and edge units endow the azine-linked pyrene frameworks with extremely high sensitivity and selectivity in chemosensing, for example, the selective detection of 2,4,6-trinitrophenol explosive. We anticipate that the extension of the present azine-linked strategy would not only increase the structural diversity but also expand the scope of functions based on this highly stable class of covalent organic frameworks.

- Visible Light-Promoted Metal-Free C-H Activation: Diarylketone-Catalyzed Selective Benzylic Mono- and Difluorination
  Xia, J.-B.; Zhu, C.; Chen, C. *J. Am. Chem. Soc.* **2013**, *135*, 17494-17500.
  Abstract:



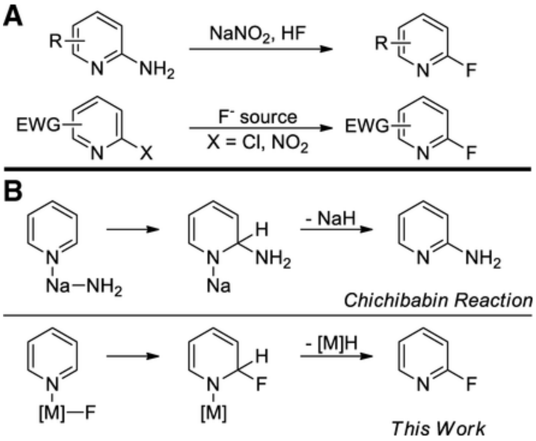
We report herein an operationally simple method for the direct conversion of benzylic C-H groups to C-F. We show that visible light can activate diarylketones to abstract a benzylic hydrogen atom selectively. Adding a fluorine radical donor yields the benzylic fluoride and regenerates the catalyst. The selective formation of mono- and difluorination products can be achieved by catalyst control. 9-Fluorenone catalyzes benzylic C-H monofluorination, while xanthone catalyzes benzylic C-H difluorination. The scope and efficiency of this new C-H fluorination method are significantly better than those of the existing methods. This is also the first report of selective C-H gem-difluorination.

- Colloidal analogs of molecular chain stoppers
  Klinkova, A.; Thérien-Aubin, H.; Choueiri, R. M.; Rubinstein, M.; Kumacheva, E. *Proc. Natl. Acad. Sci. U. S. A.* **2013,** *110*, 18775-18779.
  Abstract:



A similarity between chemical reactions and self-assembly of nanoparticles offers a strategy that can enrich both the synthetic chemistry and the nanoscience fields. Synthetic methods should enable quantitative control of the structural characteristics of nanoparticle ensembles such as their aggregation number or directionality, whereas the capability to visualize and analyze emerging nanostructures using characterization tools can provide insight into intelligent molecular design and mechanisms of chemical reactions. We explored this twofold concept for an exemplary system including the polymerization of bifunctional nanoparticles in the presence of monofunctional colloidal chain stoppers. Using reaction-specific design rules, we synthesized chain stoppers with controlled reactivity and achieved quantitative fine-tuning of the self-assembled structures. Analysis of the nanostructures provided information about polymerization kinetics, side reactions, and the distribution of all of the species in the reaction system. A quantitative model was developed to account for the reactivity, kinetics, and side reactions of nanoparticles, all governed by the design of colloidal chain stoppers. This work provided the ability to test theoretical models developed for molecular polymerization.

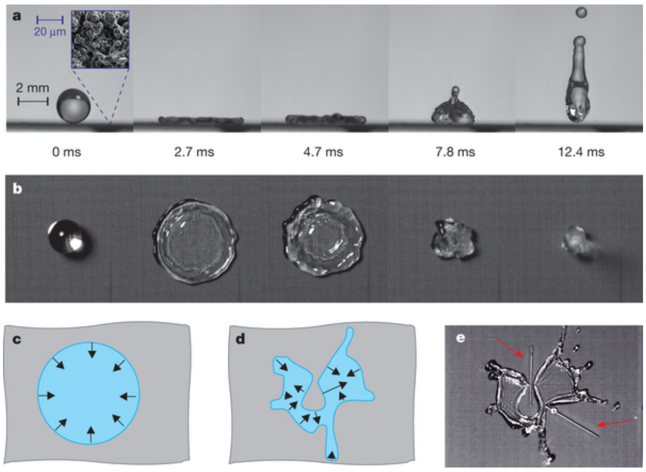
- Selective C-H Fluorination of Pyridines and Diazines Inspired by a Classic Amination Reaction
  Fier, P. S.; Hartwig, J. F. *Science* **2013,** *342*, 956-960.
  Abstract:



Fluorinated heterocycles are prevalent in pharmaceuticals, agrochemicals, and materials. However, reactions that incorporate fluorine into heteroarenes are limited in scope and can be hazardous. We present a broadly applicable and safe method for the site-selective fluorination of a single carbon-hydrogen bond in pyridines and diazines using commercially available silver(II) fluoride. The reactions occur at ambient temperature within 1 hour with exclusive selectivity for fluorination adjacent to nitrogen. The mild conditions allow access to fluorinated derivatives of medicinally important compounds, as well as a range of 2-substituted pyridines prepared by subsequent nucleophilic displacement of fluoride. Mechanistic studies demonstrate that the pathway of a classic pyridine amination can be adapted for selective fluorination of a broad range of nitrogen heterocycles.

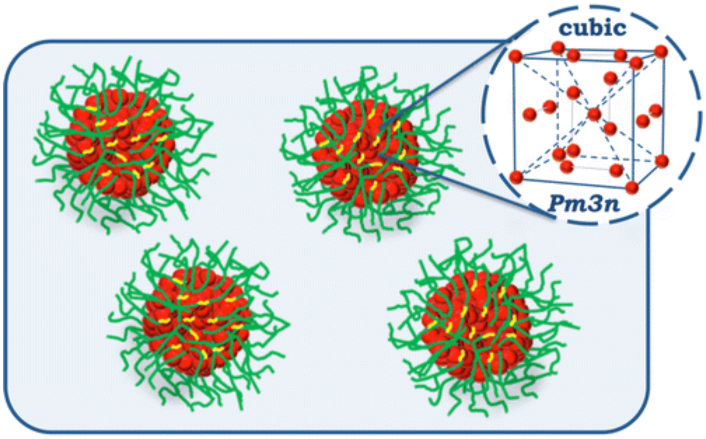
- Reducing the contact time of a bouncing drop

Bird, J. C.; Dhiman, R.; Kwon, H.-M.; Varanasi, K. K. *Nature* **2013,** *503*, 385-388.
Abstract:



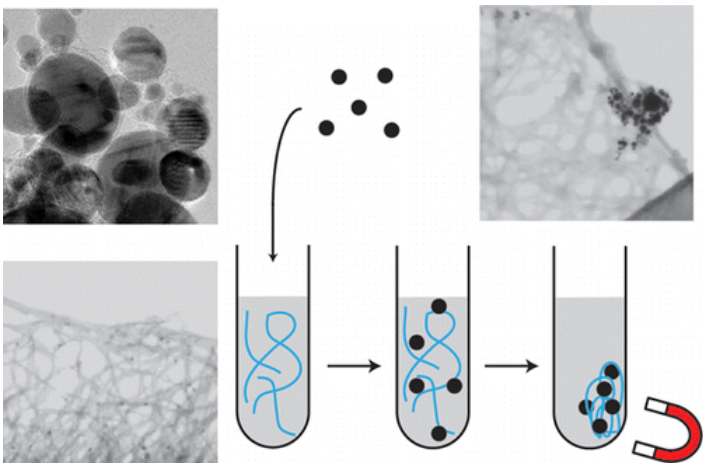
Surfaces designed so that drops do not adhere to them but instead bounce off have received substantial attention because of their ability to stay dry, self-clean and resist icing. A drop striking a non-wetting surface of this type will spread out to a maximum diameter and then recoil to such an extent that it completely rebounds and leaves the solid material. The amount of time that the drop is in contact with the solid—the ‘contact time’—depends on the inertia and capillarity of the drop, internal dissipation and surface–liquid interactions. And because contact time controls the extent to which mass, momentum and energy are exchanged between drop and surface, it is often advantageous to minimize it. The conventional approach has been to minimize surface–liquid interactions that can lead to contact line pinning; but even in the absence of any surface interactions, drop hydrodynamics imposes a minimum contact time that was conventionally assumed to be attained with axisymmetrically spreading and recoiling drops. Here we demonstrate that it is possible to reduce the contact time below this theoretical limit by using superhydrophobic surfaces with a morphology that redistributes the liquid mass and thereby alters the drop hydrodynamics. We show theoretically and experimentally that this approach allows us to reduce the overall contact time between a bouncing drop and a surface below what was previously thought possible.

- Self-Assembly of Complex Salts of Cationic Surfactants and Anionic–Neutral Block Copolymers. Dispersions with Liquid-Crystalline Internal Structure
  Vitorazi, L.; Berret, J.-F.; Loh, W. *Langmuir* **2013**, *46*, 14024-14033.
  Abstract:



We report the synthesis of complex salts made from the cationic surfactant dodecyltrimethylammonium and diblock copolymers poly(acrylic acid)-*block*-poly(acrylamide) of different molecular weights. In water, the complex salts self-assemble into stable hierarchical aggregates with a dense core and a diffuse shell. In contrast to earlier reports, the surfactant/polymer aggregates exhibit a liquid crystalline structure of *Pm*3*n* cubic symmetry. The crystal structure is analogous to that obtained with homopolymer. Size and aggregation numbers were estimated from a combination of light and small-angle X-ray scattering experiments. It is found that the size of the aggregates decreases with increasing diblock asymmetry. The complex salt methodology presents many advantages, among which to be insensitive to the preparation conditions and to the mixing pathway.

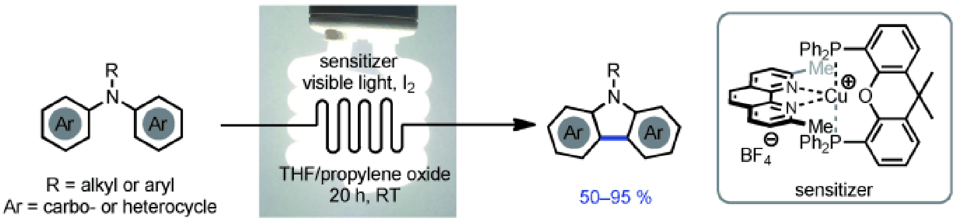
- Rapid Surface–Biostructure Interaction Analysis Using Strong Metal-Based Nanomagnets
  Rotzetter, A. C. C.; Schumacher, C. M.; Zako, T.; Stark, W. J.; Maeda, M. *Langmuir* **2013**, *46*, 14117-14123.
  Abstract:



Nanomaterials are increasingly suggested for the selective adsorption and extraction of complex compounds in biomedicine. Binding of the latter requires specific surface modifications of the nanostructures. However, even complicated macromolecules such as proteins can afford affinities toward basic surface characteristics such as hydrophobicity, topology, and electrostatic charge. In this study, we address these more basic physical interactions. In a model system, the interaction of bovine serum albumin and amyloid β 42 fibrillar aggregates with carbon-coated cobalt nanoparticles, functionalized with various polymers differing in character, was studied. The possibility of rapid magnetic separation upon binding to the surface represents a valuable tool for studying surface interactions and selectivities. We find that the surface interaction of Aβ 42 fibrillar aggregates is mostly hydrophobic in nature. Because bovine serum albumin (BSA) is conformationally adaptive, it is known to bind surfaces with widely differing properties (charge, topology, and hydrophobicity). However, the rate of tight binding (no desorption upon washing) can vary largely depending on the extent of necessary conformational changes for a specific surface. We found that BSA can only bind slowly to polyethylenimine-coated nanomagnets. Under competitive conditions (high excess BSA compared to that for β 42 fibrillar aggregates), this effect is beneficial for targeting the fibrillar species. These findings highlight the possibility of selective extractions from complex media when advantageous basic physical surface properties are chosen.

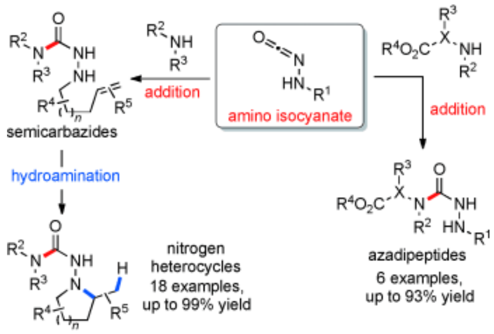
- A Visible-Light-Mediated Synthesis of Carbazoles

Hernandez-Perez, A. C.; Collins, S. K. *Angew. Chem. Int. Ed*. **2013**, *52*, 12696–12700.
<u>Abstract:</u>



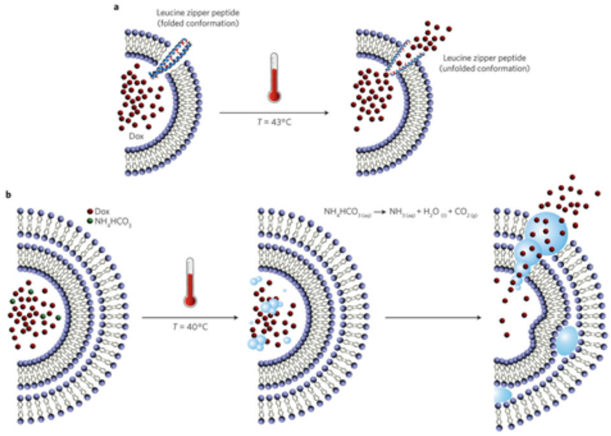
The photosynthetic preparation of *N*-aryl- and *N*-alkyl-bearing carbazoles utilizes continuous flow, visible light, and an in situ formed Cu-based sensitizer (see picture). The method is mild and efficient, and allows the straightforward synthesis of a variety of carbazoles with different substituents, heterocycles, and complex carbon architectures.

- Diversity-Oriented Synthesis of Hydrazine-Derived Compounds from Amino Isocyanates Generated In Situ
  Clavette, C.; Vincent Rocan, J.-F.; Beauchemin, A. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12705–12708.
  <u>Abstract:</u>



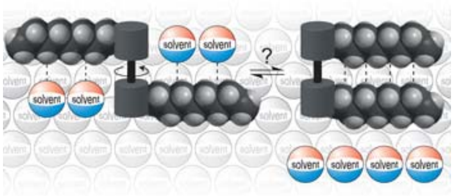
Behind the mask: Nitrogen-substituted isocyanates are rare and their synthetic potential is virtually untapped. Simple masked precursors can form amphoteric amino isocyanate intermediates in situ, and allows the synthesis of complex hydrazine derivatives upon addition with amines. This reactivity was used in a cascade substitution/hydroamination sequence, and in the assembly of azadipeptide analogues.

- Stimuli-responsive nanocarriers for drug delivery
  Mura, S.; Nicolas, J.; Couvreur, P. *Nature Mater*. **2013**, *12*, 991–1003.
  <u>Abstract:</u>



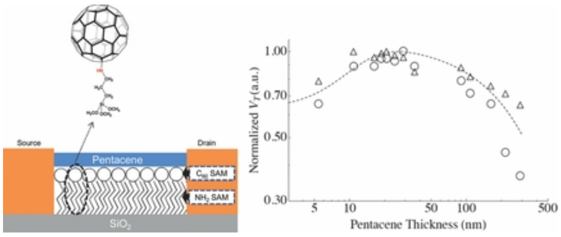
Spurred by recent progress in materials chemistry and drug delivery, stimuli-responsive devices that deliver a drug in spatial-, temporal- and dosage-controlled fashions have become possible. Implementation of such devices requires the use of biocompatible materials that are susceptible to a specific physical incitement or that, in response to a specific stimulus, undergo a protonation, a hydrolytic cleavage or a (supra)molecular conformational change. In this Review, we discuss recent advances in the design of nanoscale stimuli-responsive systems that are able to control drug biodistribution in response to specific stimuli, either exogenous (variations in temperature, magnetic field, ultrasound intensity, light or electric pulses) or endogenous (changes in pH, enzyme concentration or redox gradients).

- How much do van der Waals dispersion forces contribute to molecular recognition in solution?
  Yang, L.; Adam, C.; Nichol, G. S.; Cockroft, S. L. *Nature Chem*. **2013**, *5*, 1006–1010.
  Abstract:



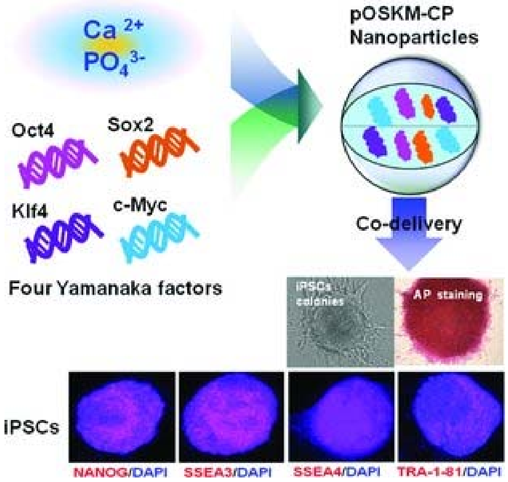
The emergent properties that arise from self-assembly and molecular recognition phenomena are a direct consequence of non-covalent interactions. Gas-phase measurements and computational methods point to the dominance of dispersion forces in molecular association, but solvent effects complicate the unambiguous quantification of these forces in solution. Here, we have used synthetic molecular balances to measure interactions between apolar alkyl chains in 31 organic, fluorous and aqueous solvent environments. The experimental interaction energies are an order of magnitude smaller than estimates of dispersion forces between alkyl chains that have been derived from vaporization enthalpies and dispersion-corrected calculations. Instead, it was found that cohesive solvent–solvent interactions are the major driving force behind apolar association in solution. The results suggest that theoretical models that implicate important roles for dispersion forces in molecular recognition events should be interpreted with caution in solvent-accessible systems.

- Simultaneous Study of Exciton Diffusion/Dissociation and Charge Transport in a Donor-Acceptor Bilayer: Pentacene on a C60-terminated Self-Assembled Monolayer
  Park, B.; Cho, S. E.; Kim, Y.; Lee, W. J.; You, N.-H.; In, I.; Reichmanis, E. *Adv. Mater*. **2013**, *25*, 6453-6458.
  Abstract:



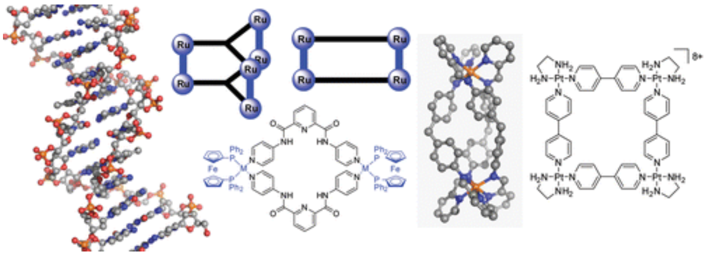
In-situ photoinduced threshold voltage measurement is a sensitive probe for exploring charge transport and exciton diffusion simultaneously, the main determinants of the power conversion efficiency in organic photovoltaic devices. The exciton diffusion length in a pentacene film deposited onto a C60-terminated self-assembled monolayer is measured. The methodology and analysis presented here can be applied in the design and engineering of electron/donor acceptor interfaces for photovoltaic devices.

- Non-Viral Co-Delivery of the Four Yamanaka Factors for Generation of Human Induced Pluripotent Stem Cells via Calcium Phosphate Nanocomposite Particles
  Cao, X.; Deng, W.; Qui, R.; Yu, Q.; Li, J.; Yang, Y.; Cao, Y.; Gao, X.; Xu, X.; Yu, J. *Adv. Funct. Mater*. **2013**, *23*, 6403-6411.
  Abstract:



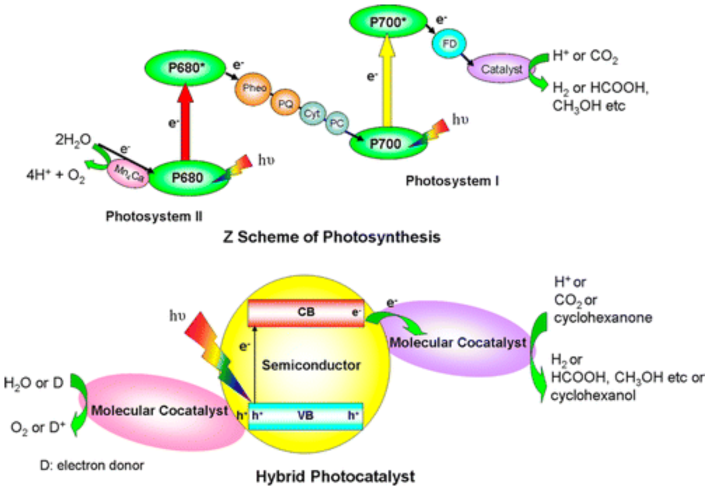
Generating of induced pluripotent stem cells (iPSCs) can be achieved by ectopic expression of defined transcription factor sets. However, most instances of iPSC induction have been achieved using viral vectors, which carry the risk of unpredictable genetic dysfunction. Here, for the first time, a non-viral vector based on calcium phosphate nanoparticles for the generation of virus-free iPSCs from human umbilical cord mesenchymal stem cells (HUMSCs) via co-delivery of the four plasmids (Oct4, Sox2, Klf4, and c-Myc) is reported. As a result, a total of 98 colonies from 200 000 cells have been obtained, with a reprogramming efficiency of 0.049%. The iPSCs shows positive expression of pluripotency markers, including OCT4, SSEA-3, SSEA-4, NANOG, and TRA-1-81. Moreover, the iPSCs are able to differentiate into all three germ layers in vitro. Subcutaneous injection of the iPSCs into immunocompromised mice results in the formation of teratomas containing a variety of tissues from all three germ layers. These findings indicate that co-delivery of the four Yamanaka factors via plasmid-encapsulated calcium phosphate nanoparticles can provide a simple, safe, and efficient method for the generation of virus-free iPSCs, which is crucial for their future clinical applications in the field of regenerative medicine.

- Biomedical and Biochemical Applications of Self-Assembled Metallacycles and Metallacages
  Cook, T. R.; Vajpayee, V.; Lee, M. H.; Stang, P. J; Chi, K.-W. *Acc. Chem. Res.* **2013**, *46*, 2464–2474.
  Abstract:



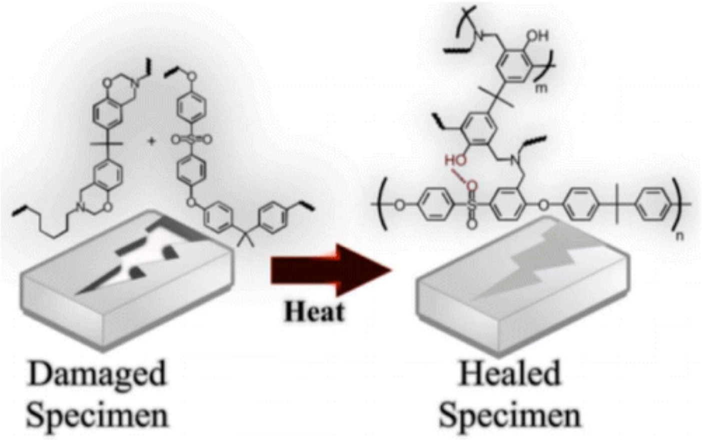
Metal ions and metal complexes with organic molecules are ubiquitous in nature. Bulk metal ions of Na, K, Mg, and Ca constitute as much as 1% of human body weight. The remaining trace ions, most commonly of Fe, Ni, Cu, Mn, Zn, Co, Mo, and V, make up 0.01% by weight, but their importance in biological processes cannot be overstated. Although nature is limited to the use of bioavailable metal ions, many rarer transition metals can elicit novel biological responses when they interact with biomolecules. For this reason, metal–biomolecule complexes are of interest in medicinal applications. A well-known example is cisplatin, which contains Pt, rare in nature, but highly effective in this context as an anticancer drug in the form of cis-$Pt(NH_3)_2Cl_2$ and analogous Pt(II) complexes. This and other examples have led to strong interest in discovering new metalloanticancer drugs. In this Account, we describe recent developments in this area, particularly, using coordination-driven self-assembly to form tunable supramolecular coordination complexes (SCCs) with biomedical applications. Coordination-driven self-assembly describes the spontaneous formation of metal–ligand bonds in solution, transforming molecular building blocks into single, 2D metallacycles, or 3D metallacages depending on the directionality of the precursors used. Such SCCs have well-defined internal cavities and simple pre- or post-self-assembly functionalizations. They are highly tunable both spatially and electronically. Metal ions are necessary structural elements for the directional bonding approach, which can be exploited to provide biological activity to an SCC, particularly for Pt- and Ru-based structures. Since these two metals are not only among the most commonly used for coordination-driven self-assembly but are also the basis for a number of small molecule anticancer agents, researchers have evaluated a growing number of SCCs for their antitumor properties. The biological application of SCCs is still an emergent field of study, but the examples discussed in this Account confirm that supramolecular scaffolds have relevance to a wide variety of biochemical and biomedical targets. SCCs can serve as anticancer agents, act as selective sensors for biologically important analytes, or interact with DNA and proteins. The myriad of possible SCCs and their almost limitless modularity and tunability without significant synthetic penalty suggests that the biological applications of such species will continue along this already promising path.

- Hybrid Artificial Photosynthetic Systems Comprising Semiconductors as Light Harvesters and Biomimetic Complexes as Molecular Cocatalysts
  Wen, F.; Li, C. *Acc. Chem. Res.* **2013**, *46,* 2355–2364.
  Abstract:



Solar fuel production through artificial photosynthesis may be a key to generating abundant and clean energy, thus addressing the high energy needs of the world’s expanding population. As the crucial components of photosynthesis, the artificial photosynthetic system should be composed of a light harvester (e.g., semiconductor or molecular dye), a reduction cocatalyst (e.g., hydrogenase mimic, noble metal), and an oxidation cocatalyst (e.g., photosystem II mimic for oxygen evolution from water oxidation). Solar fuel production catalyzed by an artificial photosynthetic system starts from the absorption of sunlight by the light harvester, where charge separation takes place, followed by a charge transfer to the reduction and oxidation cocatalysts, where redox reaction processes occur. One of the most challenging problems is to develop an artificial photosynthetic solar fuel production system that is both highly efficient and stable. The assembly of cocatalysts on the semiconductor (light harvester) not only can facilitate the charge separation, but also can lower the activation energy or overpotential for the reactions. An efficient light harvester loaded with suitable reduction and oxidation cocatalysts is the key for high efficiency of artificial photosynthetic systems. In this Account, we describe our strategy of hybrid photocatalysts using semiconductors as light harvesters with biomimetic complexes as molecular cocatalysts to construct efficient and stable artificial photosynthetic systems. We chose semiconductor nanoparticles as light harvesters because of their broad spectral absorption and relatively robust properties compared with a natural photosynthesis system. Using biomimetic complexes as cocatalysts can significantly facilitate charge separation via fast charge transfer from the semiconductor to the molecular cocatalysts and also catalyze the chemical reactions of solar fuel production. The hybrid photocatalysts supply us with a platform to study the photocatalytic mechanisms of H_2/O_2 evolution and CO_2 reduction at the molecular level and to bridge natural and artificial photosynthesis. We demonstrate the feasibility of the hybrid photocatalyst, biomimetic molecular cocatalysts, and semiconductor light harvester for artificial photosynthesis and therefore provide a promising approach for rational design and construction of highly efficient and stable artificial photosynthetic systems.

- Polybenzoxazine Precursors As Self-Healing Agents for Polysulfones
  Taskin, O. S.; Kiskan, B.; Yagci, Y. *Macromolecules* **2013**, *46*, 8773–8778.
  Abstract:



In this work, a novel self-healing system based on the use of polybenzoxazine precursor (PBP) as a healing additive is presented. PBP (M_n = 2300 g/mol, M_w/M_n = 2.6) is facilely synthesized in a reasonable yield by Mannich type polycondensation of bisphenol A, 1,6-diaminohexane with paraformaldehyde. The additive PBP faintly undergoes a thermal ring-opening reaction when contained in polysulfone (PSU) films. Thermal treatment at 160 °C enables PBP to chemically bind to PSU chains and form networks through the Friedel–Crafts reaction, demonstrating a novel self-healing behavior. The extent of the recovery was studied using a stress–elongation (%) test and found to be 55%. Thermal properties of the polybenzoxazine precursor and the healed sample were investigated.

- Cholinium-Based Poly(ionic liquid)s: Synthesis, Characterization, and Application as Biocompatible Ion Gels and Cellulose Coatings
  Isik, M.; Gracia, R.; Kollnus, L. C.; Tomé, L. C.; Marrucho, I. M.; Mecerreyes, D. *ACS Macro Lett.* **2013**, *2*, 975–979.
  Abstract:

Cholinium-based ionic liquid methacrylic monomers having halide, lactate and acetate counter-anions were synthesized and polymerized by using conventional free radical polymerization. The polymer properties were characterized by NMR, SEC/GPC, TGA, and DSC and compared among eight different cationic polymethacrylic analogs. Polycations with different methacrylic alkylammonium backbones having lactate anion displayed comparatively better thermal stability than those having the acetate counter-anions and they also exhibited lower glass transition temperatures than their counterparts having acetate and halide counteranions. As an application, cholinium lactate methacrylate ionic liquid monomer was used to prepare ion gels by photopolymerization. Interestingly, these are the first examples of ion gels which are fully composed of low toxicity and biocompatible cholinium ionic liquids. Furthermore, the same ionic liquid monomer, cholinium lactate methacrylate, showed the ability to dissolve cellulose. This facilitated the preparation of transparent poly(ionic liquid)/cellulose composite coatings by photopolymerization.