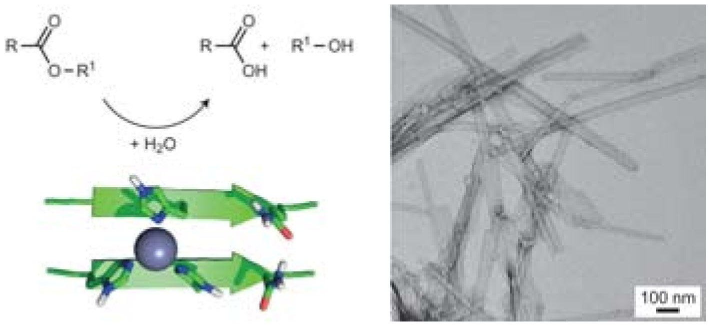
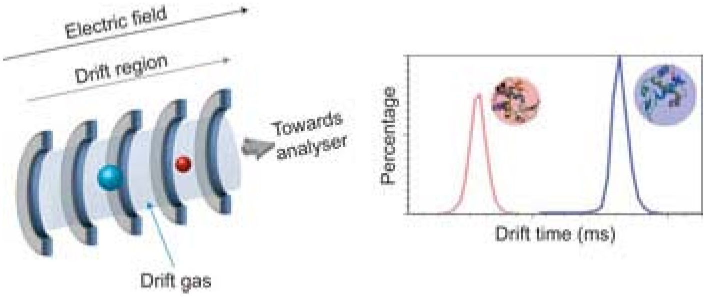
- Short peptides self-assemble to produce catalytic amyloids
  Rufo, C. M.; Moroz, Y. S.; Moroz, O. V.; Stöhr, J.; Smith, T. A.; Hu, X.; DeGrado, W. F.; Korendovych, I. V. *Nature Chem.* **2014**, *6*, 303-309.
  Abstract:



Enzymes fold into unique three-dimensional structures, which underlie their remarkable catalytic properties. The requirement to adopt a stable, folded conformation is likely to contribute to their relatively large size (>10,000 Da). However, much shorter peptides can achieve well-defined conformations through the formation of amyloid fibrils. To test whether short amyloid-forming peptides might in fact be capable of enzyme-like catalysis, we designed a series of seven-residue peptides that act as Zn^{2+}-dependent esterases. Zn^{2+} helps stabilize the fibril formation, while also acting as a cofactor to catalyse acyl ester hydrolysis. These results indicate that prion-like fibrils are able to not only catalyse their own formation, but they can also catalyse chemical reactions. Thus, they might have served as intermediates in the evolution of modern-day enzymes. These results also have implications for the design of self-assembling nanostructured catalysts including ones containing a variety of biological and non-biological metal ions.

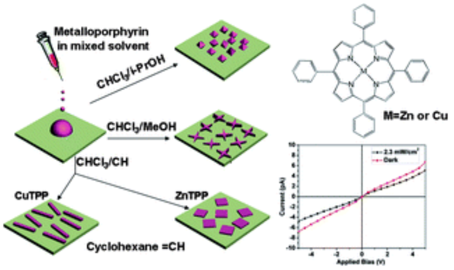
- The power of ion mobility-mass spectrometry for structural characterization and the study of conformational dynamics
  Lanucara, F.; Holman, S. W.; Gray, C. J.; Eyers, C. E. *Nature Chem.* **2014**, *6*, 281-294.
  Abstract:



Mass spectrometry is a vital tool for molecular characterization, and the allied technique of ion mobility is enhancing many areas of (bio)chemical analysis. Strong synergy arises between these two techniques because of their ability to ascertain complementary information about gas-phase ions. Ion mobility separates ions (from small molecules up to megadalton protein complexes) based on their differential mobility through a buffer gas. Ion mobility-mass spectrometry (IM-MS) can thus act as a tool to separate complex mixtures, to resolve ions that may be indistinguishable by mass spectrometry alone, or to determine structural information (for example rotationally averaged cross-sectional area), complementary to more traditional structural approaches. Finally, IM-MS can be used to gain insights into the conformational dynamics of a system, offering a unique means of

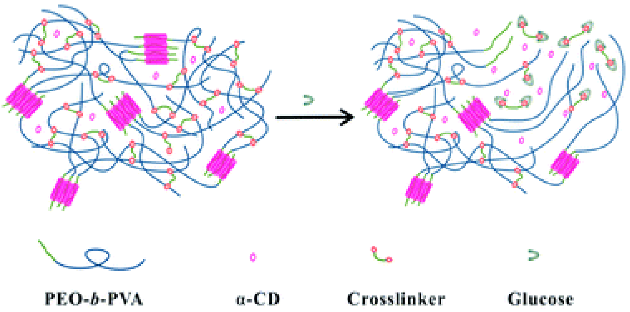
characterizing flexibility and folding mechanisms. This Review critically describes how IM-MS has been used to enhance various areas of chemical and biophysical analysis.

- Controlled self-assembly and photovoltaic characteristics of porphyrin derivatives on a silicon surface at solid–liquid interfaces
  Cai, J.; Chen, H.; Huang, J.; Wang, J.; Tian, D.; Dong, H.; Jiang, L. *Soft Matter* **2014**, *10,* 2612-2618.
  Abstract:



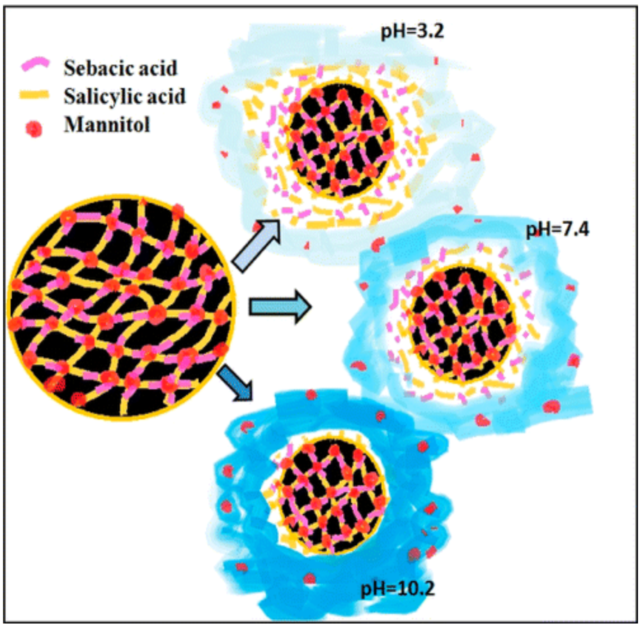
Two meso-tetraphenylporphyrin (H2TPP) derivatives with different central metal ions, namely ZnTPP, CuTPP, were synthesized, and characterized by a series of spectroscopic methods. Their self-assembly behaviors in mixed solvents without surfactant were systematically investigated. The morphology of the thus produced nanoarchitectures could be efficiently controlled. Nanoslices can be manufactured when a volume of cyclohexane is involved, octahedrons can be produced when a mixed solvent of chloroform and isopropanol is employed, while four-leaf clover-shaped structures can be produced with a large volume of methanol injected. The nanostructures have been characterized by electronic absorption, scanning electron microscopy (SEM) and photoelectric conversion techniques. The internal structures of the nanostructures are well described by XRD. The nanostructures exhibit a power conversion under illumination intensity of 2.3 mW cm^{-2}. The present result appears to represent an effort toward controlling the morphology of self-assembled nanostructures of porphyrin derivatives via synthesis through introduction of metal–ligand and solvent interaction. Nevertheless, the fundamental study will be helpful to understand photoinduced energy/charge transport in an organic interface and this might also serve as promising building blocks for nanoscale power sources for potential application in solar energy technologies and organic electronics and optoelectronics.

- Glucose-responsive hydrogels based on dynamic covalent chemistry and inclusion complexation
  Yang, T.; Ji, R.; Deng, X.-X.; Du, F.-S.; Li, Z.-C. *Soft Matter* **2014**, *10,* 2671-2678.
  Abstract:



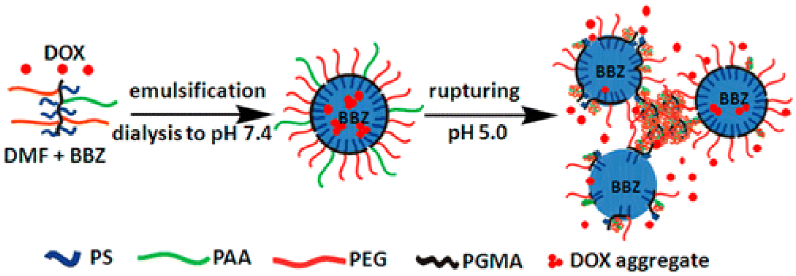
A novel glucose-responsive hydrogel system based on dynamic covalent chemistry and inclusion complexation was described. Hydrogels are formed by simply mixing the solutions of three components: poly(ethylene oxide)-b-poly vinyl alcohol (PEO-b-PVA) diblock polymer, α-cyclodextrin (α-CD) and phenylboronic acid (PBA)-terminated PEO crosslinker. Dynamic covalent bonds between PVA and PBA provide sugar-responsive crosslinking, and the inclusion complexation between PEO and α-CD can promote hydrogel formation and enhance hydrogel stability. The ratios of the three components have a remarkable effect on the gelation time and the mechanical properties of the final gels. In rheological measurements, the hydrogels are demonstrated to possess solid-like behaviour and good structural recovery ability after yielding. The sugar-responsiveness of the hydrogels was examined by protein loading and release experiments, and the results indicate that this property is also dependent on the compositions of the gels; at a proper component ratio, a new glucose-responsive hydrogel system operating at physiological pH can be obtained. The combination of good biocompatibility of the three components and the easy preparation of hydrogels with tunable glucose-responsiveness may enable an alternative design of hydrogel systems that finds potential applications in biomedical and pharmaceutical fields, such as treatment of diabetes.

- Cross-Linked, Biodegradable, Cytocompatible Salicylic Acid Based Polyesters for Localized, Sustained Delivery of Salicylic Acid: An In Vitro Study
  Chandorkar, Y.; Bhagat, R. K.; Madras, G.; Basu, B. *Biomacromolecules* **2014**, *15*, 863–875.
  Abstract:



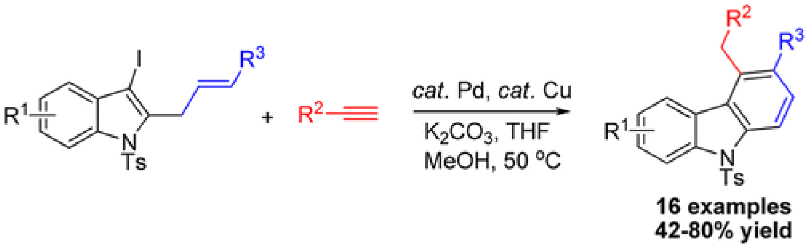
In order to suppress chronic inflammation while supporting cell proliferation, there has been a continuous surge toward development of polymers with the intention of delivering anti-inflammatory molecules in a sustained manner. In the above backdrop, we report the synthesis of a novel, stable, cross-linked polyester with salicylic acid (SA) incorporated in the polymeric backbone and propose a simple synthesis route by melt condensation. The as-synthesized polymer was hydrophobic with a glass transition temperature of 1 °C, which increases to 17 °C upon curing. The combination of NMR and FT-IR spectral techniques established the ester linkages in the as-synthesized SA-based polyester. The pH-dependent degradation rate and the rate of release of salicylic acid from the as-synthesized SA-based polymer were studied at physiological conditions in vitro. The polyester underwent surface erosion and exhibited linear degradation kinetics in which a change in degradation rate is observed after 4–10 days and 24% mass loss was recorded after 4 months at 37 °C and pH 7.4. The delivery of salicylic acid also showed a similar change in slopes, with a sustained release rate of 3.5% in 4 months. The cytocompatibility studies of these polyesters were carried out with C2C12 murine myoblast cells using techniques like MTT assay and flow cytometry. Our results strongly suggest that SA-based polyester supports cell proliferation for 3 days in culture and do not cause cell death (<7%), as quantified by propidium iodide (PI) stained cells. Hence, these polyesters can be used as implant materials for localized, sustained delivery of salicylic acid and have applications in adjuvant cancer therapy, chronic wound healing, and as an alternative to commercially available polymers like poly(lactic acid) and poly(glycolic acid) or their copolymers.

- pH-Responsive Nanoemulsions for Controlled Drug Release
  Liu, F.; Lin, S.; Zhang, Z.; Hu, J.; Liu, G.; Tu, Y.; Yang, Y.; Zou, H.; Mo, Y.; Miao, L. *Biomacromolecules* **2014**, *15*, 968–977.
  Abstract:



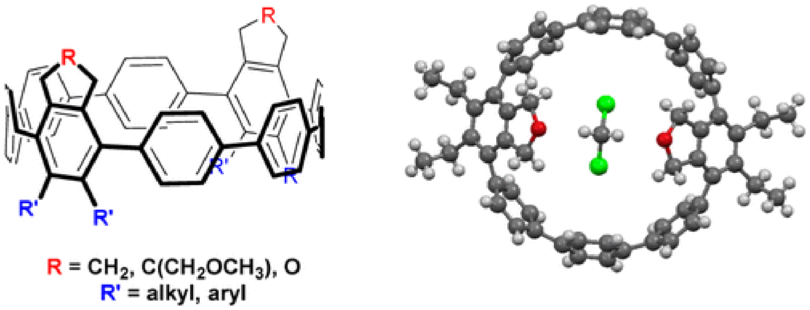
Three ternary graft copolymers bearing polystyrene (PS), poly(ethylene glycol) methyl ether (MPEG), and poly(acrylic acid) (PAA) side chains were synthesized and characterized. At pH = 7.4, these copolymers stabilized doxorubicin (DOX)-containing benzyl benzoate (BBZ) nanoemulsion droplets in water and formed a compact polymer layer to inhibit DOX release. Upon lowering the solution pH to 5.0, the AA groups dissociated less and became less soluble. Moreover, the neutralized AA groups formed presumably H-bonded complexes with the EG units, reducing the solubility of the EG units. This dual action drastically shifted the hydrophilic and hydrophobic balance of the copolymer and caused the original stabilizing polymer layer to rupture and the nanoemulsion droplets to aggregate, releasing DOX. The rate and extent of DOX release could be increased by matching the numbers of PAA and MPEG chains per graft copolymer. In addition, these nanoemulsions were not toxic and entered human carcinoma cells, releasing DOX there. Thus, these nanoemulsions have potential as drug delivery vehicles.

- Efficient Carbazole Synthesis via Pd/Cu-Cocatalyzed Cross-Coupling/Isomerization of 2-Allyl-3-iodoindoles and Terminal Alkynes
  Zhu, C.; Ma, S. *Org. Lett.* **2014,** *16*, 1542-1545.
  Abstract:



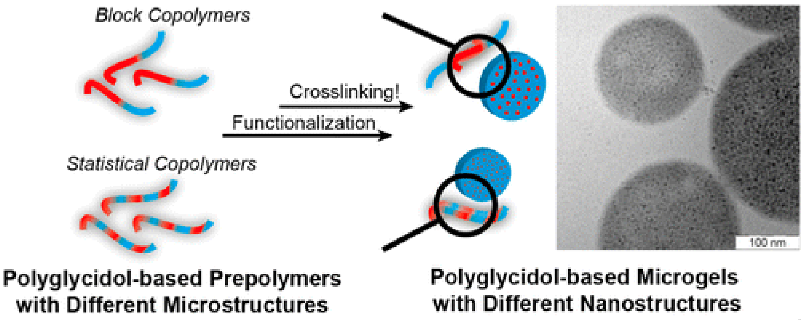
The Pd/Cu-cocatalyzed one-pot reaction of 2-allyl-3-iodo-1-tosyl-1*H*-indoles and terminal alkynes afforded carbazoles highly efficiently via sequential carbon–carbon coupling, isomerization, cyclization, and aromatization forming a benzene ring. Both Pd and Cu are responsible for the coupling step, while K_2CO_3 was observed to be critical for the subsequent cyclization.

- Synthesis of Substituted [8]Cycloparaphenylenes by [2 + 2 + 2] Cycloaddition
  Tran-Van, A.-F.; Huxol, E.; Basler, J. M.; Neuburger, M.; Adjizian, J.-J.; Ewels, C. P.; Wegner, H. A. *Org. Lett.* **2014,** *16*, 1594-1597.
  Abstract:



A new modular approach to the smallest substituted cycloparaphenylenes (CPPs) is presented. This versatile method permits access to substituted CPPs, choosing the substituent at a late stage of the synthesis. Variously substituted [8]CPPs have been synthesized, and their properties analyzed. The structural characteristics of substituted CPPs are close to those of unsubstituted CPPs. However, their optoelectronic behavior differs remarkably due to the larger torsion angle between the phenyl units.

- Polyglycidol-Based Prepolymers to Tune the Nanostructure of Microgels
  Schulte, B.; Walther, A.; Keul, H.; Möller, M. *Macromolecules* **2014**, *47*, 1633–1645.
  Abstract:

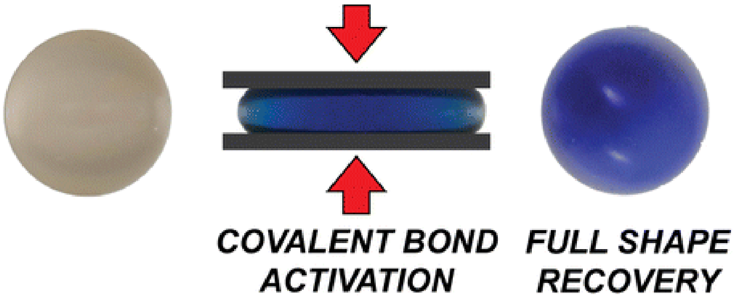


The use of prepolymers for microgel synthesis via miniemulsification allows predefining the chemical functionality and the nanostructure of microgels. We report on tailor-made polyglycidol-based prepolymers using three protected glycidol monomers (allyl glycidyl ether, AGE; ethoxy ethyl glycidyl ether, EEGE; and tert-butyl glycidyl ether, tBGE). AGE with its pendant double bonds serves as site for cross-linking or functionalization, whereas the EEGE and tBGE building blocks represent precursors for hydroxyl functionalities. Following the prepolymer approach, we design statistical and block copolymers to control the nanostructure of the microgel. Cross-linking of the prepolymers is achieved in miniemulsions under UV irradiation in a thiol–ene click type reaction addressing the allyl groups with 2,2′-(ethylenedioxy)diethanethiol. Analysis with cryo-TEM reveals that microgels derived from poly(glycidol)-block-poly(AGE) show larger hydrophobic domains than microgels derived from statistical copolymers. Additionally, the cross-linking of pH responsive tBGE/AGE prepolymers with different microstructures leads to microgels with nanostructures differing in local charge distributions.

- Mechanochemical Activation of Covalent Bonds in Polymers with Full and Repeatable Macroscopic Shape Recovery

  Gossweiler, G. R.; Hewage. G. B.; Soriano, G.; Wang, Q.; Welshofer, G. W.; Zhao, X.; Craig, S. L. *ACS Macro Lett.* **2014**, *3*, 216–219.

  Abstract:

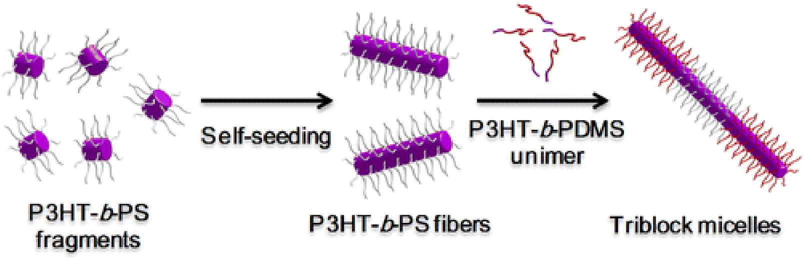


Covalent mechanochemistry within bulk polymers typically occurs with irreversible deformation of the parent material. Here we show that embedding mechanophores into an elastomeric poly(dimethylsiloxane) (PDMS) network allows for covalent bond activation under macroscopically reversible deformations. Using the colorimetric mechanophore spiropyran, we show that bond activation can be repeated over multiple cycles of tensile elongation with full shape recovery. Further, localized compression can be used to pattern strain-induced chemistry. The platform enables the reversibility of a secondary strain-induced color change to be characterized. We also observe mechanical acceleration of a flex-activated retro-Diels–Alder reaction, allowing a chemical signal to be released in response to a fully reversible deformation.

- Uniform, High Aspect Ratio Fiber-like Micelles and Block Co-micelles with a Crystalline π-Conjugated Polythiophene Core by Self-Seeding

  Qian, J.; Li, X.; Lunn, D. J.; Gwyther, J.; Hudson, Z. M.; Kynaston, E.; Rupar, P. A.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2014**, *136*, 4121-4124.

  Abstract:

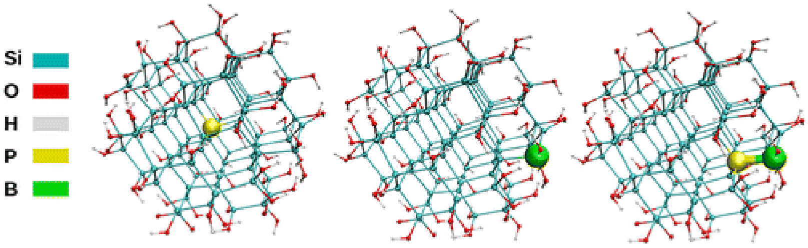


Monodisperse fiber-like micelles with a crystalline π-conjugated polythiophene core with lengths up to ca. 700 nm were successfully prepared from the diblock copolymer poly(3-hexylthiophene)-block-polystyrene using a one-dimensional self-seeding technique. Addition of a polythiophene block copolymer with a different corona-forming block to the resulting nanofibers led to the formation of segmented B-A-B triblock co-micelles by crystallization-driven seeded growth. The key to these advances appears to be the formation of a relatively defect-free crystalline micelle core under the self-seeding conditions.

- Preferential Positioning of Dopants and Co-Dopants in Embedded and Freestanding Si Nanocrystals

Guerra, R.; Ossicini, S. *J. Am. Chem. Soc.* **2014,** *136*, 4404–4409.

Abstract:

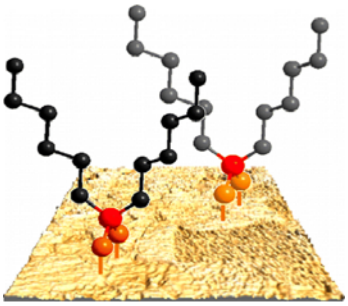


In this work we aim at understanding the effect of n- and p-type substitutional doping in the case of matrix-embedded and freestanding Si nanocrystals. By means of ab initio calculations we identify the preferential positioning of the dopants and its effect on the structural properties with respect to the undoped case. Subsequently, we consider the case of phosphorus and boron co-doped nanocrystals showing that, against the single-doping situation, the energetics strongly favors the binding of the impurities at the nanocrystal surface. Indeed we demonstrate that the polar B–P bond forms a stable permanent electric dipole that radially points inward in the nanocrystal. Such a noteworthy characteristic and its physical consequences are discussed alongside new potential applications.

- The Unusual Self-Organization of Dialkyldithiophosphinic Acid Self-Assembled Monolayers on Ultrasmooth Gold

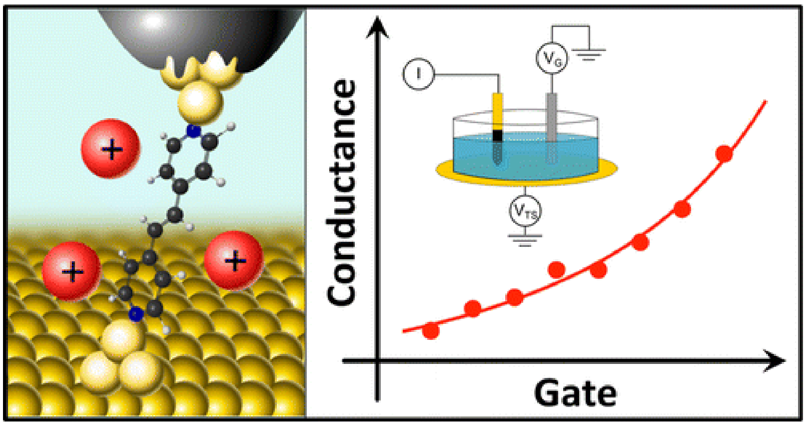
  Miller, M. S.; San Juan, R. R.; Ferrato, M.-A.; Carmichael, T. B. *J. Am. Chem. Soc.* **2014**, *136*, 4212-4222.

  Abstract:



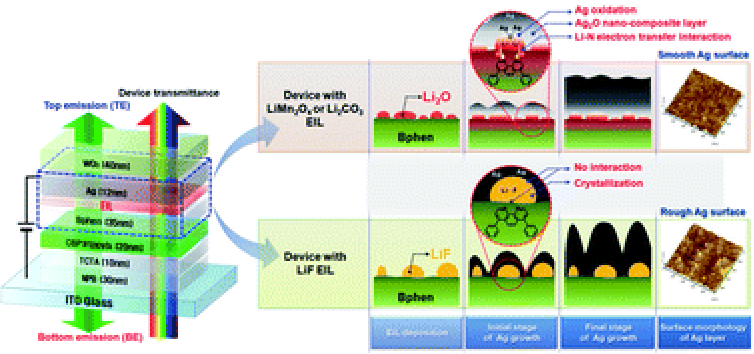
We report the formation and characterization of self-assembled monolayers (SAMs) of dialkyldithiophosphinic acid adsorbates $[CH_3(CH_2)n]_2P(S)SH$ (R_2DTPA) (n = 5, 9, 11, 13, 15) on ultrasmooth gold substrates prepared by the template stripping method. The SAMs were characterized using X-ray photoelectron spectroscopy, reflection–absorption infrared spectroscopy, contact angle measurements, lateral force microscopy, and electrochemical impedance spectroscopy. The data show these SAMs exhibit an unusual trend in alkyl chain crystallinity; SAMs formed from adsorbates with short alkyl chains (n = 5) are ordered and crystalline, and the alkyl groups become increasingly disordered and liquidlike as the number of methylene units is increased. This trend is the opposite of the typical behavior exhibited by *n*-alkanethiolate SAMs, in which the alkyl layer becomes more crystalline and ordered as the alkyl chain length is increased. We discuss four factors that operate together to determine how R_2DTPA self-organize within SAMs on TS gold: (i) adsorbate–substrate interactions; (ii) gold substrate morphology; (iii) lateral van der Waals interactions between alkyl groups; and (iv) steric demands of the alkyl groups. We also present a model for the structures of these SAMs on the basis of consideration of the data and the structural parameters of a model $^{n}Bu_2DTPA$ adsorbate. In this model, interdigitation of short alkyl chains stabilizes a trans-extended, crystalline arrangement and produces an ordered alkyl layer. As the alkyl chain length is increased, the increased steric demands of the alkyl groups lead to liquidlike, disorganized alkyl layers.

- Tunable Charge Transport in Single-Molecule Junctions via Electrolytic Gating
  Capozzi, B.; Chen, Q.; Darancet, P.; Kotiuga, M.; Buzzeo, M.; Neaton, J. B.; Nuckolls, C.; Venkataraman, L. *Nano Lett.* **2014**, *14*, 1400–1404.
  Abstract



We modulate the conductance of electrochemically inactive molecules in single-molecule junctions using an electrolytic gate to controllably tune the energy level alignment of the system. Molecular junctions that conduct through their highest occupied molecular orbital show a decrease in conductance when applying a positive electrochemical potential, and those that conduct though their lowest unoccupied molecular orbital show the opposite trend. We fit the experimentally measured conductance data as a function of gate voltage with a Lorentzian function and find the fitting parameters to be in quantitative agreement with self-energy corrected density functional theory calculations of transmission probability across single-molecule junctions. This work shows that electrochemical gating can directly modulate the alignment of the conducting orbital relative to the metal Fermi energy, thereby changing the junction transport properties.

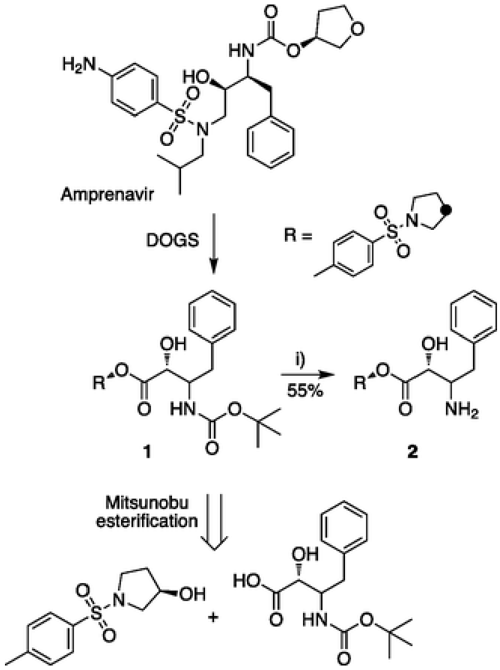
- An efficient nano-composite layer for highly transparent organic light emitting diodes
  Kim, G. W.; Lampande, R.; Boizot, J.; Kim, G. H.; Choe, D. C.; Kwon, J. H. *Nanoscale* **2014**, *6*, 3810–3817.
  Abstract:



We report highly transparent and low resistive new cathode structures, which basically consist of nano-composite layer/Ag/WO3 for transparent organic light-emitting diode (TOLED) applications. Our new cathode structure exhibits an extremely high transmittance of 91.2% at 550 nm, a low sheet resistance of 5.4 Ω [square]−1, and excellent electron injection properties. Such a high transmittance

along with a low resistivity of the fabricated new cathode could be explained by surface-modifying behavior with the generation of a nano-composite thin silver oxide layer during Ag deposition. Chemical interaction at the interface between the electron injection layer and the electron transport layer results in good electron injection properties in TOLEDs. The fabricated TOLEDs with our new cathode structures have a full device transmittance of 85–87% at 550 nm.

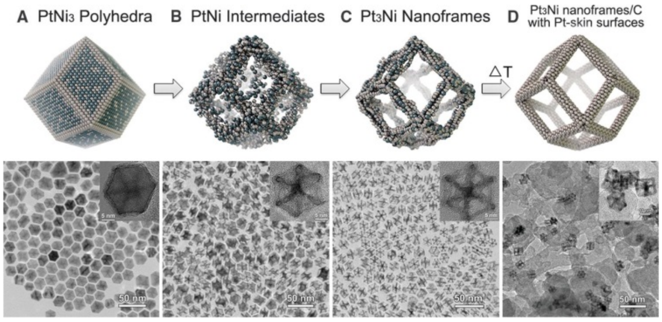
- Identifying the macromolecular targets of de novo-designed chemical entities through self-organizing map consensus
  Reker, D.; Rodrigues, T.; Schneider, P.; Schneider, G. *Proc. Natl. Acad. Sci. U. S. A.* **2014,** *111*, 4067-4072.
  Abstract:



De novo molecular design and in silico prediction of polypharmacological profiles are emerging research topics that will profoundly affect the future of drug discovery and chemical biology. The goal is to identify the macromolecular targets of new chemical agents. Although several computational tools for predicting such targets are publicly available, none of these methods was explicitly designed to predict target engagement by de novo-designed molecules. Here we present the development and practical application of a unique technique, self-organizing map–based prediction of drug equivalence relationships (SPiDER), that merges the concepts of self-organizing maps, consensus scoring, and statistical analysis to successfully identify targets for both known drugs and computer-generated molecular scaffolds. We discovered a potential off-target liability of fenofibrate-related compounds, and in a comprehensive prospective application, we identified a multitarget-modulating profile of de novo designed molecules. These results demonstrate that SPiDER may be used to identify innovative compounds in chemical biology and in the early stages of drug discovery, and help investigate the potential side effects of drugs and their repurposing options.

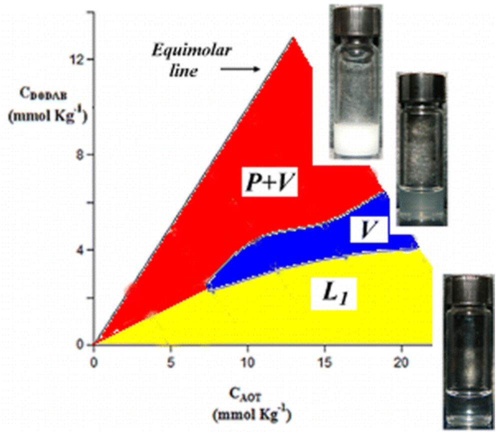
- Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces
  Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M.; Chi, M.; More, K. L.; Li, Y.; Markovic, N. M.; Somorjai, G. A.; Yang, P.; Stamenkovic, V. R. *Science* **2014,** *343*, 1339-1343.

Abstract:



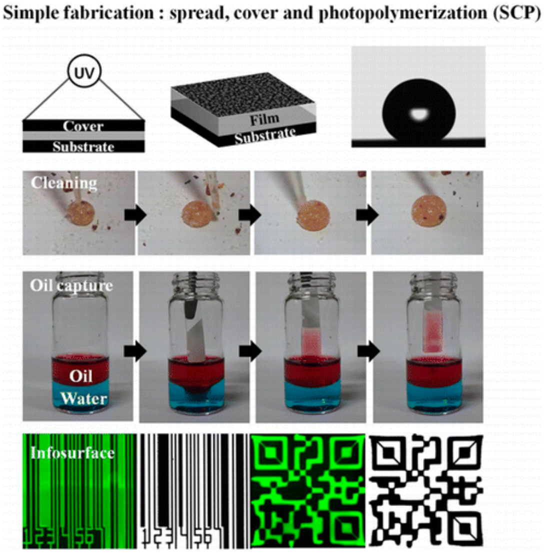
Control of structure at the atomic level can precisely and effectively tune catalytic properties of materials, enabling enhancement in both activity and durability. We synthesized a highly active and durable class of electrocatalysts by exploiting the structural evolution of platinum-nickel (Pt-Ni) bimetallic nanocrystals. The starting material, crystalline $PtNi_3$ polyhedra, transforms in solution by interior erosion into Pt_3Ni nanoframes with surfaces that offer three-dimensional molecular accessibility. The edges of the Pt-rich $PtNi_3$ polyhedra are maintained in the final Pt_3Ni nanoframes. Both the interior and exterior catalytic surfaces of this open-framework structure are composed of the nanosegregated Pt-skin structure, which exhibits enhanced oxygen reduction reaction (ORR) activity. The Pt_3Ni nanoframe catalysts achieved a factor of 36 enhancement in mass activity and a factor of 22 enhancement in specific activity, respectively, for this reaction (relative to state-of-the-art platinum-carbon catalysts) during prolonged exposure to reaction conditions.

- Binding of a Protein or a Small Polyelectrolyte onto Synthetic Vesicles
  Sciscione, F.; Pucci, C.; La Mesa, C. *Langmuir* **2014**, *10*, 2810–2819.
  Abstract:



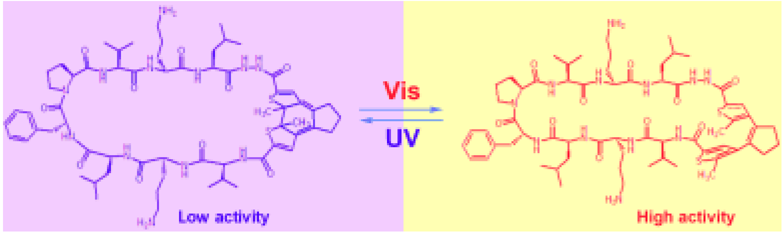
Catanionic vesicles were prepared by mixing nonstoichiometric amounts of sodium bis(2-ethylhexyl) sulfosuccinate and dioctyldimethylammonium bromide in water. Depending on the concentration and mole ratios between the surfactants, catanionic vesicular aggregates are formed. They have either negative or positive charges in excess and are endowed with significant thermodynamic and kinetic stability. Vesicle characterization was performed by dynamic light scattering and electrophoretic mobility. It was inferred that vesicle size scales in inverse proportion with its surface charge density and diverges as the latter quantity approaches zero and/or the mole ratio equals unity. Therefore, both variables are controlled by the anionic/cationic mole ratio. Small-angle X-ray scattering, in addition, indicates that vesicles are unilamellar. Selected anionic vesicular systems were reacted with poly-l-lysine hydrobromide or lysozyme. Polymer binding continues until complete neutralization of the negatively charged sites on the vesicles surface is attained, as inferred by electrophoretic mobility. Lipoplexes are formed as a result of significant electrostatic interactions between cationic polyelectrolytes and negatively charged vesicles.

- A Rapid One-Step Fabrication of Patternable Superhydrophobic Surfaces Driven by Marangoni Instability
  Kang, S.-M., Hwang, S.; Jin, S.-H.; Choi, C.-H.; Kim, J.; Park, B. J.; Lee, D.; Lee, C.S. *Langmuir* **2014**, *10*, 2828–2834.
  Abstract:



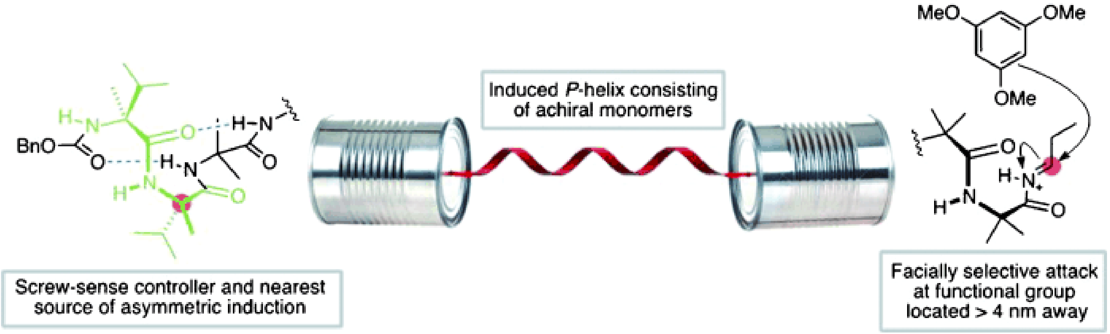
We present a facile and inexpensive approach without any fluorinated chemistry to create superhydrophobic surface with exceptional liquid repellency, transportation of oil, selective capture of oil, optical bar code, and self-cleaning. Here we show experimentally that the control of evaporation is important and can be used to form superhydrophobic surface driven by Marangoni instability: the method involves in-situ photopolymerization in the presence of a volatile solvent and porous PDMS cover to afford superhydrophobic surfaces with the desired combination of micro- and nanoscale roughness. The porous PDMS cover significantly affects Marangoni convection of coating fluid, inducing composition gradients at the same time. In addition, the change of concentration of ethanol is able to produce versatile surfaces from hydrophilic to superhydrophobic and as a consequence to determine contact angles as well as roughness factors. In conclusion, the control of evaporation under the polymerization provides a convenient parameter to fabricate the superhydrophobic surface, without application of fluorinated chemistry and the elegant nanofabrication technique.

- Controlling Biological Activity with Light: Diarylethene-Containing Cyclic Peptidomimetics
  Babii, O.; Afonin, S.; Berditsch, M.; Reiβer, S.; Mykhailiuk, P. K.; Kubyshkin, V. S.; Steinbrecher, T.; Ulrich, A. S.; Komarov, I. V. *Angew. Chem. Int. Ed.* **2014**, *53*, 3292–3295.
  Abstract:



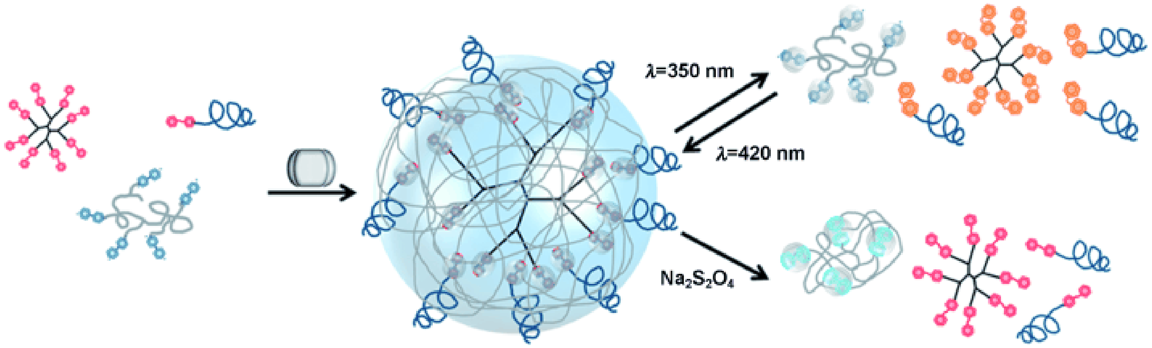
Photobiological processes in nature are usually triggered by nonpeptidic chromophores or by modified side chains. A system is presented in which the polypeptide backbone itself can be conformationally switched by light. An amino acid analogue was designed and synthesized based on a reversibly photoisomerizable diarylethene scaffold. This analogue was incorporated into the cyclic backbone of the antimicrobial peptide gramicidin S at several sites. The biological activity of the resulting peptidomimetics could then be effectively controlled by ultraviolet/visible light within strictly defined spatial and temporal limits.

- Remote Stereocontrol Transmitted through Helicity
  Johnston, C. P.; Smith, M. D. *Angew. Chem. Int. Ed.* **2014**, *53*, 3315–3317.
  Abstract:



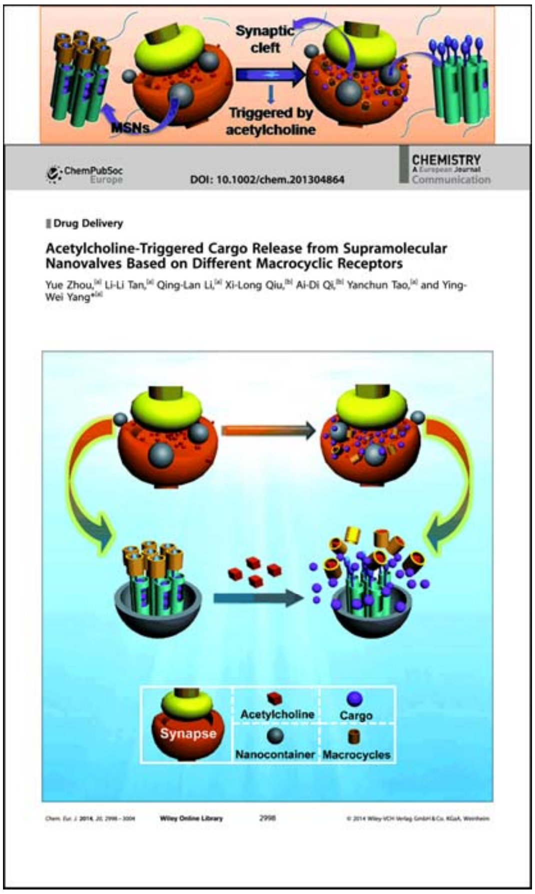
Near…far…wherever you are! Two chiral residues at the N-terminus of a helical foldamer are sufficient to induce a significant helical screw-sense preference. The capacity of this helix to transmit stereochemical information is exemplified by highly stereoselective transformations conducted over nanometer distances.

- Dual Stimuli-Responsive Self-Assembled Supramolecular Nanoparticles
  Stoffelen, C.; Voskuhl, J.; Jonkheijm, P.; Huskens, J.; *Angew. Chem. Int. Ed.* **2014**, *53*, 3400–3404.
  Abstract:



Supramolecular nanoparticles (SNPs) encompass multiple copies of different building blocks brought together by specific noncovalent interactions. The inherently multivalent nature of these systems allows control of their size as well as their assembly and disassembly, thus promising potential as biomedical delivery vehicles. Here, dual responsive SNPs have been based on the ternary host–guest complexation between cucurbit[8]uril (CB[8]), a methyl viologen (MV) polymer, and mono- and multivalent azobenzene (Azo) functionalized molecules. UV switching of the Azo groups led to fast disruption of the ternary complexes, but to a relatively slow disintegration of the SNPs. Alternating UV and Vis photoisomerization of the Azo groups led to fully reversible SNP disassembly and reassembly. SNPs were only formed with the Azo moieties in the *trans* and the MV units in the oxidized states, respectively, thus constituting a supramolecular AND logic gate.

- Acetylcholine-Triggered Cargo Release from Supramolecular Nanovalves Based on Different Macrocyclic Receptors
  Zhou, Y.; Tan, L.-L.; Li, Q.-L.; Qiu, X.-L.; Qi, A.-D.; Tao, Y.; Yang, Y.-W. *Chem. Eur. J.* **2014**, *20*, 2998–3004.
  Abstract:



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Communication

Drug Delivery

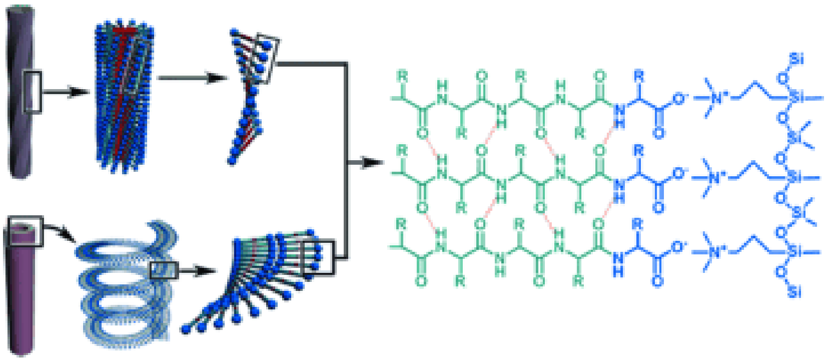
Acetylcholine-Triggered Cargo Release from Supramolecular Nanovalves Based on Different Macrocyclic Receptors

Yue Zhou,[a] Li-Li Tan,[a] Qing-Lan Li,[a] Xi-Long Qiu,[b] Ai-Di Qi,[b] Yanchun Tao,[a] and Ying-Wei Yang*[a]

Chem. Eur. J. **2014**, 20, 2998 – 3004 **Wiley Online Library** 2998 © 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

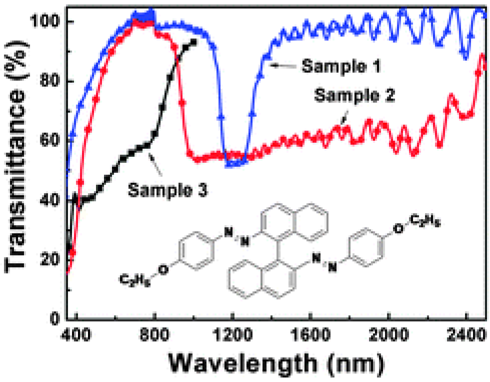
Acetylcholine (ACh), a neurotransmitter located in cholinergic synapses, can trigger cargo release from mesoporous silica nanoparticles equipped with calixarene- or pillarene-based nanovalves by removing macrocycles from the stalk components. The amount and speed of cargo release can be controlled by varying the concentration of ACh in solution or changing the type of gating macrocycle. Although this proof-of-concept study is far from a real-life application, it provides a possible route to treat diseases related to the central nervous system.

- Design of Amphiphilic Peptide Geometry towards Biomimetic Self-Assembly of Chiral Mesoporous Silica
  Huang, Z.; Yao, Y.; Che, S. *Chem. Eur. J.* **2014**, *20*, 3273–3276.
  Abstract:



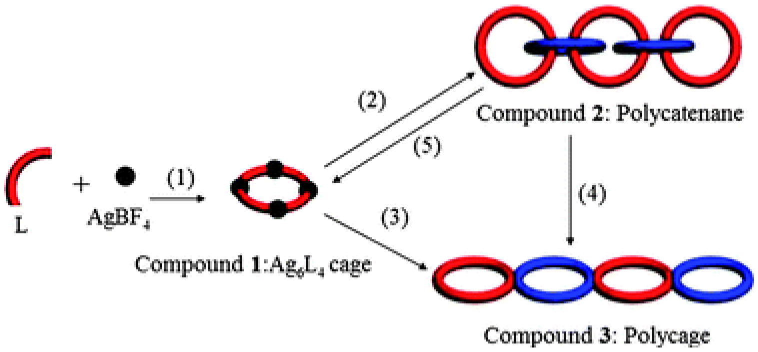
In nature, diatoms and sponges are exquisite examples of well-defined structures produced by silica biomineralisation, in which proteins play an important role. However, the artificial peptide templating route for the silica mesostructure remains a formidable and unsolved challenge. Herein, we report our effort on the design of amphiphilic peptides for synthesising a highly ordered two-dimensional (2D)-hexagonal and lamellar chiral silica mesostructure using trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride as the co-structure directing agent (CSDA). The geometry of the peptide was designed by adding proline residues into the hydrophobic chain of the peptide to break the β-sheet conformation by weakening the intermolecular hydrogen bonds; this led to the mesophase transformation from the most general lamellar structure to the 2D hexagonal *P*6*mm* mesostructure by increasing the amphiphilic molecules packing parameter *g*. Enantiomerically pure chiral mesostructures were formed thanks to the intrinsic chirality and relatively strong intermolecular hydrogen bonds of peptides.

- Broadband reflection of polymer-stabilized chiral nematic liquid crystals induced by a chiral azobenzene compound
  Chen, X.; Wang, L.; Chen, Y.; Li, C.; Hou, G.; Liu, X.; Zhang, X.; He, W.; Yang, H. *Chem. Commun.* **2014**, *50,* 691-694.
  Abstract:



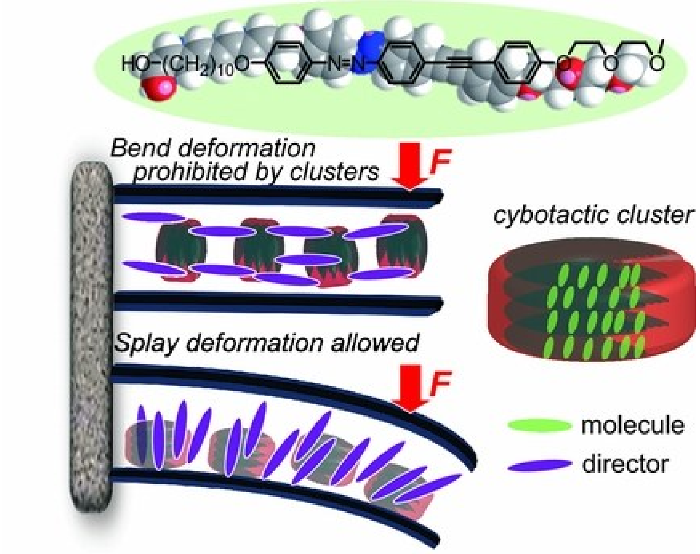
A chiral nematic liquid crystal-photopolymerizable monomer-chiral azobenzene compound composite was prepared and then polymerized under UV irradiation. The reflection wavelength of the composite can be extended to cover the 1000-2400 nm range and also be adjusted to the visible light region by controlling the concentration of chiral compounds.

- A controllable and dynamic assembly system based on discrete metallocages
  Chen, Q.; Jiang, F.; Yuan, D.; Lyu, G.; Chen, L.; Hong, M. *Chem. Sci.* **2014**, *5,* 483-488.
  Abstract:



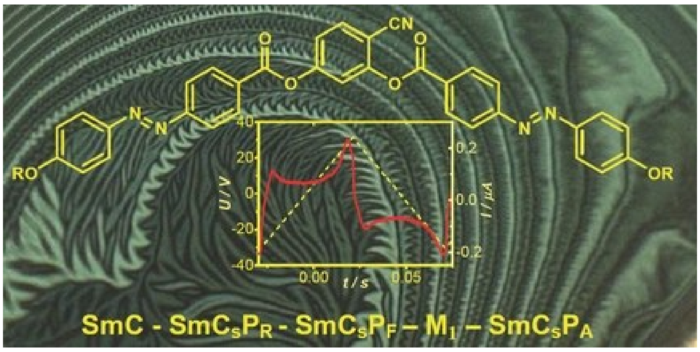
A novel self-assembly system has been developed, in which Ag$_6$L$_4$ cages can not only effectively assemble into a polycatenane containing multiple mechanical bonds in their supersaturated (MeOH-CHCl$_3$) solution in a kinetically solution through a thermodynamically-controlled assembly process. Moreover, the newly constructed multiple mechanical bonds can also be opened and transformed into metal-metal interactions through reconstruction of the kinetically-controlled product into the thermodynamically controlled product in the (MeOH-CHCl$_3$) system, while the more strongly polarized DMSO solution can only open these multiple mechanical bonds.

- Highly Elastic Liquid Crystals with a Sub-nanonewton Bending Elastic Constant Mediated by the Resident Molecular Assemblies
  Aya, S.; Obara, H.; Pociecha, D.; Araoka, F.; Okano, K.; Ishikawa, K.; Gorecka, E.; Takezoe, T. Y. H. *Adv. Mater*. **2014**, 26, 1918–1922.
  Abstract:



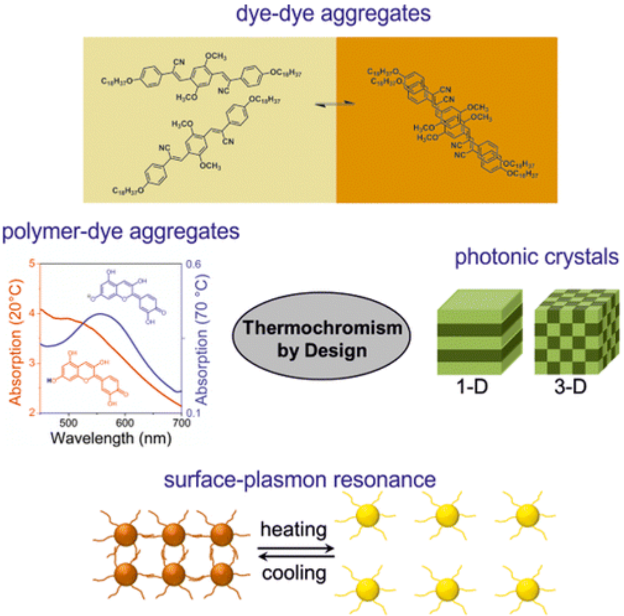
A surprisingly high bending elastic constant (K_{33}) is obtained in a newly synthesized compound shown here. Mixtures containing a few percent of this compound confirm the influence of the unusual K_{33} values, and show an improved electro-optic response. The origin of the huge K_{33} is discussed based on the formation of a smectic cluster structure formed in the nematic phase.

- 4-Cyanoresorcinol-Based Bent-Core Mesogens with Azobenzene Wings: Emergence of Sterically Stabilized Polar Order in Liquid Crystalline Phases
  Alaasar, M.; Prehm, M.; May, K.; Eremin, A.; Tschierske, C. *Adv. Funct. Mater.* **2014**, 24, 1703–1717.
  Abstract:



Development of polar order in tilted smectic liquid crystalline phases (SmC) of bent-core mesogens is found to take place with increasing polar domain size in a series of distinct phases via a paraelectric and a new randomized polar SmC phase (SmCsPR) to a ferroelectric phase, which then becomes modulated and finally changes to an antiferroelectric phase.

- Thermochromic Polymers—Function by Design
  Seeboth, A.; Lötzsch, D.; Ruhmann, R.; Muehling, O. A. *Chem. Rev.* **2014**, *114*, 3037-3068.
  Abstract:



Thermochromism denotes the phenomenon of a color change with dependence on temperature. The red color of the ruby, for example, transforms on heating, when exceeding sufficient temperature, into a shiny green and returns upon cooling. Known since antiquity, this phenomenon has been studied by scientists for centuries. In 1963 and 1968, reviews written by Day appeared reporting on reversible and irreversible thermochromism by single compounds as well as by organic or inorganic composites. In the last decades, the field of thermochromism has made tremendous progress. Thermochromic composites or pigments based on leuco dyes or cholesteric liquid crystals as well as their incorporation into polymers have become a state of the art technology and were described in detail. Within the group of polymers with inherent thermochromic properties conjugated polymers were studied extensively. The investigations on these thermochromic material classes seem to have elucidated their specific potential and limitations. Thus only marginal stimuli can be expected from them in the future.

The strategy to design thermochromic systems by physical or chemical interaction of their nonthermochromic components encourages the topic as never before. As a consequence the following systems will be highlighted in the present review:

- photonic crystals including Bragg stacks and crystalline colloidal arrays
- nanoparticle based effects: surface plasmon absorption and quantum dots
- dye–dye or polymer–dye aggregation–disaggregation mechanisms

In cases in which the same strategies were applied to develop novel thermoresponsive fluorophoric polymers these are also reported.

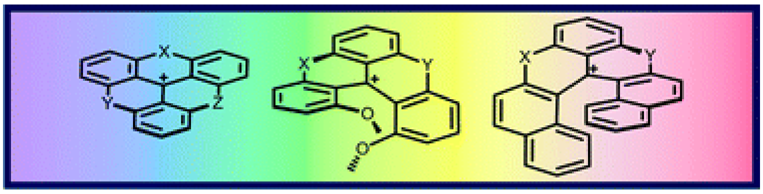
Pioneering works in the field of polymers with stimuli-responsive colorimetric properties, especially with thermochromic and/or mechanochromic properties were reported by the groups of Asher, Weder, and Pucci. The origin of the respective thermochromic effects, the specific design strategies, state of the art, structure–property-relationships, and the strengths and weaknesses of the different material classes will be evaluated critically.

To give an overview of the widespread field of thermochromism, section 1.1 will present a classification of polymers with thermoresponsive optical properties according to their thermoresponsive effect on light while in section 1.2 thermochromic polymers will be classified into inherent and doped systems.

- Cationic triangulenes and helicenes: synthesis, chemical stability, optical properties and extended applications of these unusual dyes

  Bosson, J.; Gouina, J.; Lacour, J. *Chem. Soc. Rev.* **2014**, *43*, 2824-2840.

  <u>Abstract:</u>

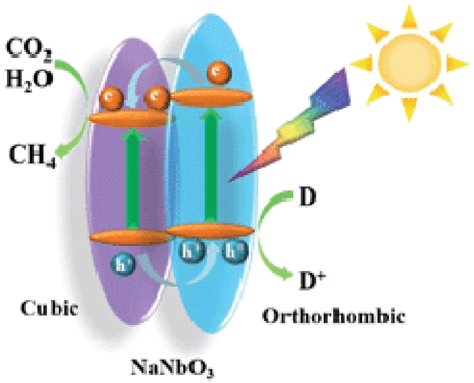


Cationic triangulenes and helicenes are highly stable carbocations with planar and helical conformations respectively. These moieties are effective dyes with original absorption and emission properties. Over the last decade, they have received greater attention and are considered as valuable tools for the development of innovative applications. In this review, the synthesis of these unique compounds is presented together with their core chemical and physical properties. Representative applications spanning from surface sciences to biology and chemistry are presented.

- Constructing cubic–orthorhombic surface-phase junctions of $NaNbO_3$ towards significant enhancement of CO_2 photoreduction

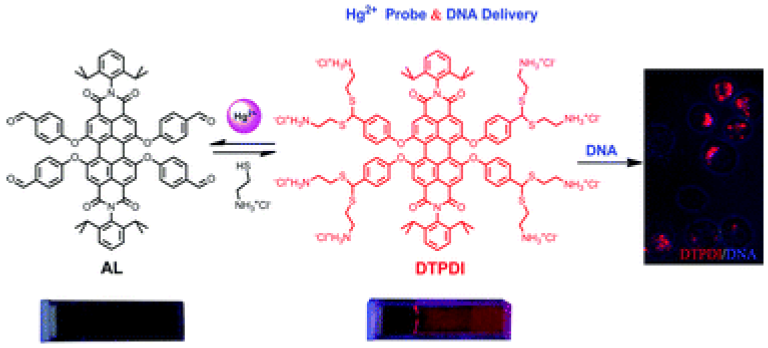
  Li, P.; Xu, H.; Liu, L.; Kako, T.; Umezawa, N.; Abe, H.; Ye, J. *J. Mater. Chem. A.* **2014**, *2*, 5606–5609.

  <u>Abstract:</u>



A NaNbO$_3$ photocatalyst with cubic–orthorhombic surface-junctions was synthesized by a polymerized-complex method. Compared with cubic and orthorhombic NaNbO$_3$, the activity of mixed-phase NaNbO$_3$ is enhanced by 30% and 200% in reducing CO$_2$ into CH$_4$, respectively. The enhancement of photoactivity over mixed-phase NaNbO$_3$ was attributed to the cubic–orthorhombic surface-junctions which improved the charge separation.

- A multifunctional perylenediimide derivative (DTPDI) can be used as a recyclable specific Hg^{2+} ion sensor and an efficient DNA delivery carrier
  Liu, K.; Xu, Z.; Yin, M.; Yang, W.; He, B.; Wei, W.; Shen, J. *J. Mater. Chem B* **2014**, *2,* 2093–2096.
  <u>Abstract:</u>



Multifunctional dithioacetal-modified perylenediimide (DTPDI) is synthesized as a highly sensitive and selective fluorescent chemosensor for recyclable Hg^{2+} detection and an effective DNA carrier. The central PDI chromophore allows the tracing of cell uptake by fluorescence microscopy, dithioacetals enable the detection of Hg^{2+}, and peripheral amine hydrochloride salts increase the water solubility and also serve as positive charges for noncovalent binding of negatively charged DNA. In addition to serve as a recyclable fluorescent probe for Hg^{2+} detection, DTPDI can be rapidly internalized into live cells with low cytotoxicity and high DNA delivery efficacy.