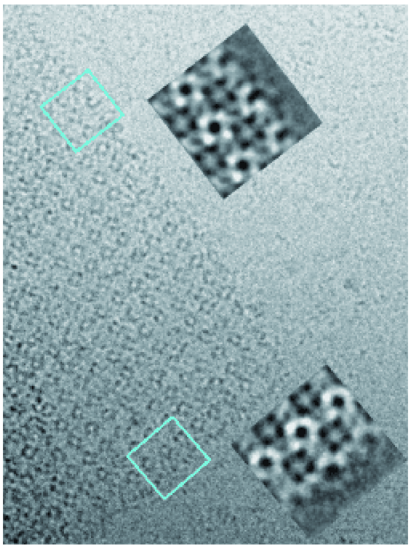
- Conformational Transitions at an S-Layer Growing Boundary Resolved by Cryo-TEM
  Comolli, L. R.; Siegerist, C. E.; Shin, S.-H.; Bertozzi, C.; Regan, W.; Zettl, A.; De Yoreo, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 4829 –4832.
  Abstract:

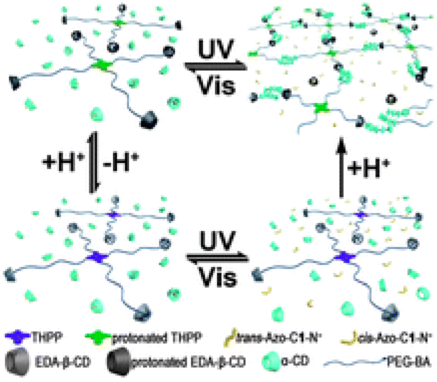


Snapshots of growth: The use of a single graphene layer as the support for S-layer self-assembly of proteins provides an ideal, robust flat surface to image the expanding boundary by flash freezing and cryo-TEM, capturing the conformational states present at the expanding boundary (see figure). Image alignment and averaging provide a view of the steps leading to subunit recruitment and maturation in the self-assembly process.

- Supramolecular Thiophene Nanosheets
  Zheng, Y.; Zhou, H.; Liu, D.; Floudas, G.; Wagner, M.; Koynov, K.; Mezger, M.; Butt, H.-J.; Ikeda, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 4845 –4848.
  Abstract:

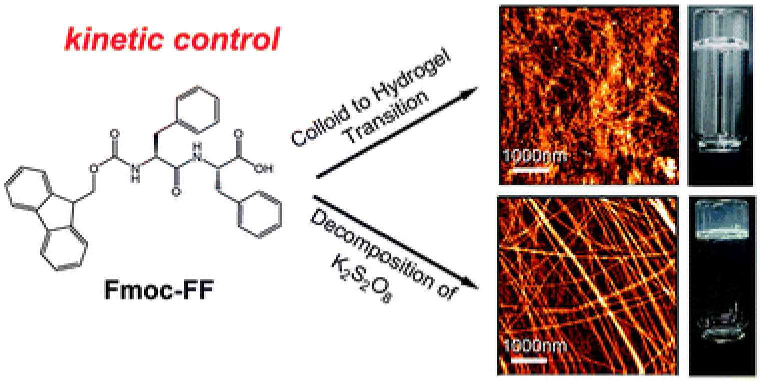
Alternating copolymers consisting of phenyl-capped bithiophene (red units) and oligo(ethylene glycol) hierarchically self-assemble into nanosheets through polymer folding in some organic solvents. The lateral size of the nanosheet is controllable by temperature and concentration of the solution. The nanosheet surface can be chemically modified by using copper-catalyzed Huisgen cycloaddition without disrupting the nanosheet structure.

- Dual stimuli-responsive supramolecular pseudo-polyrotaxane hydrogels
  Zhou, L.; Li, J.; Luo, Q.; Zhu, J.; Zou, H.; Gao, Y.; Wang, L.; Xu, J.; Dong, Z.; Liu, J. *Soft Matter* **2013,** *9*, 4635-4641.
  Abstract:



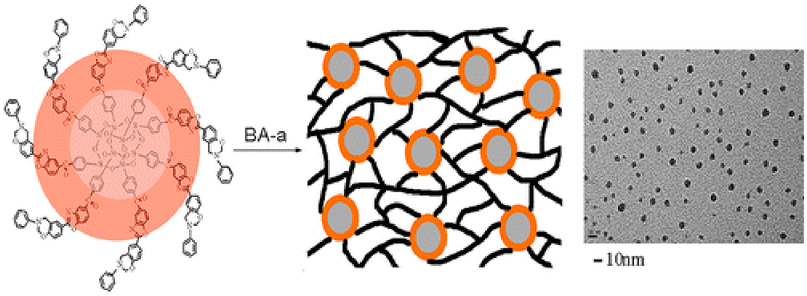
THPP-(PEG$_{2000}$-BA)$_4$, a four-branched molecule end-decorated with benzaldehyde (BA), was successfully designed and synthesized. It can form physical pseudo-polyrotaxane (PPR) hydrogels in the presence of α-cyclodextrins (α-CDs). The branched structure of the THPP core promotes gel formation with a small amount of host and guest. Moreover, these resulting hydrogels are dual stimuli-responsive, which can be observed by physically macroscopical phenomena and ^{1}H NMR spectra. Since BA can react with amine to form a pH-responsive Schiff-base which possesses a dynamic covalent nature, it is anticipated that the formation of gels can be modulated by pH. When THPP-(PEG$_{2000}$-BA)$_4$ was blocked by the relatively large molecule 6-*N*-ethylenediamine-6-deoxy functionalized β-CD (EDA-β-CD) gelation did not take place. However, the addition of an acid resulted in gelation since the benzoic imine bonds can hydrolyze under acidic conditions and α-CDs can thus pass through BA to thread on the polyethylene glycol (PEG) chains. When a strongly competitive guest, 1-[*p*-(phenylazo)benzyl]-bromide (Azo-C**1**-N$^+$), was added to the gel, a gel-to-sol transition was observed due to the disassembly of inclusion complexes between α-CDs and PEG chains. Simultaneously, this gel shows a photo-responsive capacity because of the presence of azobenzene. Therefore, the cycles of gel–sol transitions were achieved through pH- and photo-stimuli. This kind of hydrogel is promising for use in many fields, such as biology and electronics.

- Two approaches for the engineering of homogeneous small-molecule hydrogels
  Ding, B.; Li, Y.; Qin, M.; Ding, Y.; Cao, Y.; Wang, W. *Soft Matter* **2013,** *9*, 4672-4680.
  Abstract:



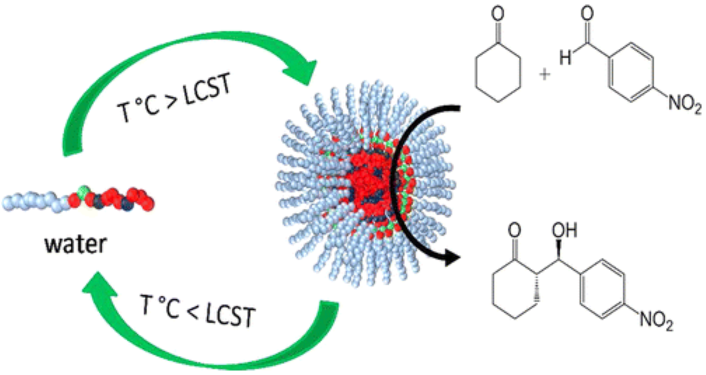
Small-molecule hydrogelators have been widely used to engineer supramolecular hydrogels for biomedical applications. Typically, a change of the solubility of small molecules in solvent is used to trigger the gelation process. This requires a switch of pH or solvent by mixing two different types of solutions. However, due to the intrinsic ragged free energy landscape that underlies the self-assembly process and the high viscosity of the solution that limits the diffusion, the hydrogels made by these methods are often limited by their inhomogeneity and irreproducible physical properties. It is therefore desirable to circumvent these drawbacks and produce homogeneous hydrogels. Conversely, only a few studies have been done towards this direction. In this article, we present two novel approaches to engineer homogeneous hydrogels. One is based on the nano-dispersed colloids to hydrogel transition and the other is based on the decomposition of potassium persulfate to mildly change the pH. These two methods allow kinetically controlling the self-assembly process and the resulting hydrogels are indeed more homogeneous and reproducible. Moreover, the structural and morphological characterizations suggest that the structures of the hydrogels prepared by different approaches are distinct from each other, leading to diverse macroscopic mechanical properties. These results suggest that besides the thermodynamics, the self-assembly kinetics also plays an important role in determining the properties of the final assembled hydrogels. We propose that it is possible to rationally tune the physical properties of the hydrogels by simply control the self-assembly kinetics without changing the structure of the small-molecule hydrogelators.

- A New Benzoxazine Containing Benzoxazole-Functionalized Polyhedral Oligomeric Silsesquioxane and the Corresponding Polybenzoxazine Nanocomposites
  Zhang, K.; Zhuang, Q.; Liu, X.; Yang, G.; Cai, R.; Han, Z. *Macromolecules* **2013**, *46*, 2696-2704.
  Abstract:



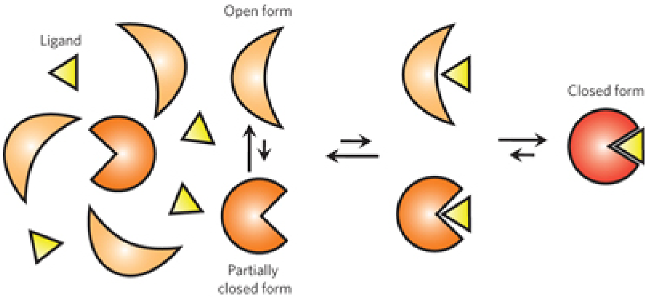
A new benzoxazole-modified $[PhSiO_{1.5}]_8$(OPS) benzoxazine (OPS–Bz) was synthesized and used to prepare polyhedral oligomeric silsesquioxane (POSS)/polybenzoxazine (PBz) nanocomposites. Fourier transform infrared spectroscopy (FTIR), ^{1}H NMR, ^{29}Si NMR, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to characterize the structure of OPS–Bz. The high resolution transmission electron microscopy images of POSS/PBz(30/70) nanocomposites showed a well separated nanostructure of POSS with a typical phase size of 3–10 nm. POSS was highly dispersed in the polymer matrix because of the benzoxazole groups around the OPS molecular, in which the rigid benzoxazole groups increased the distance among the POSS molecules and reduced the aggregation of POSS nanoparticles. The TGA study showed these nanocomposites possess good thermal stability. Moreover, the dielectric constants and dielectric loss of these POSS/PBz nanocomposites were low and changed slightly at room temperature in the frequency range of 10 Hz to 1 MHz.

- Thermoresponsive Polymer-Supported l-Proline Micelle Catalysts for the Direct Asymmetric Aldol Reaction in Water
  Zayas, H. A.; Lu, A.; Valade, D.; Amir, F.; Jia, Z.; O'Reilly, R. K.; Monteiro, M. J. *ACS Macro Lett.* **2013**, *2*, 327-331.
  Abstract:



L-Proline moieties bound to a thermoresponsive polymer nanoreactor efficiently directed the asymmetric aldol reaction in water with excellent yields and enantioselectivity (ee). The reactions were efficient at higher temperatures in direct contrast to the low yields and ee values found when the reaction was carried out in a DMF/water mixture due to the location of the L-proline moieties within the hydrophobic pocket inside the core of the nanoreactors. This ideal environment formed for catalysis allows control over the water content as well as enhancing interactions between the carboxylic acid of L-proline and the aldehyde substrate. The nanoreactors were disassembled to fully water-soluble polymers by lowering the temperature to below the lower critical solution temperature (LCST) of the polymer, resulting in precipitation of the product in near pure form. The product was isolated by centrifugation and the polymer/water solution reused in additional catalytic cycles by heating the polymer above its LCST and thus reforming the nanoreactors. Although a small decrease in yield after five cycles was observed, the selectivity (anti/syn ratio and ee) remained high.

- A single-molecule dissection of ligand binding to a protein with intrinsic dynamics
  Kim, E.; Lee, S.; Jeon, A.; Choi, J. M.; Lee, H.-S.; Hohng, S.; Kim, H.-S. *Nature Chem. Biol.* **2013**, *9*, 313–318.
  Abstract:

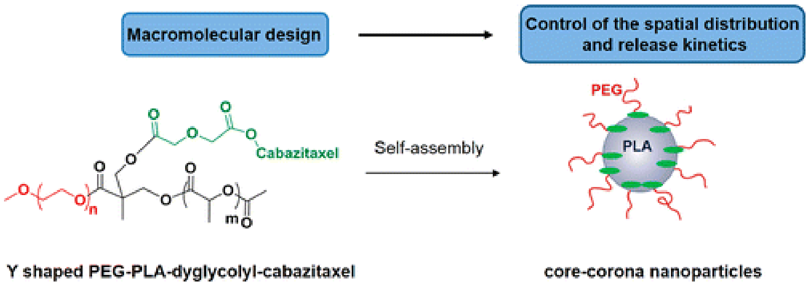


Protein dynamics have been suggested to have a crucial role in biomolecular recognition, but the precise molecular mechanisms remain unclear. Herein, we performed single-molecule fluorescence resonance energy transfer measurements for wild-type maltose-binding protein (MBP) and its variants to demonstrate the interplay of conformational dynamics and molecular recognition. Kinetic analysis provided direct evidence that MBP recognizes a ligand through an 'induced-fit' mechanism, not through the generally proposed selection mechanism for proteins with conformational dynamics such as MBP. Our results indicated that the mere presence of intrinsic dynamics is insufficient for a 'selection' mechanism. An energetic analysis of ligand binding implicated the critical role of conformational dynamics in facilitating a structural change that occurs upon ligand binding.

- Y-Shaped mPEG-PLA Cabazitaxel Conjugates: Well-Controlled Synthesis by Organocatalytic Approach and Self-Assembly into Interface Drug-Loaded Core–Corona Nanoparticles

Bensaid, F.; Thillaye du Boullay, O.; Amgoune, A.; Pradel, C.; Reddy, L. H.; Didier, E.; Sablé, S.; Louit, G.; Bazile, D.; Bourissou, D. *Biomacromolecules* **2013**, *14*, 1189-1198.

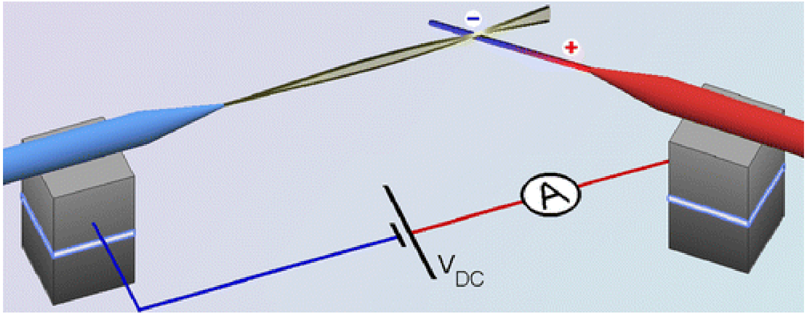
Abstract:



A well-defined poly(ethylene glycol) methyl ether-*b*-poly(lactic acid) copolymer (mPEG-PLA) featuring a new, Y-shaped, architecture with a hydroxyl functional group between the two blocks has been prepared and thoroughly characterized. The functional copolymer was then readily coupled to diglycolyl-cabazitaxel. The resulting copolymer conjugates assembled into stable and monodisperse nanoparticles (NPs) in aqueous suspension. The architecture of the copolymer conjugate is shown to impact the spatial distribution of the drug within the nanoparticles. With the Y-shaped architecture, cabazitaxel was found localized at the interface of the hydrophobic PLA core and the hydrophilic mPEG corona of the NPs, as substantiated by variable temperature NMR analysis of the nanoparticles in D_2O. Preliminary in vitro release studies reveal dependence on the architecture of the copolymer conjugate. This new approach offers promising perspectives to finely tune the position of the active ingredient in polymeric nanoparticles.

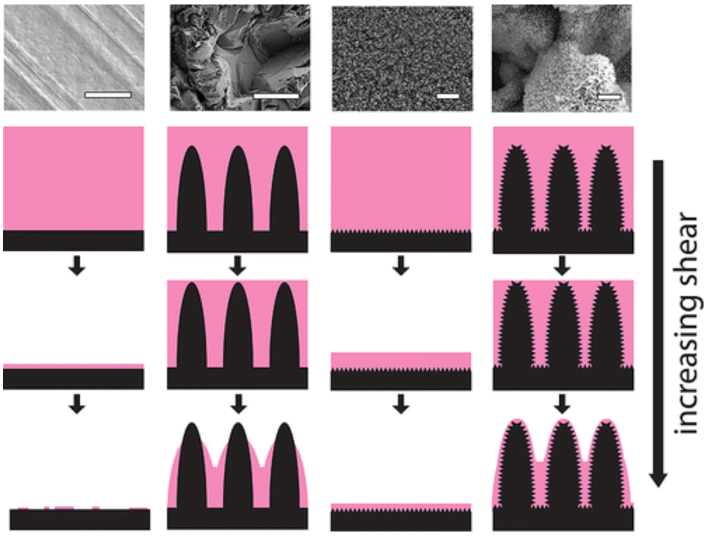
- Ultra Low Power Consumption for Self-Oscillating Nanoelectromechanical Systems Constructed by Contacting Two Nanowires
  Barois, T.; Ayari, A.; Vincent, P.; Perisanu, S.; Poncharal, P.; Purcell, S. T. *Nano Lett.* **2013**, *13*, 1451-1456.

  Abstract:



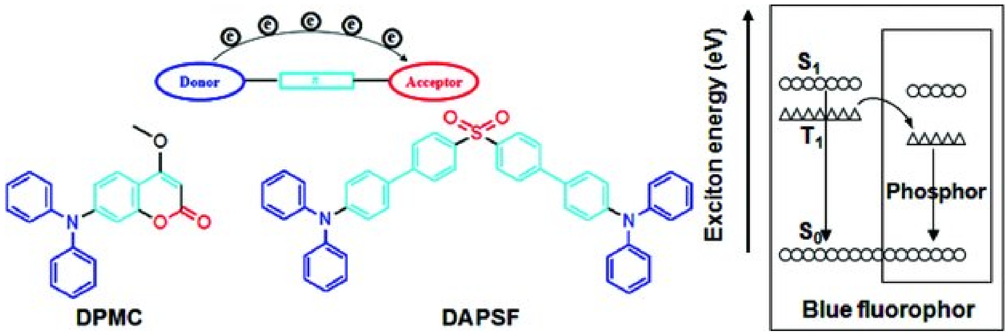
We report here the observation of a new self-oscillation mechanism in nanoelectromechanical systems (NEMS). A highly resistive nanowire was positioned to form a point-contact at a chosen vibration node of a silicon carbide nanowire resonator. Spontaneous and robust mechanical oscillations arise when a sufficient DC voltage is applied between the two nanowires. An original model predicting the threshold voltage is used to estimate the piezoresistivity of the point-contact in agreement with the observations. The measured input power is in the pW-range which is the lowest reported value for such systems. The simplicity of the contacting procedure and the low power consumption open a new route for integrable and low-loss self-excited NEMS devices.

- Hierarchical or Not? Effect of the Length Scale and Hierarchy of the Surface Roughness on Omniphobicity of Lubricant-Infused Substrates
  Kim, P.; Kreder, M. J.; Alvarenga, J.; Aizenberg, J. *Nano Lett.* **2013**, *13*, 1793-1799.
  Abstract:



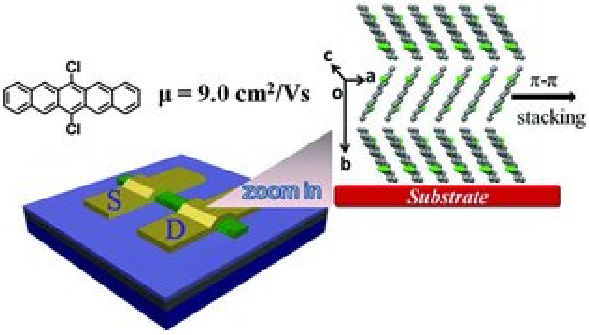
Lubricant-infused textured solid substrates are gaining remarkable interest as a new class of omni-repellent nonfouling materials and surface coatings. We investigated the effect of the length scale and hierarchy of the surface topography of the underlying substrates on their ability to retain the lubricant under high shear conditions, which is important for maintaining nonwetting properties under application-relevant conditions. By comparing the lubricant loss, contact angle hysteresis, and sliding angles for water and ethanol droplets on flat, microscale, nanoscale, and hierarchically textured surfaces subjected to various spinning rates (from 100 to 10 000 rpm), we show that lubricant-infused textured surfaces with uniform nanofeatures provide the most shear-tolerant liquid-repellent behavior, unlike lotus leaf-inspired superhydrophobic surfaces, which generally favor hierarchical structures for improved pressure stability and low contact angle hysteresis. On the basis of these findings, we present generalized, low-cost, and scalable methods to manufacture uniform or regionally patterned nanotextured coatings on arbitrary materials and complex shapes. After functionalization and lubrication, these coatings show robust, shear-tolerant omniphobic behavior, transparency, and nonfouling properties against highly contaminating media.

- Novel Efficient Blue Fluorophors with Small Singlet-Triplet Splitting: Hosts for Highly Efficient Fluorescence and Phosphorescence Hybrid WOLEDs with Simplified Structure
  Zheng, C.-J.; Wang, J.; Ye, J.; Lo, M.-F.; Liu, X.-K.; Fung, M.-K.; Zhang, X.-H.; Lee, C.-S. *Adv. Mater.* **2013**, *25*, 2205–2211.
  Abstract:



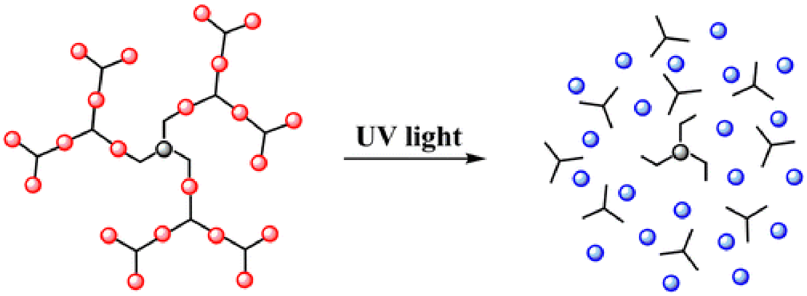
The exact hosts for F-P hybrid WOLEDs have been first demonstrated following a new design strategy for blue fluorophors with small singlet-triplet splitting. Two novel compounds DPMC and DAPSF exhibit efficient blue fluorescence, high triplet energies and good conductivities. These merits allow us to use new simplified device designs to achieve high efficiency, slow efficiency roll-off and stable emission color.

- High-Performance Organic Field-Effect Transistors Based on Single and Large-Area Aligned Crystalline Microribbons of 6,13-Dichloropentacene
  Wang, M.; Li, J.; Zhao, G.; Wu, Q.; Huang, Y.; Hu, W.; Gao, X.; Li, H.; Zhu, D. *Adv. Mater.* **2013**, *25*, 2229–2233.
  Abstract:



Single and large-area aligned crystalline microribbons of 6,13-dichloropentacene (DCP) are prepared. The ribbons display excellent charge transport properties with a mobility of up to 9.0 cm^2 V^{-1} s^{-1} in ambient conditions, one of the highest values reported for organic semiconductors. The slipped π-π stacking with large intermolecular overlap is responsible for the high mobility of DCP ribbons.

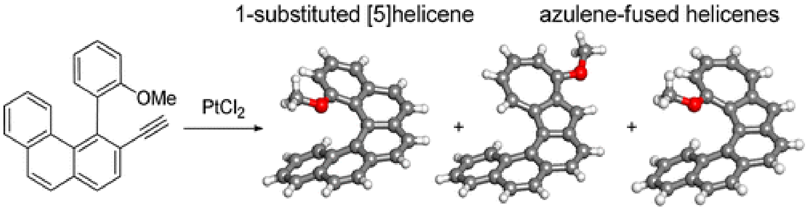
- Synthesis and Degradation of Backbone Photodegradable Polyester Dendrimers
  Nazemi, A.; Schon, T. B.; Gillies, E. R. *Org. Lett.* **2013***, 15,* 1830-1833.
  Abstract:



Dendrimers with fully photodegradable backbones were synthesized through the incorporation of photodegradable o-nitrobenzyl esters into a new dendrimer monomer based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA). Dendrons were synthesized using a divergent approach, and were subsequently coupled to a core molecule in the final step. Photodegradation was performed and it was demonstrated that the molecules degrade to release bis-MPA. The accessibility of these molecules opens new avenues for the preparation of well-defined, fully photodegradable materials.

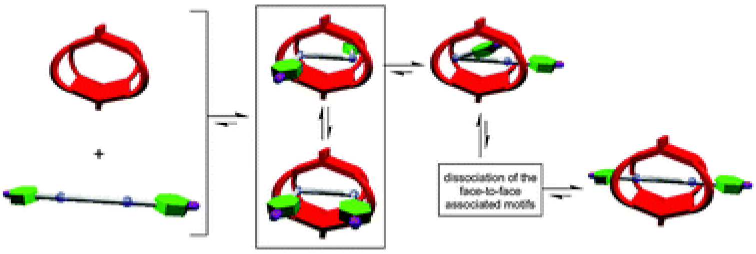
- Synthesis of [5]Helicenes with a Substituent Exclusively on the Interior Side of the Helix by Metal-catalyzed Cycloisomerization

Yamamoto, K.; Okazumi, M.; Suemune, H.; Usui, K. *Org. Lett.* **2013**, *15*, 1806-1809.
Abstract:



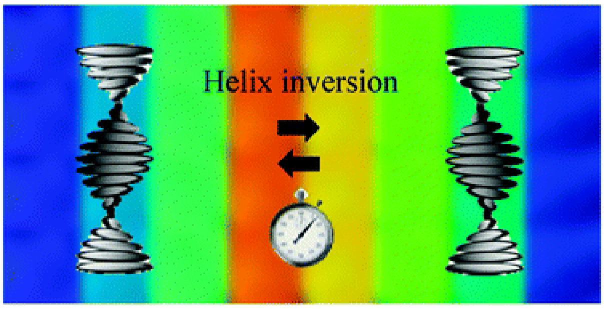
[5]Helicenes with a substituent exclusively oriented toward the interior curvature of the helix are synthesized by metal-catalyzed cycloisomerization. In addition, novel azulene-fused helicenes have been found through cycloisomerization studies. These [5]helicenes shows a high enough configurationally stability to allow resolution by HPLC on a chiral stationary phase.

- Observation of face-to-face host–guest associated states prior to threading of dialkylammonium ions into the DB24C8-like openings of a molecular cage
  Chuang, C.-J.; Yen, M.-L.; Lai, C.-C.; Liu, Y.-H.; Penga, S.-M.; Chiu, S.-H. *Chem. Commun*. **2013**, *49*, 4199-4201.
  Abstract:



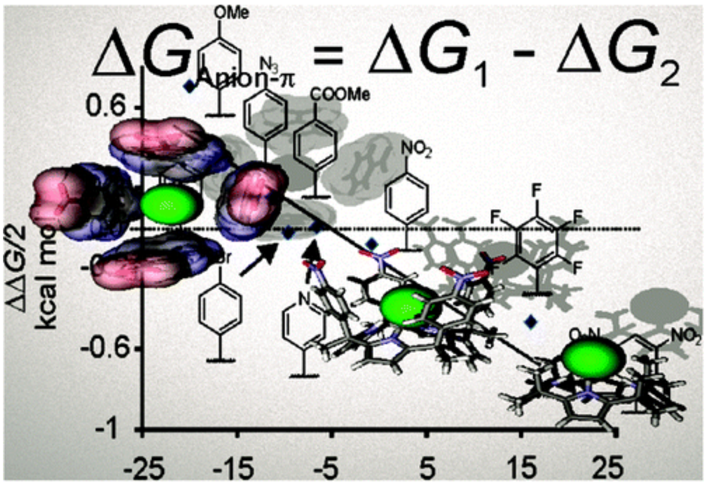
The threading of bis(dialkylammonium) ions through the DB24C8-like openings of a molecular cage proceeds through a stepwise mechanism: formation of a face-to-face complex between the NH2+ centers and the crown ether, significant dissociation of this complex, and passage of the terminus of the cation through the macrocycle.

- Time-programmed helix inversion in phototunable liquid crystals
  Aßhoff, S. J.; Iamsaard, S.; Bosco, A.; Cornelissen, J. J. L. M.; Feringa, B. L.; Katsonis, N. *Chem. Commun*. **2013**, *49*, 4256-4258.
  Abstract :



Doping cholesteric liquid crystals with photo-responsive molecules enables controlling the colour and polarisation of the light they reflect. However, accelerating the rate of relaxation of these photo-controllable liquid crystals remains challenging. Here we show that the relaxation rate of the cholesteric helix is fully determined by helix inversion of the molecular dopants.

- Experimental Quantification of Anion−π Interactions in Solution Using Neutral Host–Guest Model Systems
  Ballester, P. *Acc. Chem. Res.* **2013**, *46*, 874–884.
  Abstract:



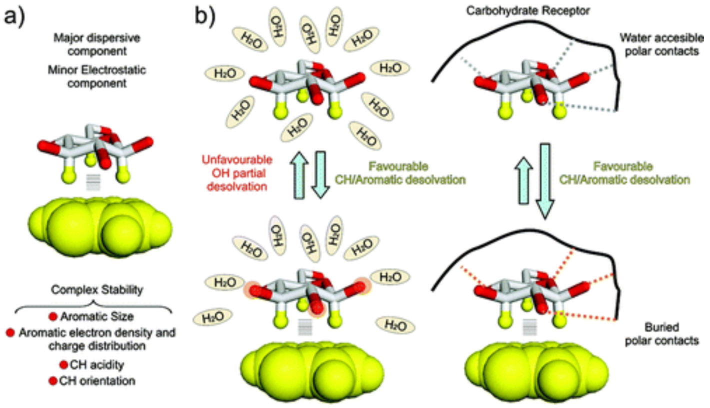
Chemical intuition suggests that anions and π-aromatic systems would repel each other. Typically, we think of cations as being attracted to electron-rich π-systems of aromatic rings, and the cation−π interaction, a well-established noncovalent interaction, plays an important role in nature. Therefore the anion−π interaction can be considered the opposite of the cation−π interaction. Computational studies of simple models of anion−π interactions have provided estimates of the factors that govern the binding geometry and the binding energy, leading to a general consensus about the nature of these interactions. In order to attract an anion, the charge distribution of the aromatic system has to be reversed, usually through the decoration of the aromatic systems with strongly electron-withdrawing groups. Researchers have little doubt about the existence of attractive anion−π interactions in the gas phase and in the solid state. The bonding energies assigned to anion−π interactions from quantum chemical calculations and gas phase experiments are significant and compare well with the values obtained for cation−π interactions. In solution, however, there are few examples of attractive anion−π interactions.

In this Account, I describe several examples of neutral molecular receptors that bind anions in solution either solely through anion−π interactions or as a combination of anion−π interactions and hydrogen bonding. In the latter cases, the strength of the anion−π interaction is indirectly detected as a modulation of the stronger hydrogen bonding interaction (enforced proximity). The dissection of the energy contribution of the anion−π interaction to the overall binding is complex, which requires the use of appropriate reference systems.

This Account gives an overview the experimental efforts to determine the binding energies that can be expected from anion−π interactions in solution with examples that center around the recognition of halides. The studies show that anion−π interactions also exist in solution, and the free energy of binding estimated for these attractive interactions is less than 1 kcal/mol for each substituted phenyl groups. The quantification of anion−π interactions in solution relies on the use of molecular recognition model systems; therefore researchers need to consider how the structure of the model system can alter the magnitude of the observed energy values. In addition, the recognition of anions in solution requires the use of salts (ion pairs) as precursors, which complicates the analysis of the titration data and the corresponding estimate of the binding strength. In solution, the weak binding energies suggest that anion−π interactions are not as significant for the selective or enhanced binding

of anions but offer potential applications in catalysis and transport within functional synthetic and biological systems.

- Carbohydrate–Aromatic Interactions
  Asensio, J. L.; Ardá, A.; Cañada, F. J.; Jiménez-Barbero, J. *Acc. Chem. Res.* **2013**, *46*, 946–954.
  Abstract:



The recognition of saccharides by proteins has far reaching implications in biology, technology, and drug design. Within the past two decades, researchers have directed considerable effort toward a detailed understanding of these processes. Early crystallographic studies revealed, not surprisingly, that hydrogen-bonding interactions are usually involved in carbohydrate recognition. But less expectedly, researchers observed that despite the highly hydrophilic character of most sugars, aromatic rings of the receptor often play an important role in carbohydrate recognition.

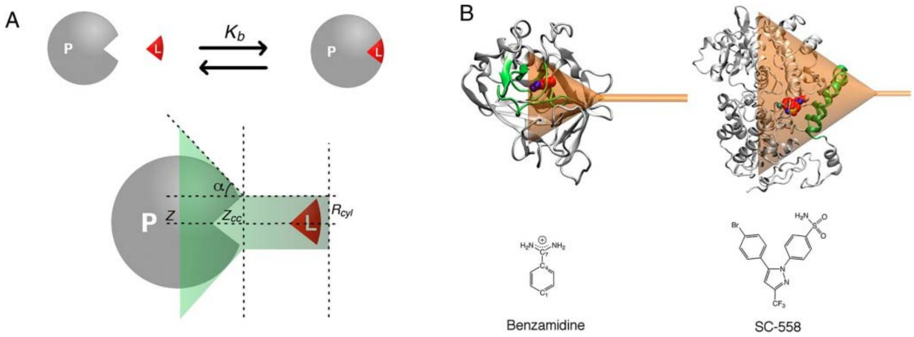
With further research, scientists now accept that noncovalent interactions mediated by aromatic rings are pivotal to sugar binding. For example, aromatic residues often stack against the faces of sugar pyranose rings in complexes between proteins and carbohydrates. Such contacts typically involve two or three CH groups of the pyranoses and the π electron density of the aromatic ring (called CH/π bonds), and these interactions can exhibit a variety of geometries, with either parallel or nonparallel arrangements of the aromatic and sugar units.

In this Account, we provide an overview of the structural and thermodynamic features of protein–carbohydrate interactions, theoretical and experimental efforts to understand stacking in these complexes, and the implications of this understanding for chemical biology. The interaction energy between different aromatic rings and simple monosaccharides based on quantum mechanical calculations in the gas phase ranges from 3 to 6 kcal/mol range. Experimental values measured in water are somewhat smaller, approximately 1.5 kcal/mol for each interaction between a monosaccharide and an aromatic ring. This difference illustrates the dependence of these intermolecular interactions on their context and shows that this stacking can be modulated by entropic and solvent effects. Despite their relatively modest influence on the stability of carbohydrate/protein complexes, the aromatic platforms play a major role in determining the specificity of the molecular recognition process.

The recognition of carbohydrate/aromatic interactions has prompted further analysis of the properties that influence them. Using a variety of experimental and theoretical methods, researchers have worked to quantify carbohydrate/aromatic stacking and identify the features that stabilize these complexes. Researchers have used site-directed mutagenesis, organic synthesis, or both to incorporate modifications in the receptor or ligand and then quantitatively analyzed the structural and thermodynamic features of these interactions. Researchers have also synthesized and

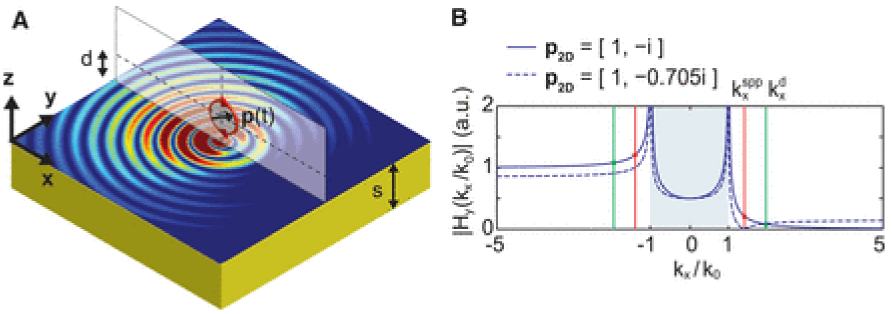
characterized artificial receptors and simple model systems, employing a reductionistic chemistry-based strategy. Finally, using quantum mechanics calculations, researchers have examined the magnitude of each property's contribution to the interaction energy.

- Funnel metadynamics as accurate binding free-energy method
  Limongelli, V.; Bonomi, M., Parrinello, M. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 6358-6363.
  Abstract:



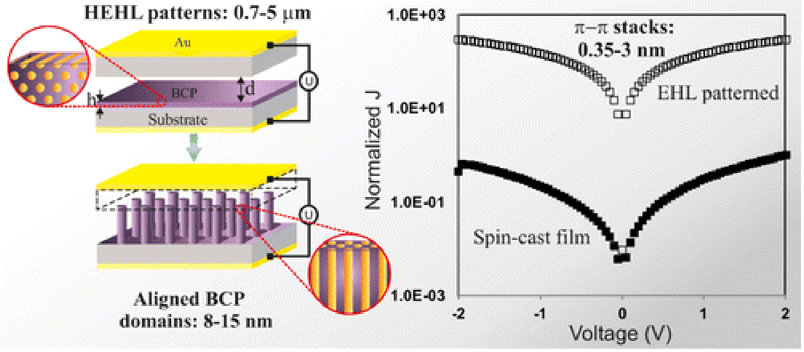
A detailed description of the events ruling ligand/protein interaction and an accurate estimation of the drug affinity to its target is of great help in speeding drug discovery strategies. We have developed a metadynamics-based approach, named funnel metadynamics, that allows the ligand to enhance the sampling of the target binding sites and its solvated states. This method leads to an efficient characterization of the binding free-energy surface and an accurate calculation of the absolute protein–ligand binding free energy. We illustrate our protocol in two systems, benzamidine/trypsin and SC-558/cyclooxygenase 2. In both cases, the X-ray conformation has been found as the lowest free-energy pose, and the computed protein–ligand binding free energy in good agreement with experiments. Furthermore, funnel metadynamics unveils important information about the binding process, such as the presence of alternative binding modes and the role of waters. The results achieved at an affordable computational cost make funnel metadynamics a valuable method for drug discovery and for dealing with a variety of problems in chemistry, physics, and material science.

- Near-Field Interference for the Unidirectional Excitation of Electromagnetic Guided Modes
  Rodríguez-Fortuño, F. J.; Marino, G.; Ginzburg, P.; O'Connor, D.; Martínez, A.; Wurtz, G. A.; Zayats, A. V. *Science* **2013**, *340,* 328-330.
  Abstract:



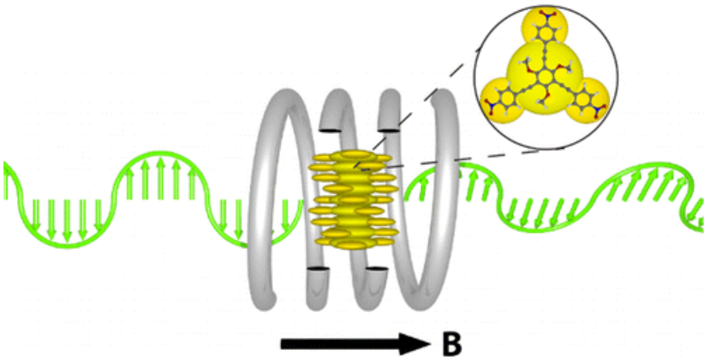
Wave interference is a fundamental manifestation of the superposition principle with numerous applications. Although in conventional optics, interference occurs between waves undergoing different phase advances during propagation, we show that the vectorial structure of the near field of an emitter is essential for controlling its radiation as it interferes with itself on interaction with a mediating object. We demonstrate that the near-field interference of a circularly polarized dipole results in the unidirectional excitation of guided electromagnetic modes in the near field, with no preferred far-field radiation direction. By mimicking the dipole with a single illuminated slit in a gold film, we measured unidirectional surface-plasmon excitation in a spatially symmetric structure. The surface wave direction is switchable with the polarization.

- Hierarchical Orientation of Crystallinity by Block-Copolymer Patterning and Alignment in an Electric Field
  Goldberg-Oppenheimer, P.; Kabra, D.; Vignolini, S.; Hüttner, S.; Sommer, M.; Neumann, K.; Thelakkat, M.; Steiner, U. *Chem. Mater.* **2013**, *25*, 1063-1070.
  Abstract:



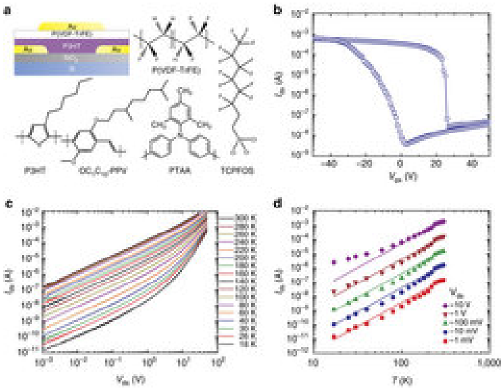
Electron and hole conducting 10-nm-wide polymer morphologies hold great promise for organic electro-optical devices such as solar cells and light emitting diodes. The self-assembly of block-copolymers (BCPs) is often viewed as an efficient way to generate such materials. Here, a functional block copolymer that contains perylene bismide (PBI) side chains which can crystallize via π–π stacking to form an electron conducting microphase is patterned harnessing hierarchical electrohydrodynamic lithography (HEHL). HEHL film destabilization creates a hierarchical structure with *three* distinct length scales: (1) micrometer-sized polymer pillars, containing (2) a 10-nm BCP microphase morphology that is aligned perpendicular to the substrate surface and (3) on a molecular length scale (0.35–3 nm) PBI π–π-stacks traverse the HEHL-generated plugs in a continuous fashion. The good control over BCP and PBI alignment inside the generated vertical microstructures gives rise to liquid-crystal-like optical dichroism of the HEHL patterned films, and improves the electron conductivity across the film by 3 orders of magnitude.

- Giant Faraday Rotation in Mesogenic Organic Molecules
  Vandendriessche, S.; Van Cleuvenbergen, S.; Willot, P.; Hennrich, G.; Srebro, M.; Valev, V. K.; Koeckelberghs, G.; Clays, K.; Autschbach, J.; Verbiest, T. *Chem. Mater.* **2013**, *25*, 1139-1143.
  Abstract:



Faraday rotation, the rotation of the polarization of light due to a magnetic field in the direction of propagation of the light, is used in applications ranging from quantum memory to the detection of biomagnetic fields. For these applications large Faraday rotation is necessary, but absorption of light is detrimental. In search of these properties, we have characterized the Verdet constant of a so far unexplored class of mesogenic organic molecules. We report their spectra and provide an interpretation. A Verdet constant of almost 2.5×10^5 deg T^{-1} m^{-1} is found around 520 nm. This Verdet constant is 3 orders of magnitude larger than the largest known for organic molecules in a region without spectral features. We attribute this enormous Faraday rotation to resonant enhancement by a triplet excitation that does not appear in the linear absorption spectrum and to near-resonant enhancement by low-energy singlet excitations. Furthermore we are able to switch the Faraday rotation by changing the liquid crystal phase of the compound. These results demonstrate a new class of Faraday rotating materials with great potential to replace current materials and improve existing applications. The inherent flexibility in the synthesis of this class of molecules opens a new field of research in Faraday rotation.

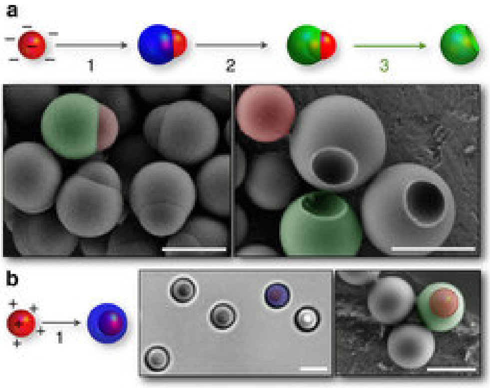
- Polaron hopping mediated by nuclear tunnelling in semiconducting polymers at high carrier density
  Asadi, K.; Kronemeijer, A. J.; Cramer, T.; Jan Anton Koster, L.; Blom, P. W. M.; de Leeuw, D. M. *Nat Commun* **2013**, *4*, 1710.
  <u>Abstract:</u>



The transition rate for a single hop of a charge carrier in a semiconducting polymer is assumed to be thermally activated. As the temperature approaches absolute zero, the predicted conductivity becomes infinitesimal in contrast to the measured finite conductivity. Here we present a uniform description of charge transport in semiconducting polymers, including the existence of absolute-zero ground-state oscillations that allow nuclear tunnelling through classical barriers. The resulting expression for the macroscopic current shows a power-law dependence on both temperature and voltage. To suppress the omnipresent disorder, the predictions are experimentally verified in semiconducting polymers at high carrier density using chemically doped in-plane diodes and ferroelectric field-effect transistors. The renormalized current-voltage characteristics of various polymers and devices at all temperatures collapse on a single universal curve, thereby demonstrating the relevance of nuclear tunnelling for organic electronic devices.

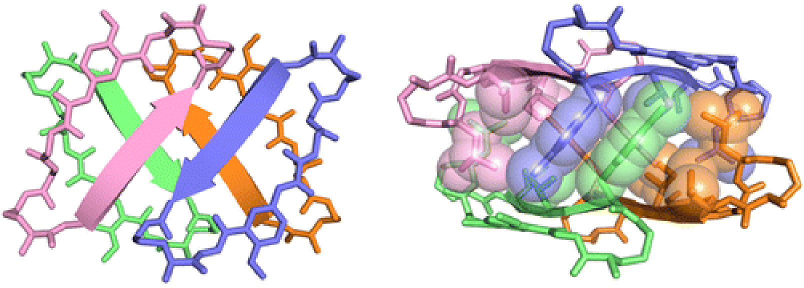
- Shaping colloids for self-assembly
  Sacanna, S.; Korpics, M.; Rodriguez, K.; Colón-Meléndez, L.; Kim, S.-H.; Pine, D. J.; Yi, G.-R. *Nat Commun* **2013**, *4*, 1688.

Abstract:



The creation of a new material often starts from the design of its constituent building blocks at a smaller scale. From macromolecules to colloidal architectures, to granular systems, the interactions between basic units of matter can dictate the macroscopic behaviour of the resulting engineered material and even regulate its genesis. Information can be imparted to the building units by altering their physical and chemical properties. In particular, the shape of building blocks has a fundamental role at the colloidal scale, as it can govern the self-organization of particles into hierarchical structures and ultimately into the desired material. Herein we report a simple and general approach to generate an entire zoo of new anisotropic colloids. Our method is based on a controlled deformation of multiphase colloidal particles that can be selectively liquified, polymerized, dissolved and functionalized in bulk. We further demonstrate control over the particle functionalization and coating by realizing patchy and Janus colloids.

- The Supramolecular Chemistry of β-Sheets
  Cheng, P.-N.; Pham, J. D.; Nowick, J. S. *J. Am. Chem. Soc.* **2013***, 135*, 5477–5492.
  Abstract:

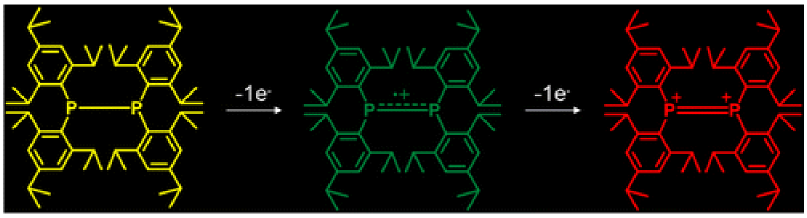


Interactions among β-sheets occur widely in protein quaternary structure, protein–protein interaction, and protein aggregation and are central in Alzheimer's and other amyloid-related diseases. This Perspective looks at the structural biology of these important yet under-appreciated interactions from a supramolecular chemist's point of view. Common themes in the supramolecular interactions of β-sheets are identified and richly illustrated though examples from proteins, amyloids, and chemical model systems. β-Sheets interact through edge-to-edge hydrogen bonding to form extended layers and through face-to-face hydrophobic or van der Waals interactions to form layered sandwich-like structures. Side chains from adjacent layers can fit together through simple hydrophobic contacts or can participate in complementary interdigitation or knob–hole interactions. The layers can be aligned, offset, or rotated. The right-handed twist of β-sheets provides additional opportunities for stabilization of edge-to-edge contacts and rotated layered structures.

- Stable Tetraaryldiphosphine Radical Cation and Dication

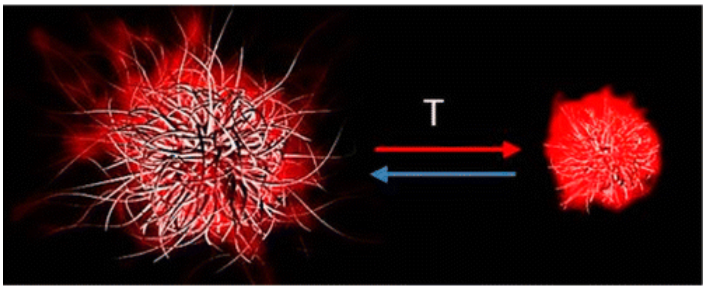
Pan, X.; Su, Y.; Chen, X.; Zhao, Y.; Li, Y.; Zuo, J.; Wang, X. *J. Am. Chem. Soc.* **2013***, 135,* 5561–5564.

Abstract:



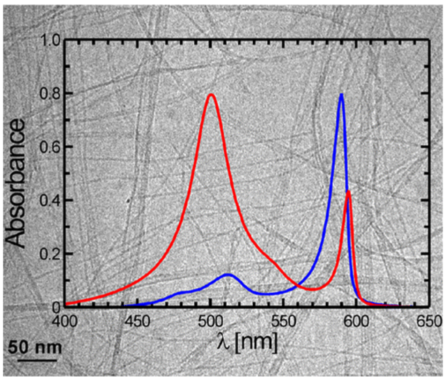
Salts containing tetraaryldiphosphine radical cation 1•+ and dication 12+ have been isolated and structurally characterized. Radical 1•+ has a relaxed pyramidal geometry, while dication 12+ prefers a planar, olefin-like geometry with a two-electron π bond. The alteration of the geometries of the tetraaryldiphosphine upon oxidation is rationalized by the nature of the bonding. The EPR spectrum showed that the spin density of radical 1•+ is mainly localized on phosphorus atoms, which is supported by theoretical calculation.

- Enhanced Electrogenerated Chemiluminescence in Thermoresponsive Microgels
  Pinaud, F.; Russo, L.; Pinet, S.; Gosse, I.; Ravaine, V.; Sojic, N. *J. Am. Chem. Soc.*, **2013**, *135*, 5517–5520.
  Abstract:



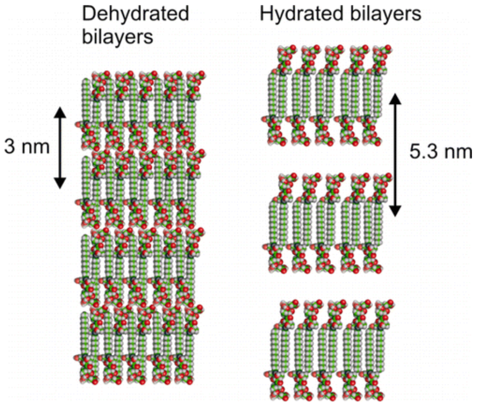
The electrochemistry, photoluminescence and electrogenerated chemiluminescence of thermoresponsive redox microgels were investigated. For the first time, reversible ECL enhancement is demonstrated in stimuli-responsive 100-nm microgel particles. Such an unexpected amplification reached 2 orders of magnitude, and it is intrinsically correlated with the collapse of the microgel particles. The swell–collapse transition decreases the average distance between adjacent redox sites and favors the electron-transfer processes in the microgels resulting in the enhanced ECL emission.

- Supramolecular Structure of TTBC J-Aggregates in Solution and on Surface
  Berlepsch, H.; Böttcher, C. *Langmuir* **2013**, *29*, 4948–4958.
  Abstract:



The aggregation behavior of cationic 5,5′,6,6′-tetrachloro-1,1′,3,3′-tetraethylbenzimidacarbocyanine with chloride (TTBC-Cl) or iodide counterions (TTBC-I) in aqueous solution is investigated by absorption, linear dichroism, and fluorescence spectroscopies, as well as cryogenic transmission electron microscopy (cryo-TEM) and atomic force microscopy (AFM). TTBC-Cl is found to form J-aggregates with a classical Davydov-split absorption band (type I spectrum) even under different preparation conditions. These aggregates remain stable for months. Unlike the chloride salt, the iodide salt TTBC-I forms two different types of J-aggregates depending on the pH of the aqueous solution. The TTBC-I aggregates prepared in pure water (pH = 6) are characterized by a single redshifted absorption band (type III spectrum), whereas those prepared in alkaline solution at pH = 13 show a typical Davydov-split (type I) absorption band. Despite differences in counterions, preparation method, stability, and spectroscopic behavior, cryo-TEM reveals an identical tubular architecture for all these J-aggregates. Among the new structure models discussed here is a cylindrical brickwork layer of dye molecules for single-banded J-aggregates (type III). For Davydov-split aggregates (type I), a molecular herringbone-like pattern is proposed instead. Moreover, absorption spectra have revealed an additional single redshifted absorption band (type II spectrum) that is assigned to a surface aggregate and is induced by a specific interaction of the dye cation with the negatively charged cuvette wall. AFM measurements of analogous preparations on negatively charged mica surfaces have supported this interpretation and revealed the formation of monolayered sheet structures.

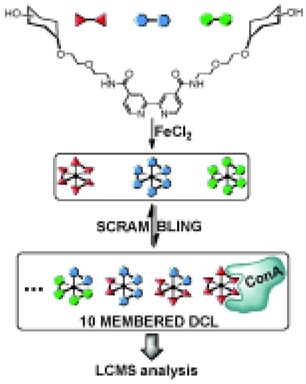
- Coassembly in Binary Mixtures of Peptide Amphiphiles Containing Oppositely Charged Residues
  Hamley, I. W.; Dehsorkhi , A.; Castelletto, V. *Langmuir* **2013**, *29*, 5050–5059.
  Abstract:



The self-assembly in water of designed peptide amphiphile (PA) C_{16}-ETTES containing two anionic residues and its mixtures with C_{16}-KTTKS containing two cationic residues has been investigated. Multiple spectroscopy, microscopy, and scattering techniques are used to examine ordering extending from the β-sheet structures up to the fibrillar aggregate structure. The peptide amphiphiles both comprise a hexadecyl alkyl chain and a charged pentapeptide headgroup containing two charged residues. For C_{16}-ETTES, the critical aggregation concentration was determined by fluorescence experiments. FTIR and CD spectroscopy were used to examine β-sheet formation. TEM revealed highly extended tape nanostructures with some striped regions corresponding to bilayer structures viewed edge-on. Small-angle X-ray scattering showed a main 5.3 nm bilayer spacing along with a 3 nm spacing. These spacings are assigned respectively to predominant hydrated bilayers and a fraction of dehydrated bilayers. Signs of cooperative self-assembly are observed in the mixtures, including

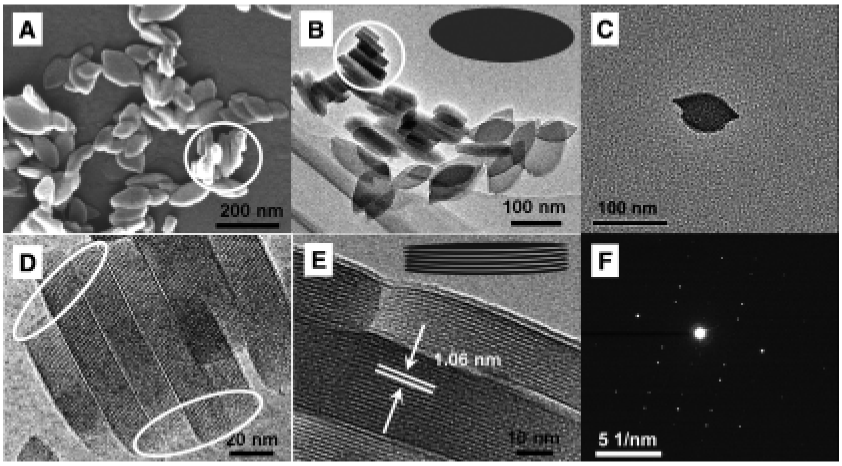
reduced bundling of peptide amphiphile aggregates (extended tape structures) and enhanced β-sheet formation.

- Dynamic Multivalency for Carbohydrate–Protein Recognition through Dynamic Combinatorial Libraries Based on Fe^{II}–Bipyridine Complexes
  Reeh, P.; Mendoza, J. *Chem. Eur. J.* **2013**, *17*, 5259-5262.
  <u>Abstract:</u>



Molecular recognition: Dynamic combinatorial libraries (DCLs) exploiting multivalency effects and metal coordination have been employed for carbohydrate–protein recognition. The interaction of a three-component DCL based on 2,2′-bipyridine (bipy)–Fe^{II} complexes with concanavalin A (ConA; see scheme) results in enhanced binding by multivalent presentation with a bias towards mannose-containing library components.

- Synthesis and Properties of Oval-Shaped Iron Oxide/Ethylene Glycol Mesostructured Nanosheets
  Wang, X.; Yang, Y.; Zhai, T.; Zhong, Y.; Gu, Z.; Cao, Y. C.; Zhao, Y.; Ma, Y.; Yao, J. *Chem. Eur. J.* **2013**, *17*, 5442-5449.
  <u>Abstract:</u>



We have demonstrated a new and facile bottom-up protocol for the effective synthesis of oval-shaped iron oxide/ethylene glycol (FeO_x/EG) mesostructured nanosheets. Deprotonated ethylene glycol molecules are intercalated into iron oxide layers to form an interlayer distance of 10.6 Å. These materials display some peculiar magnetic properties, such as the low Morin temperature T_M and ferromagnetism below this T_M value. CdSe/ZnS nanoparticles can be loaded onto these mesostructured nanosheets to produce nanocomposites that combine both magnetic and fluorescence functions. In addition, iron oxide/propanediol (or butanediol) mesostructured materials with increased interlayer distances can also be synthesized. The developed synthetic strategy may be extended toward the creation of other ultrathin mesostructured nanosheets.