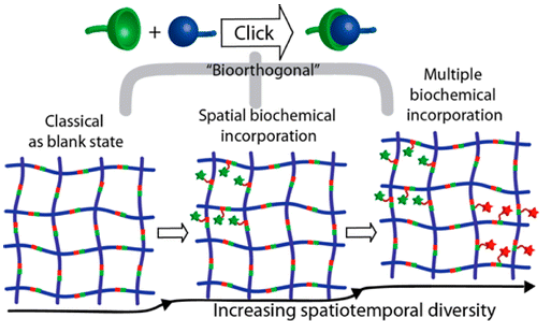
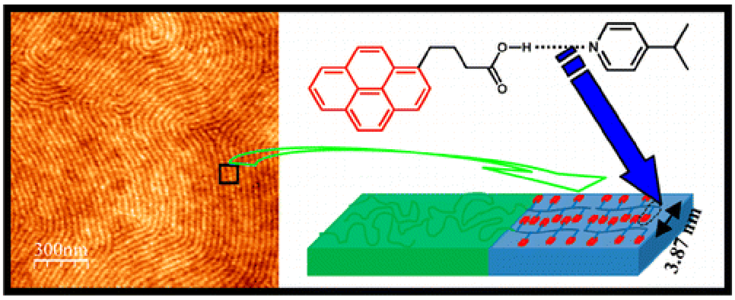
- Bioorthogonal Click Chemistry: An Indispensable Tool to Create Multifaceted Cell Culture Scaffolds
  Azagarsamy, M. A.; Anseth, K. S. *ACS Macro Lett.* **2013**, *2*, 5-9.
  Abstract:



Over the past decade, bioorthogonal click chemistry has led the field of biomaterial science into a new era of diversity and complexity by its extremely selective, versatile, and biocompatible nature. In this viewpoint, we seek to emphasize recent endeavors of exploiting this versatile chemistry toward the development of poly(ethylene glycol) hydrogels as cell culture scaffolds. In these cell-laden materials, the orthogonality of these reactions has played an effective role in allowing the creation of diverse biochemical patterns in complex biological environments that provide new found opportunities for researchers to delineate and control cellular phenotypes more precisely than ever.

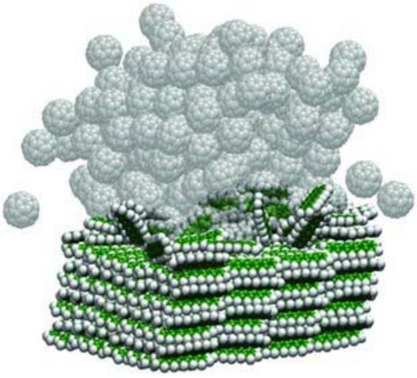
- A Synergistic Coassembly of Block Copolymer and Fluorescent Probe in Thin Film for Fine-Tuning the Block Copolymer Morphology and Luminescence Property of the Probe Molecules
  Kuila, B. K.; Chakraborty, C.; Malik, S. *Macromolecules* **2013**, *46*, 484-492.
  Abstract:



Here, we investigate a synergistic coassembly of a block copolymer, polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP), and a fluorescent probe molecule, pyrenebutyric acid (PBA), in thin film using block copolymer supramolecular assembly (SMA) strategy for a wide range of compositions tuned by varying the molar ratio (r) of PBA and 4VP units. The PBA molecules form supramolecules with PS-*b*-P4VP through H-bonding between the carboxylic acid group of 1-pyrenebutyric acid and pyridine ring of P4VP. For compositions r = 0, 0.1, 0.25, and 0.5, the SMAs exhibit cylindrical morphology, whereas for r = 0.75 and 1, the SMAs generate lamellar morphology. Interestingly, it has been observed that the orientation of the microdomains depends on the solvent used for annealing and can be switched reversibly on exposing the SMA films to corresponding solvent. In a nonselective solvent like chloroform, the microdomains are oriented normal to the substrate, whereas in a selective solvent like 1,4-dioxane, the microdomains are oriented parallel. The synergistic coassembly of PS-*b*-P4VP and PBA in SMAs with higher molar ratio results in a structure-within-structure pattern characterized by two length scales from phase separation of block copolymer and parallel π–π stacking of the pyrene moiety of PBA molecules inside the comb block. The photophysical properties

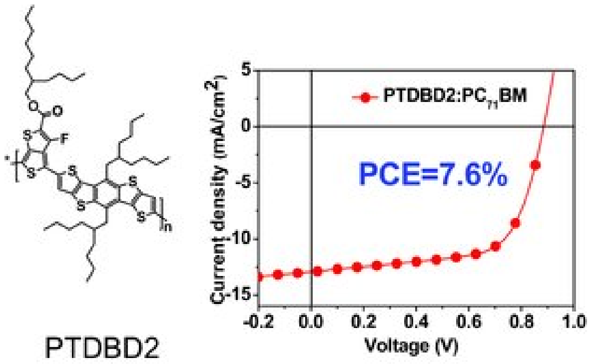
of PBA in different SMAs of varying composition were studied both in solution and in thin film state and compared to pure PBA. The UV–vis study shows the H type of aggregation of PBA molecules inside the comb block by parallel stacking of the pyrene units, and the PBA molecules orient parallel to the substrate when the microdomains are oriented normal to the substrate. The pure PBA molecules in thin film exhibit excimer emission extensively, whereas the PBA molecules in different supramolecular assemblies exhibit emission ranging from monomer to mixture of monomer and excimer. The SMA shows more intense fluorescence emission compared to pure PBA both in solution and in thin film.

- Intermixing at the Pentacene-Fullerene Bilayer Interface: A Molecular Dynamics Study
  Fu, Y.-T.; Risko, C.; Brédas, J.-L.; Zhao, Y. S.; Yao, J. *Adv. Mater.* **2013**, *25*, 878–882.
  Abstract:



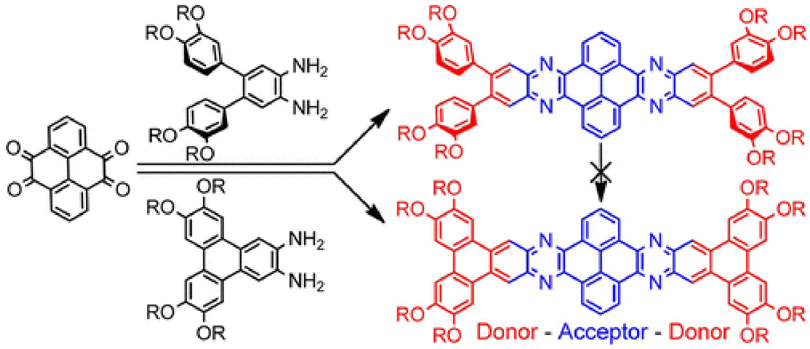
Molecular dynamics simulations of the pentacene-C_{60} donor–acceptor interface reveal the potential for miscibility and disorder in "simple" bilayer organic photovoltaic architectures. The results fall in line with growing evidence of morphological complexity at such interfaces, and will impact descriptions of the electronic processes taking place during the photovoltaic effect.

- Synthesis and Photovoltaic Effect in Dithieno[2,3-*d*:2′,3′-*d*′]Benzo[1,2-*b*:4,5-*b*′]dithiophene-Based Conjugated Polymers
  Son, H. J.; Lu, L.; Chen, W.; Xu, T.; Zheng, T.; Carsten, B.; Strzalka, J.; Darling, S. B.; Chen, L. X.; Yu, L. *Adv. Mater.* **2013**, *25*, 838–843.
  Abstract:



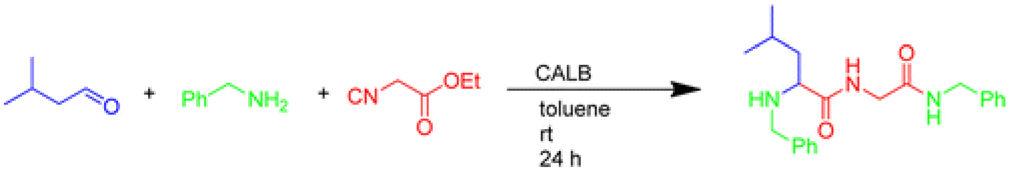
Conjugated polymers based on a heteroacene, 3,7-dialkyl-dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (DBD), are synthesized. These polymers show broad UV–vis absorption with energy bandgaps below 1.7 eV. PTDBD2, showing good miscibility in a polymer/phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) blend film, achieves a power conversion efficiency (PCE) of 7.6%. The results indicate that copolymers containing DBD are promising candidates for high-performance organic solar cells.

- Columnar Mesomorphism of Fluorescent Board-Shaped Quinoxalinophenanthrophenazine Derivatives with Donor-Acceptor Structure
  Chen, S.; Raad, F.S.; Ahmida, M.; Kaafarani, B. R.; Eichhorn, S. H. *Org. Lett.* **2013**, *15,* 558-561.
  Abstract:



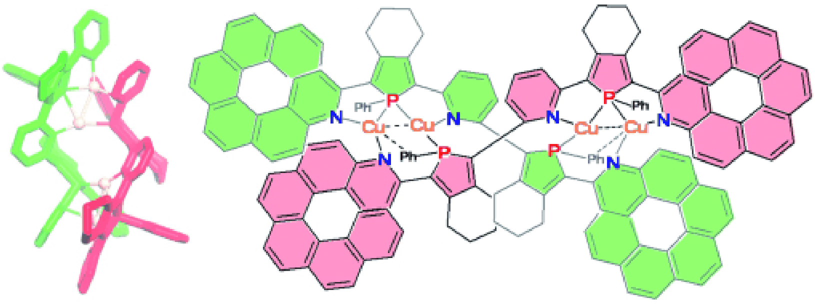
Quinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine (QPP) dyes have been studied as electron acceptor materials, fluorophores, and building blocks for self-organizing organic semiconductors. Condensation of tetraketopyrene with electron-rich diamino-terphenylene and –triphenylene derivatives generates new donoracceptor QPP derivatives that display columnar mesomorphism over wide ranges of temperature; are fluorescent in solution, liquid crystal, and solid phases; and have electron acceptor properties. Also reported are the synthesis and properties of the first diamino-(tetraalkoxy)triphenylene as a valuable new synthon.

- Model Studies on the First Enzyme-Catalyzed Ugi Reaction
  Kłossowski, S.; Wiraszka, B.; Berłozecki, S.; Ostaszewski, R. *Org. Lett.* **2013**, *15*, 566-569.
  Abstract:



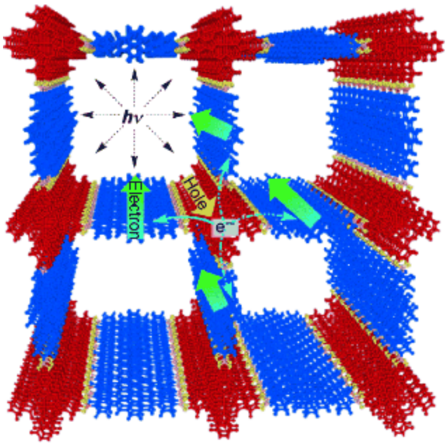
Multicomponent reactions are powerful tools for organic chemistry, and among them, the Ugi reaction provides remarkable improvement in many fields of organic chemistry such us combinatorial chemistry, medicinal chemistry, and peptide chemistry. A new, enzyme-catalyzed example of the Ugi three component reaction is presented. The studies include the selection of an enzyme as well as determination of the scope and limitations of the newly described reaction. The presented method combines the enzyme promiscuity and multicomponent reaction advantages in the first one-pot formation of dipeptide 1.

- Assembly of Helicene-Capped N,P,N,P,N-Helicands within Cu^{I} Helicates: Impacting Chiroptical Properties by Ligand–Ligand Charge Transfer
  Vreshch, V.; El Sayed Moussa, M.; Nohra, B.; Srebro, M.; Vanthuyne, N.; Roussel, C.; Autschbach, J.; Crassous, J.; Lescop, C.; Réau, R. *Angew. Chem. Int. Ed.* **2013**, *52*, 1968–1972.
  Abstract:



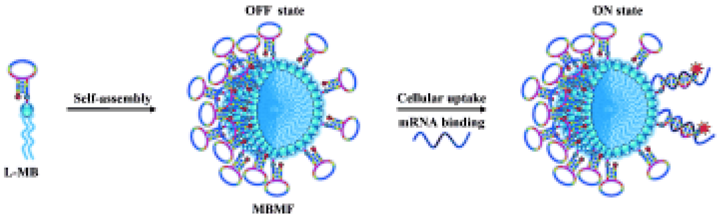
Combining helicate and helicene chemistry: Pentadentate phosphole-pyridine helicands (see scheme) coordinated to Cu^I or Ag^I centers afford configurationally stable double-stranded helicates bearing multiple bridging-phosphane coordination modes. Similarly enantiomerically pure helicene-grafted helicands afford enantiopure helicates.

- Charge Dynamics in A Donor–Acceptor Covalent Organic Framework with Periodically Ordered Bicontinuous Heterojunctions
  Jin, S.; Ding, X.; Feng, X.; Supur, M.; Furukawa, K.; Takahashi, S.; Addicoat, M.; El-Khouly, M. E.; Nakamura, T.; Irle, S.; Fukuzumi, S.; Nagai, A.; Jiang, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 2017–2021.
  <u>Abstract:</u>



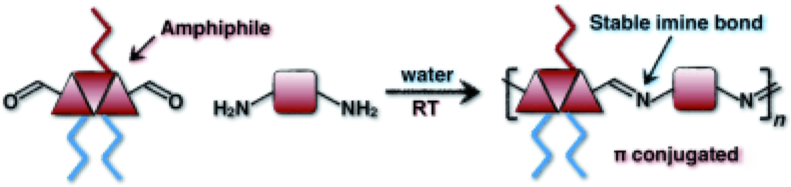
Light works: Mechanistic insights into the photochemical events and charge dynamics of a donor–acceptor covalent organic framework were given by time-resolved transient absorption spectroscopy and time-resolved electron spin resonance spectroscopy (see picture). The organic framework triggers ultrafast electron transfer and enables long-distance charge delocalization and exceptional long-term charge separation.

- DNA Micelle Flares for Intracellular mRNA Imaging and Gene Therapy
  Chen, T.; Wu, C. S.; Jimenez, E.; Zhu, Z.; Dajac, J. G.; You, M.; Han, D.; Zhang, X.; Tan, W. *Angew. Chem. Int. Ed.* **2013**, *7*, 2012-2016.
  <u>Abstract:</u>



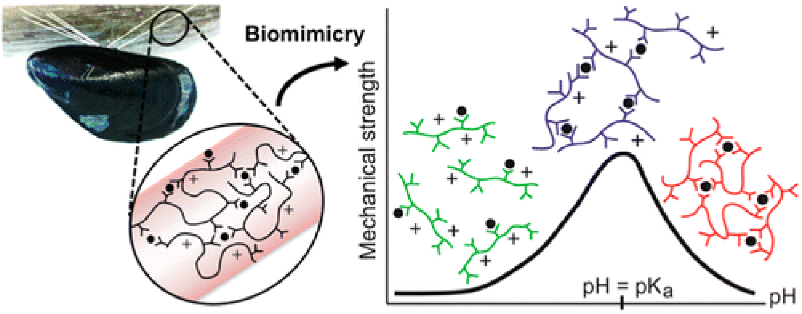
Lighting the way with DNA: Molecular beacon micelle flares (MBMFs), based on self-assembly of diacyllipid–molecular-beacon conjugates (L-MBs; see figure), have been developed for combined mRNA detection and gene therapy. These MBMFs were shown to inhibit a model gene in vitro and decrease the viability of cancer cells in culture.

- Aggregation-Driven Reversible Formation of Conjugated Polymers in Water
  Janeliunas, D.; Van Rijn, P.; Boekhoven, J.; Minkenberg, C. B.; Van Esch, J. H.; Eelkema, R. *Angew. Chem. Int. Ed.* **2013**, *7*, 1998-2001.
  Abstract:



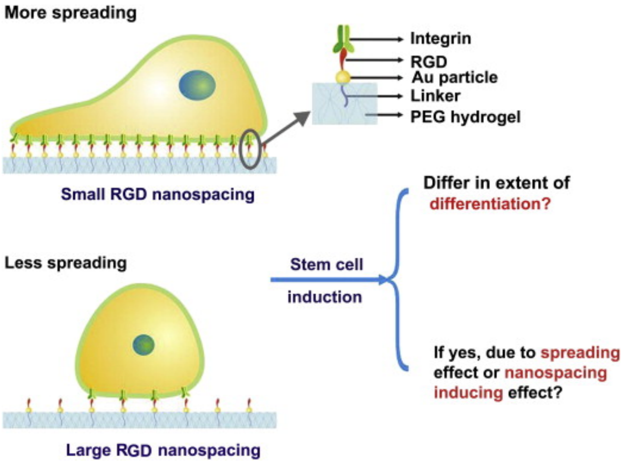
Come together: Self-assembly can drive the formation of conjugated imine polymers in water, and stabilization of otherwise unstable imine bonds is used to obtain fully π-conjugated, responsive dynamic covalent polyimines in aqueous environments. Both the optical properties and the aggregate morphology can be tuned by varying the aromatic monomers.

- Self-Healing Mussel-Inspired Multi-pH-Responsive Hydrogels
  Krogsgaard, M.; Behrens, M. A.; Pedersen, J. S.; Birkedal, H. *Biomacromolecules* **2013**, *14*, 297-301.
  Abstract:



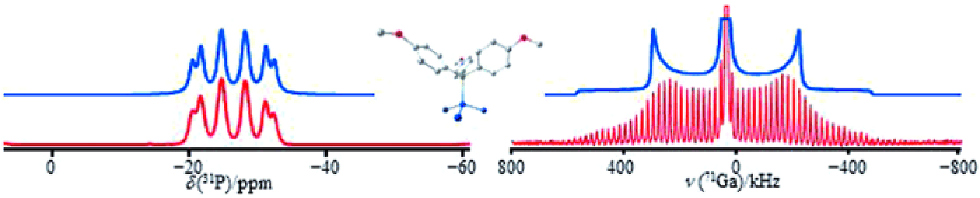
Self-healing hydrogels can be made using either reversible covalent cross-links or coordination chemistry bonds. Here we present a multi-pH-responsive system inspired by the chemistry of blue mussel adhesive proteins. By attaching DOPA to an amine-functionalized polymer, a multiresponsive system is formed upon reaction with iron. The degree of polymer cross-linking is pH controlled through the pH-dependent DOPA/iron coordination chemistry. This leads to the formation of rapidly self-healing high-strength hydrogels when pH is raised from acidic toward basic values. Close to the pK_a value, or more precisely the pI value, of the polymer, the gel collapses due to reduced repulsion between polymer chains. Thereby a bistable gel-system is obtained. The present polymer system more closely resembles mussel adhesive proteins than those previously reported and thus also serves as a model system for mussel adhesive chemistry.

- Effect of RGD nanospacing on differentiation of stem cells
  Wang, X.; Yan, C.; Ye, K.; He, Y.; Li, Z.; Ding, J. *Biomaterials* **2013**, *34*, 2865-2874.
  Abstract:



Nanopatterns of a cell-adhesive peptide arginine–glycine–aspartate (RGD) on a persistently non-fouling poly(ethylene glycol) hydrogel were prepared, and behaviours of mesenchymal stem cells (MSCs) on patterns of five RGD nanospacings from 37 to 124 nm were examined under a full level of serum for eight days. Besides cell adhesion, osteogenic and adipogenic inductions of MSCs from rat bone marrow were observed in corresponding media. We not only confirmed the nanospacing dependence of cell spreading previously reported in other cell types (non-stem cells) such as less spreading in the case of nanospacings larger than the critical 70 nm, but also found the effect of RGD nanospacing on lineage commitments of stem cells. Both osteogenic and adipogenic inductions resulted in higher differentiation extents on patterns of large nanospacings than of small nanospacings. Under co-induction in the mixed osteogenic/adipogenic media, osteogenesis was predominant over adipogenesis on patterns of large RGD nanospacings, although a less cell spreading itself was beneficial not for osteogenesis but for adipogenesis according to previous studies without nanopatterns. The effect of RGD nanospacing on lineage commitments of stem cells is unexpected and cannot be interpreted via the cell spreading effect. Thus, the differentiation of stem cells might be regulated inherently by nanospacing of bioactive ligands on the material surfaces.

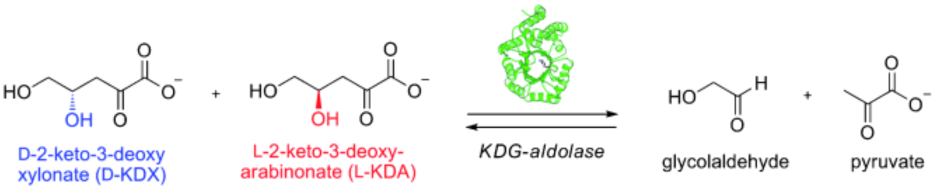
- An Investigation of 1:1 Adducts of Gallium Trihalides with Triarylphosphines by Solid-State $^{69/71}$Ga and ^{31}P NMR Spectroscopy
  Chen, F.; Ma, G.; Bernard, G. M.; Wasylishen, R. E.; Cavell, R. G.; McDonald, R.; Ferguson, M. J.
  Chem. Eur. J. **2013**, *19*, 2826–2838.
  Abstract:



Several 1:1 adducts of gallium trihalides with triarylphosphines, $X_3Ga(PR_3)$ (X=Cl, Br, and I; PR_3=triarylphosphine ligand), were investigated by using solid-state $^{69/71}$Ga and ^{31}P NMR spectroscopy at different magnetic-field strengths. The $^{69/71}$Ga nuclear quadrupolar coupling parameters, as well as the gallium and phosphorus magnetic shielding tensors, were determined. The magnitude of the ^{71}Ga quadrupolar coupling constants ($C_Q(^{71}Ga)$) range from approximately 0.9 to 11.0 MHz. The spans of the gallium magnetic shielding tensors for these complexes, δ_{11}–δ_{33}, range from approximately 30 to 380 ppm; those determined for phosphorus range from 10 to 40 ppm. For any given phosphine ligand, the gallium nuclei are most shielded for X=I and least shielded for X=Cl, a trend previously observed

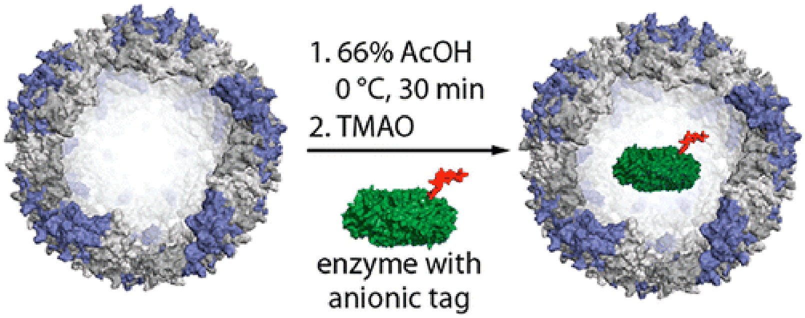
for $\mathrm{In^{III}}$–phosphine complexes. This experimental trend, attributed to spin-orbit effects of the halogen ligands, is reproduced by DFT calculations. The signs of $C_Q(^{69/71}\mathrm{Ga})$ for some of the adducts were determined from the analysis of the ^{31}P NMR spectra acquired with magic angle spinning (MAS). The $^{1}J(^{69/71}\mathrm{Ga},^{31}\mathrm{P})$ and $\Delta J(^{69/71}\mathrm{Ga}, ^{31}\mathrm{P})$ values, as well as their signs, were also determined; values of $^{1}J(^{71}\mathrm{Ga},^{31}\mathrm{P})$ range from approximately 380 to 1590 Hz. Values of $^{1}J(^{69/71}\mathrm{Ga},^{31}\mathrm{P})$ and $\Delta J(^{69/71}\mathrm{Ga},^{31}\mathrm{P})$ calculated by using DFT have comparable magnitudes and generally reproduce experimental trends. Both the Fermi-contact and spin-dipolar Fermi-contact mechanisms make important contributions to the $^{1}J(^{69/71}\mathrm{Ga},^{31}\mathrm{P})$ tensors. The ^{31}P NMR spectra of several adducts in solution, obtained as a function of temperature, are contrasted with those obtained in the solid state. Finally, to complement the analysis of NMR spectra for these adducts, single-crystal X-ray diffraction data for $\mathrm{Br_3Ga[P(}p\mathrm{\text{-}Anis)_3]}$ and $\mathrm{I_3Ga[P(}p\mathrm{\text{-}Anis)_3]}$ were obtained.

- Syntheses of 2-Keto-3-deoxy-D-xylonate and 2-Keto-3-deoxy-L-arabinonate as Stereochemical Probes for Demonstrating the Metabolic Promiscuity of *Sulfolobus solfataricus* Towards D-Xylose and L-Arabinose
  Archer, R. M.; Royer, S. F.; Mahy, W.; Winn, C. L.; Danson, M. J.; Bull, S. D. *Chem. Eur. J.* **2013**, *19*, 2895–2902.
  Abstract:



Practical syntheses of 2-keto-3-deoxy-D-xylonate (D-KDX) and 2-keto-3-deoxy-L-arabinonate (L-KDA) that rely on reaction of the anion of ethyl 2-[(*tert*-butyldimethylsilyl)oxy]-2-(dimethoxy phosphoryl) acetate with enantiopure glyceraldehyde acetonide, followed by global deprotection of the resultant *O*-silyl-enol esters, have been developed. This has enabled us to confirm that a 2-keto-3-deoxy-D-gluconate aldolase from the archaeon *Sulfolobus solfataricus* demonstrates good activity for catalysis of the retro-aldol cleavage of both these enantiomers to afford pyruvate and glycolaldehyde. The stereochemical promiscuity of this aldolase towards these enantiomeric aldol substrates confirms that this organism employs a metabolically promiscuous pathway to catabolise the C5-sugars D-xylose and L-arabinose.

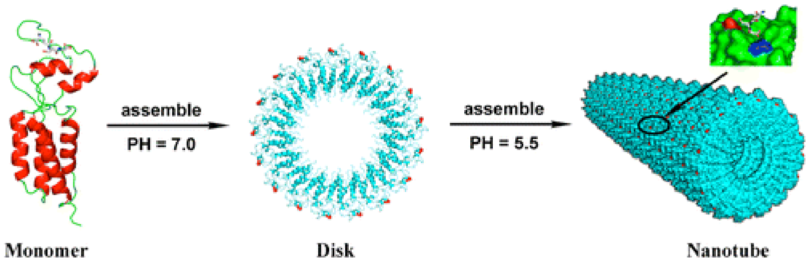
- Osmolyte-Mediated Encapsulation of Proteins inside MS2 Viral Capsids
  Glasgow, J. E.; Capehart, S. L.; Francis, M. B.; Tullman-Ercek, D. *ACS Nano* **2012**, *6*, 8658-8664.
  Abstract:



The encapsulation of enzymes in nanometer-sized compartments has the potential to enhance and control enzymatic activity, both in vivo and in vitro. Despite this potential, there is little quantitative

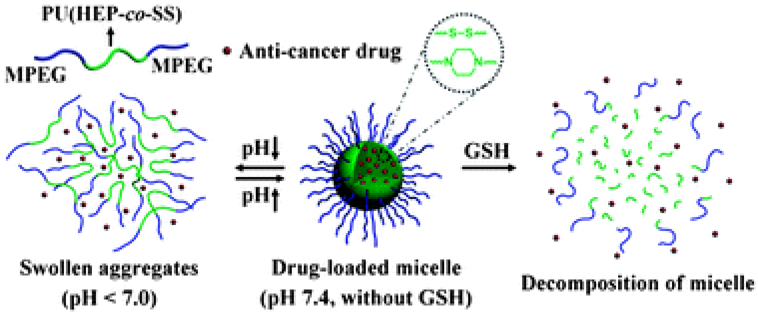
data on the effect of encapsulation in a well-defined compartment under varying conditions. To gain more insight into these effects, we have characterized two improved methods for the encapsulation of heterologous molecules inside bacteriophage MS2 viral capsids. First, attaching DNA oligomers to a molecule of interest and incubating it with MS2 coat protein dimers yielded reassembled capsids that packaged the tagged molecules. The addition of a protein-stabilizing osmolyte, trimethylamine-N-oxide, significantly increased the yields of reassembly. Second, we found that expressed proteins with genetically encoded negatively charged peptide tags could also induce capsid reassembly, resulting in high yields of reassembled capsids containing the protein. This second method was used to encapsulate alkaline phosphatase tagged with a 16 amino acid peptide. The purified encapsulated enzyme was found to have the same Km value and a slightly lower kcat value than the free enzyme, indicating that this method of encapsulation had a minimal effect on enzyme kinetics. This method provides a practical and potentially scalable way of studying the complex effects of encapsulating enzymes in protein-based compartments.

- Construction of GPx Active Centers on Natural Protein Nanodisk/Nanotube: A New Way to Develop Artificial Nanoenzyme
  Hou, C.; Luo, Q.; Liu, J.; Miao, L.; Zhang, C.; Gao, Y.; Zhang, X.; Xu, J.; Dong, Z.; Liu, J. *ACS Nano* **2012**, *6*, 8692-8701.
  Abstract:



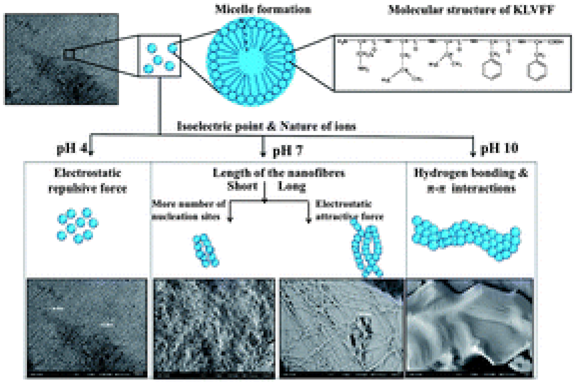
Construction of catalytic centers on natural protein aggregates is a challenging topic in biomaterial and biomedicine research. Here we report a novel construction of artificial nanoenzyme with glutathione peroxidase (GPx)-like function. By engineering the surface of tobacco mosaic virus (TMV) coat protein, the main catalytic components of GPx were fabricated on TMV protein monomers. Through direct self-assembly of the functionalized viral coat proteins, the multi-GPx centers were installed on these well-defined nanodisks or nanotubes. With the help of muti-selenoenzyme centers, the resulting organized nanoenzyme exhibited remarkable GPx activity, even approaching the level of natural GPx. The antioxidation study on subcell mitochondrial level demonstrated that virus-based nanoenzyme exerted excellent capacity for protecting cell from oxidative damage. This strategy represents a new way to develop artificial nanoenzymes.

- pH and reduction dual responsive polyurethane triblock copolymers for efficient intracellular drug delivery
  Yu, S.; He, C.; Ding, J.; Cheng, Y.; Song, W.; Zhuang, X.; Chen, X. *Soft Matter* **2013, ***9*, 2637-2645.
  Abstract:



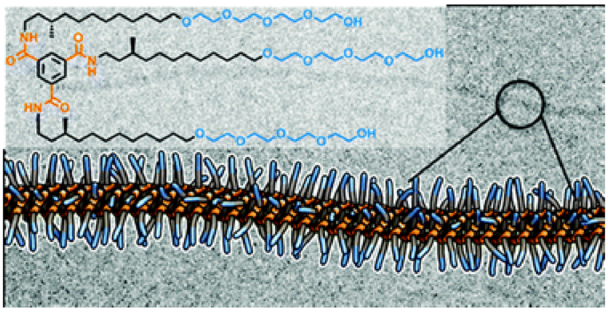
A series of pH/reduction dual responsive poly(ethylene glycol)/polyurethane triblock copolymers containing tertiary amines and disulfide bonds are reported. The polyurethane block copolymers self-assembled into stable micelles in aqueous medium at pH 7.4, which responded rapidly to both a narrow pH change within the physiologically relevant pH range and a reduction environment mimicking the intracellular space. The *in vitro* drug release from doxorubicin (DOX)-loaded polyurethane micelles was significantly accelerated by reducing the pH or by addition of an intracellular reducing agent, glutathione (GSH). Confocal laser scanning microscopy (CLSM) and flow cytometry measurements revealed that the intracellular drug release from the DOX-loaded nanoparticles was increased in the HeLa cells with enhanced intracellular GSH level. In addition, even though the polyurethane block copolymers exhibited good cytocompatibility, the DOX-loaded polyurethane micelles displayed efficient growth inhibition of HeLa and HepG2 cells, which showed a dependence on the intracellular GSH concentration. Owing to their unique responsiveness to dual biological stimuli, the biocompatible and bioreducible polyurethane block copolymers have the potential to serve as a versatile platform for intracellular drug delivery.

- Hierarchical self-assembly of Tjernberg peptide at nanoscale
  Kumaraswamy, P.; Sethuraman, S.; Krishnan, U. M. *Soft Matter* **2013,** *9*, 2684-2694.
  Abstract:



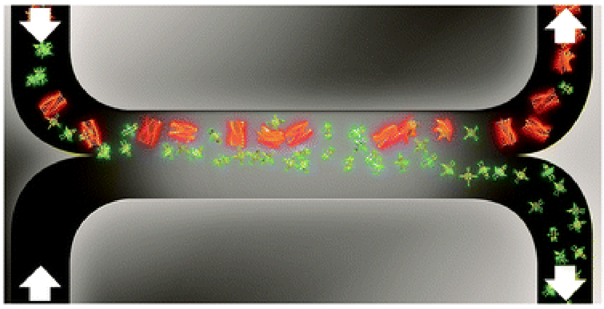
Molecular self-assembly of biomolecules, especially proteins and peptides has elucidated much interest in recent years due to the reproducibility of structures and the high degree of control on the formation kinetics and morphology by varying the self-assembling conditions. These self-assembled structures have found widespread applications in tissue engineering, drug delivery and electronics. Two pentapeptides, namely Soto peptide (LPFFD) and the Tjernberg peptide (KLVFF), have been proposed to effectively curtail amyloid plaque deposits. Being amphipathic, these molecules can undergo self-assembly that can be influenced by a host of factors including concentration, pH, proteins, salt content, *etc.* However, this facet is scarcely explored till date, which might pave way for the novel treatment strategy for Alzheimer's disease. Our data show that the peptide spontaneously forms micelles and they are rich in beta sheet structures, which is confirmed using FT-IR, SAED and thioflavin binding studies. While, acidic pH seems to have no role in the formation of higher order structures, alkaline pH promotes longitudinal and lateral stacking interactions resulting in formation of higher order structures. We also found that the hydrophobicity and hydrophilicity of the substrate also play a major role in the formation of higher order structures. Moreover, the micelles formed by the KLVFF peptide under various environmental conditions exhibits excellent surface tension lowering effects which is in good agreement with the cell proliferation data that showed the protective ability of KLVFF peptide against Aβ$_{1-42}$ cytotoxicity indicating its potential in Alzheimer's disease therapy as an aggregation blocking agent.

- Supramolecular polymerization in water harnessing both hydrophobic effects and hydrogen bond formation
  Leenders, C. M. A.; Albertazzi, L.; Mes, T.; Koenigs, M.; Palmans, A. R. A.; Meijer, E. W. *Chem. Commun*. **2013**, *49*, 1963-1965.
  Abstract:



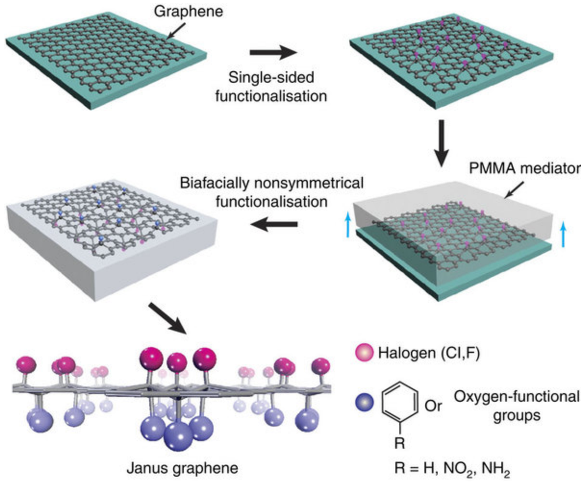
The formation of supramolecular polymers in water through rational design of a benzene-1,3,5-tricarboxamide (BTA) motif is presented. Intermolecular hydrogen bonding and hydrophobic effects cooperate in the self-assembly into long fibrillar aggregates. Minimal changes in molecular structure significantly affect the internal packing of the aggregates.

- Controlled perturbation of the thermodynamic equilibrium by microfluidic separation of porphyrin-based aggregates in a multi-component self-assembling system
  Helmich, F.; Meijer, E. W. *Chem. Commun.* **2013**, *49*, 1796-1798.
  Abstract:



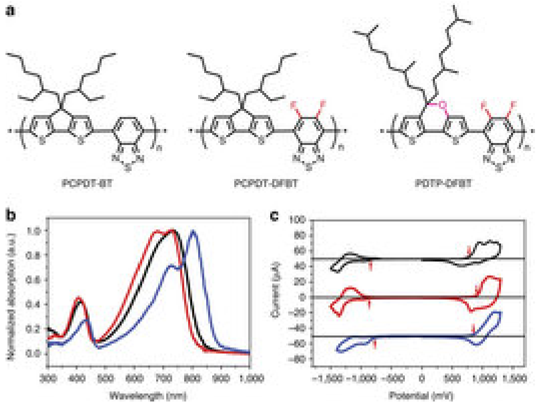
In a microfluidic H-cell, a multi-component self-assembled system is brought out-of-equilibrium by changing the bimodal composition of porphyrin stacks and pyridine-capped dimers. Driven by their different diffusivities, diffusion-controlled separation in methylcyclohexane reveals different compositions when detected in-line and off-line, which demonstrates the kinetic behaviour of this metastable system. The microfluidic technique also proves to be highly equipped to determine diffusion constants of the different assemblies.

- Janus graphene from asymmetric two-dimensional chemistry
  Zhang, L.; Yu, J.; Yang, M.; Xie, Q.; Peng, H.; Liu, Z. *Nature Communications* **2013**, *4*, 1443.
  Abstract:



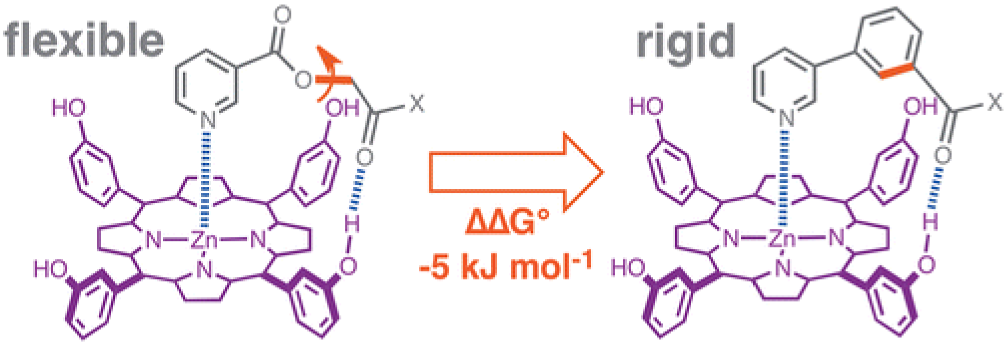
Janus materials have distinct surfaces on their opposite faces. Graphene, a two-dimensional giant molecule, provides an excellent candidate to fabricate the thinnest Janus discs and study the asymmetric chemistry of atomic-thick nanomembranes using covalent chemical functionalisation. Here we present the first experimental realisation of nonsymmetrically modified single-layer graphene—Janus graphene—which is fabricated by a two-step surface covalent functionalisation assisted by a poly(methyl methacrylate)-mediated transfer approach. Four types of Janus graphene are produced by co-grafting of halogen and aryl/oxygen-functional groups on each side. Chemical decorations on one side are found to be capable of affecting both chemical reactivity and physical wettability of the opposite side, indicative of communication between the two grafted groups. This novel asymmetric structure provides a platform for theoretical and experimental studies of two-dimensional chemistry and graphene devices with multiple functions.

- A polymer tandem solar cell with 10.6% power conversion efficiency
  You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. *Nature Communications* **2013**, *4*, 1446.
  Abstract:



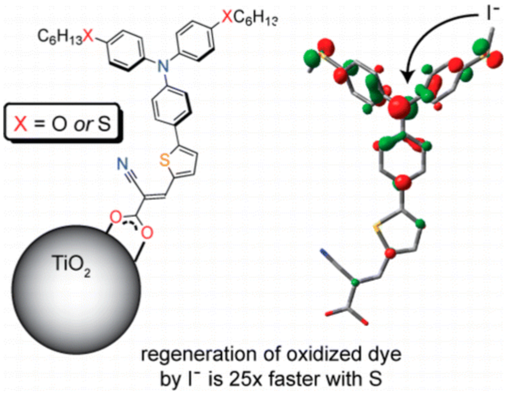
An effective way to improve polymer solar cell efficiency is to use a tandem structure, as a broader part of the spectrum of solar radiation is used and the thermalization loss of photon energy is minimized. In the past, the lack of high-performance low-bandgap polymers was the major limiting factor for achieving high-performance tandem solar cell. Here we report the development of a high-performance low bandgap polymer (bandgap <1.4eV), poly[2,7-(5,5-bis-(3,7-dimethyloctyl)-5H-dithieno[3,2-b:2′,3′-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothia diazole)] with a bandgap of 1.38eV, high mobility, deep highest occupied molecular orbital. As a result, a single-junction device shows high external quantum efficiency of >60% and spectral response that extends to 900nm, with a power conversion efficiency of 7.9%. The polymer enables a solution processed tandem solar cell with certified 10.6% power conversion efficiency under standard reporting conditions (25°C, 1,000Wm^{-2}, IEC 60904-3 global), which is the first certified polymer solar cell efficiency over 10%.

- Quantification of the Effect of Conformational Restriction on Supramolecular Effective Molarities
  Adams, H.; Chekmeneva, E.; Hunter, C. A.; Misuraca, M. C.; Navarro, C.; Turega, S. M. *J. Am. Chem. Soc.* **2013***, 135,* 1853–1863.
  Abstract:



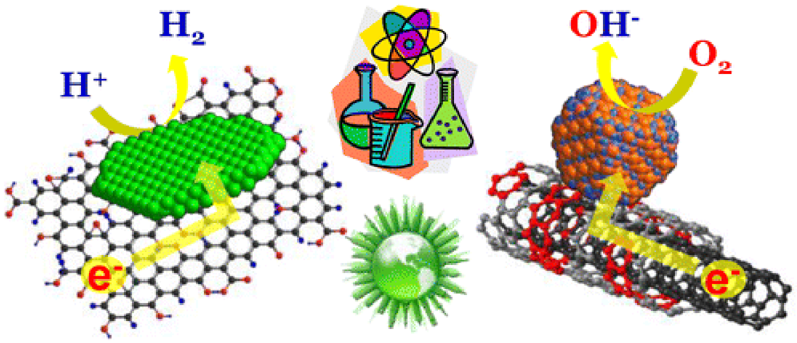
The association constants for a family of 96 closely related zinc porphyrin–pyridine ligand complexes have been measured in two different solvents, toluene and 1,1,2,2-tetrachloroethane (TCE). The zinc porphyrin receptors are equipped with phenol side arms, which can form intramolecular H-bonds with ester or amide side arms on the pyridine ligands. These association constants were used to construct 64 chemical double mutant cycles, which measure the free energy contributions of intramolecular H-bonding interactions to the overall stability of the complexes. Measurement of association constants for the corresponding intermolecular H-bonding interactions allowed determination of the effective molarities (EM) for the intramolecular interactions. Comparison of ligands that feature amide H-bond acceptors and ester H-bonds at identical sites on the ligand framework show that the values of EM are practically identical. Similarly, the values of EM are practically identical in toluene and in TCE. However, comparison of two ligand series that differ by one degree of torsional freedom shows that the values of EM for the flexible ligands are an order of magnitude lower than for the corresponding rigid ligands. This observation holds for a range of different supramolecular architectures with different degrees of receptor–ligand complementarity and suggests that in general the cost of freezing a rotor in supramolecular complexes is of the order of 5 kJ/mol.

- Atomic Level Resolution of Dye Regeneration in the Dye-Sensitized Solar Cell
  Robson, K. C. D.; Hu, K.; Meyer, G. J.; Berlinguette, C. P. *J. Am. Chem. Soc.* **2013***, 135,* 1961–1971.
  Abstract:



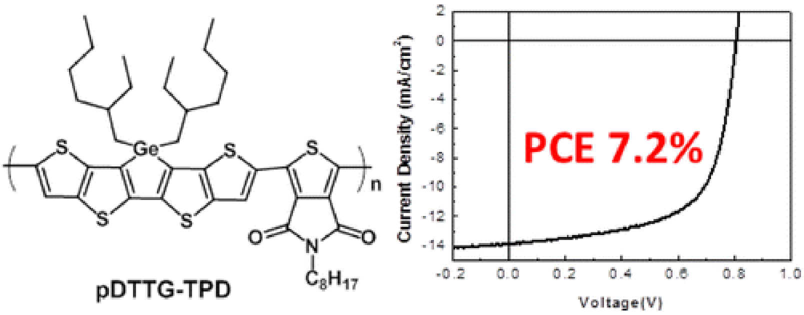
Two donor–acceptor organic dyes have been synthesized that differ only by a two-heteroatom change from oxygen to sulfur within the donor unit. The two dyes, (*E*)-3-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (**Dye-O**) and (*E*)-3-(5-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid) (**Dye-S**), were tested in solar cell devices employing both I_3^-/I^--based and $[Co(bpy)_3]^{3+/2+}$ redox mediators. Power conversion efficiencies over 6% under simulated AM 1.5 illumination (1 Sun) were achieved in both electrolytes. Despite similar optical and redox properties for the two dyes, a consistently higher open-circuit voltage (V_{oc}) was measured for **Dye-S** relative to **Dye-O**. The improved efficiency observed with **Dye-S** in an iodide redox mediator is against the commonly held view that sulfur atoms promote charge recombination attributed to inner-sphere interactions. Detailed mechanistic studies revealed that this is a consequence of a 25-fold enhancement of the regeneration rate constant that enhances the regeneration yield under open circuit conditions. The data show that a high short circuit photocurrent does not imply optimal regeneration efficiency as is often assumed.

- Strongly Coupled Inorganic/Nanocarbon Hybrid Materials for Advanced Electrocatalysis
  Liang, Y.; Li, Y.; Wang, H.; Dai, H. *J. Am. Chem. Soc.* **2013**, *135*, 2013–2036.
  Abstract:



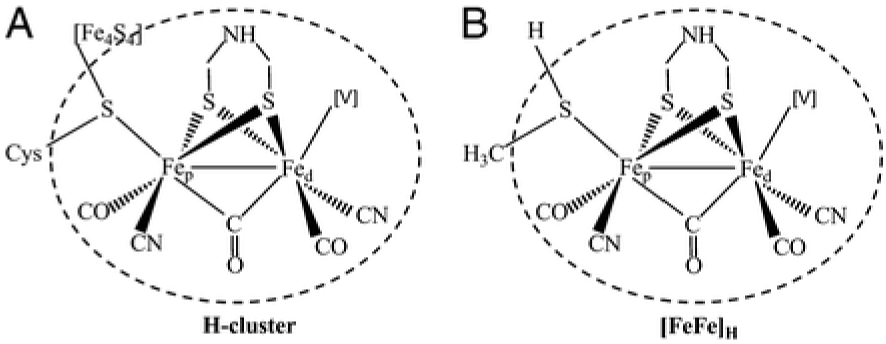
Electrochemical systems, such as fuel cell and water splitting devices, represent some of the most efficient and environmentally friendly technologies for energy conversion and storage. Electrocatalysts play key roles in the chemical processes but often limit the performance of the entire systems due to insufficient activity, lifetime, or high cost. It has been a long-standing challenge to develop efficient and durable electrocatalysts at low cost. In this Perspective, we present our recent efforts in developing strongly coupled inorganic/nanocarbon hybrid materials to improve the electrocatalytic activities and stability of inorganic metal oxides, hydroxides, sulfides, and metal–nitrogen complexes. The hybrid materials are synthesized by direct nucleation, growth, and anchoring of inorganic nanomaterials on the functional groups of oxidized nanocarbon substrates including graphene and carbon nanotubes. This approach affords strong chemical attachment and electrical coupling between the electrocatalytic nanoparticles and nanocarbon, leading to nonprecious metal-based electrocatalysts with improved activity and durability for the oxygen reduction reaction for fuel cells and chlor-alkali catalysis, oxygen evolution reaction, and hydrogen evolution reaction. X-ray absorption near-edge structure and scanning transmission electron microscopy are employed to characterize the hybrids materials and reveal the coupling effects between inorganic nanomaterials and nanocarbon substrates. Z-contrast imaging and electron energy loss spectroscopy at single atom level are performed to investigate the nature of catalytic sites on ultrathin graphene sheets. Nanocarbon-based hybrid materials may present new opportunities for the development of electrocatalysts meeting the requirements of activity, durability, and cost for large-scale electrochemical applications.

- Fused Dithienogermolodithiophene Low Band Gap Polymers for High-Performance Organic Solar Cells without Processing Additives
  Zhong, H.; Li, Z.; Deledalle, F.; Collado Fregoso, E.; Shahid, M.; Fei, Z.; Nielsen, C. B.; Yaacobi-Gross, N.; Rossbauer, S.; Anthopoulos, T. D.; Durrant, J. R.; Heeney, M. *J. Am. Chem. Soc.* **2013**, *135*, 2040–2043.
  Abstract:



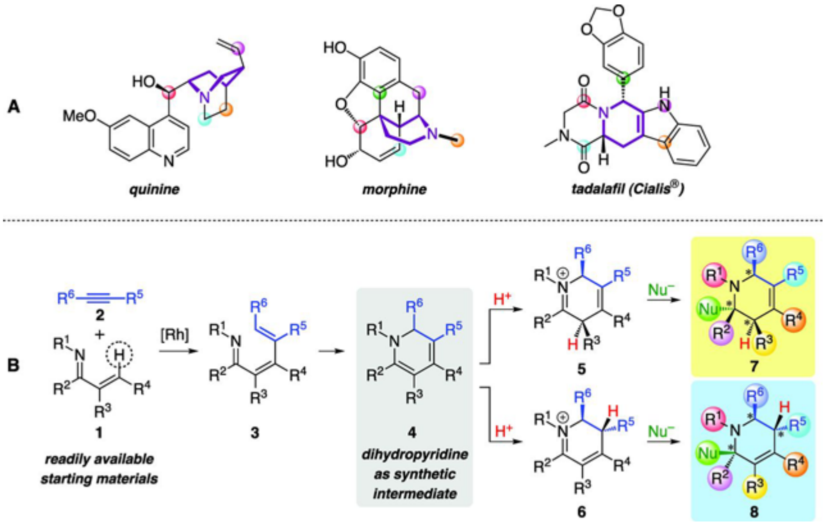
We report the synthesis of a novel ladder-type fused ring donor, dithienogermolodithiophene, in which two thieno[3,2-*b*]thiophene units are held coplanar by a bridging dialkyl germanium. Polymerization of this extended monomer with *N*-octylthienopyrrolodione by Stille polycondensation afforded a polymer, **pDTTG-TPD**, with an optical band gap of 1.75 eV combined with a high ionization potential. Bulk heterojunction solar cells based upon **pDTTG-TPD**:$PC_{71}BM$ blends afforded efficiencies up to 7.2% without the need for thermal annealing or processing additives.

- Oxygen tolerance of an *in silico*-designed bioinspired hydrogen-evolving catalyst in water
  Sit, P. H.-L.; Car, R.; Cohen, M. H.; Selloni, A. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 2017-2022.
  Abstract:



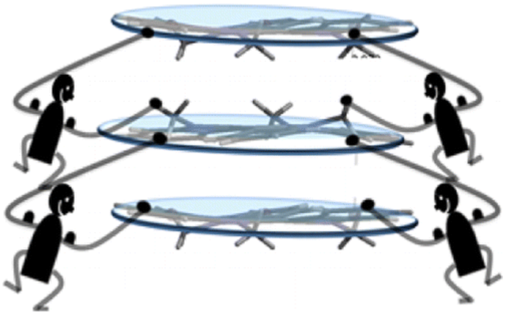
Certain bacterial enzymes, the diiron hydrogenases, have turnover numbers for hydrogen production from water as large as 10^4/s. Their much smaller common active site, composed of earth-abundant materials, has a structure that is an attractive starting point for the design of a practical catalyst for electrocatalytic or solar photocatalytic hydrogen production from water. In earlier work, our group has reported the computational design of $[FeFe]_P/FeS_2$, a hydrogenase-inspired catalyst/electrode complex, which is efficient and stable throughout the production cycle. However, the diiron hydrogenases are highly sensitive to ambient oxygen by a mechanism not yet understood in detail. An issue critical for practical use of $[FeFe]_P/FeS_2$ is whether this catalyst/electrode complex is tolerant to the ambient oxygen. We report demonstration by ab initio simulations that the complex is indeed tolerant to dissolved oxygen over timescales long enough for practical application, reducing it efficiently. This promising hydrogen-producing catalyst, composed of earth-abundant materials and with a diffusion-limited rate in acidified water, is efficient as well as oxygen tolerant.

- Proton Donor Acidity Controls Selectivity in Nonaromatic Nitrogen Heterocycle Synthesis
  Duttwyler, S.; Chen, S.; Takase, M. K.; Wiberg, K. B.; Bergman, R. G.; Ellman, J. A. *Science* 2013, *339*, 678-682.
  <u>Abstract:</u>



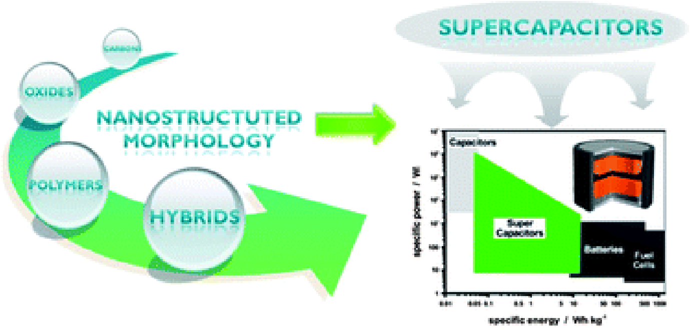
Piperidines are prevalent in natural products and pharmaceutical agents and are important synthetic targets for drug discovery and development. We report on a methodology that provides highly substituted piperidine derivatives with regiochemistry selectively tunable by varying the strength of acid used in the reaction. Readily available starting materials are first converted to dihydropyridines via a cascade reaction initiated by rhodium-catalyzed carbon-hydrogen bond activation. Subsequent divergent regio- and diastereoselective protonation of the dihydropyridines under either kinetic or thermodynamic control provides two distinct iminium ion intermediates that then undergo highly diastereoselective nucleophilic additions. X-ray structural characterization of both the kinetically and thermodynamically favored iminium ions along with density functional theory calculations provide a theoretical underpinning for the high selectivities achieved for the reaction sequences.

- High Hole Mobility in Triindole-Based Columnar phases: Removing the Bottleneck of Homogeneous Macroscopic Orientation
  Benito-Hernández, A.; Pandey, U. K.; Cavero, E.; Termine, R.; García-Frutos, E. M.; Serrano, J. L.; Golemme, A.; Gómez-Lor, B. *Chem. Mater.* **2013**, *25*, 117-121.
  <u>Abstract:</u>



We report the synthesis, mesomorphic behavior, and mobility values of a series of highly ordered *N*-substituted triindole-based columnar liquid crystals. Shortening the length of *N*-alkylic substituents from *N*-dodecyl to *N*-methyl chains results in a drastic approach of the disks within the columns and in an impressive increase in charge carrier mobility. An study of aggregation in solution provide insights into the intermolecular forces responsible of the reduction of the intrastack distance as the size of the *N*-alkyl chains is decreased and offer evidence of stabilization of the columns by the contribution of cooperative CH−π interactions. The materials presented here exhibit mobility values, even in totally misaligned columnar phases, that may compete with those of the best polycrystalline organic semiconductors, without the need of costly vacuum evaporation processes.

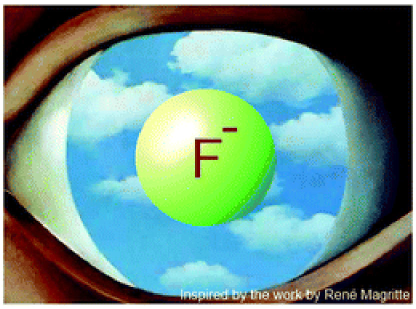
- Nanostructured morphology control for efficient supercapacitor electrodes
  Chen, S.; Xing, W.; Duan, J.; Hu, X.; Zhang Qiao, S. *J. Mater. Chem. A* **2013**, *1*, 2941-2954.
  Abstract:



The fast growing interest in portable electronic devices and electric vehicles has stimulated extensive research in high performance energy storage devices, such as supercapacitors. Nanostructured electrodes can achieve high electrochemical performances in supercapacitors owing to their high surface atom ratio, tuneable texture and unique size-dependent properties that can afford effective electrolyte diffusion and improved charge transportation and storage during charging–discharging. This review reports on the recent progress in designing and fabricating different kinds of nanostructured electrodes, including electrical double layer based electrodes such as porous carbons and graphene, and Faradic reaction based electrodes such as metal oxides/hydroxides and conductive polymers. Furthermore, the review also summarizes the advances of hybrid electrodes, which store charges by both mechanisms, such as porous carbons–metal oxides/hydroxides, porous carbons–conductive polymers, graphene–metal oxides/hydroxides, and graphene–conductive polymers. Finally, we provide some perspectives as to the future directions of this intriguing field.

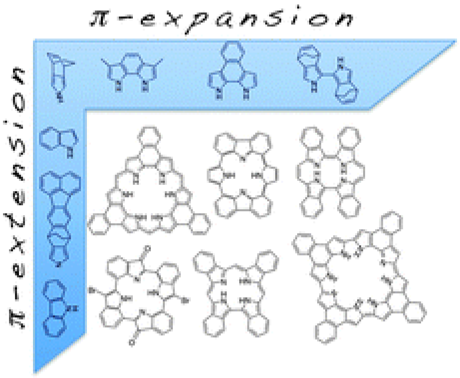
- Highlights on contemporary recognition and sensing of fluoride anion in solution and in the solid state
  Cametti, M.; Rissanen, K. *Chem. Soc. Rev.* **2013**, *42*, 2016-2038.

Abstract:



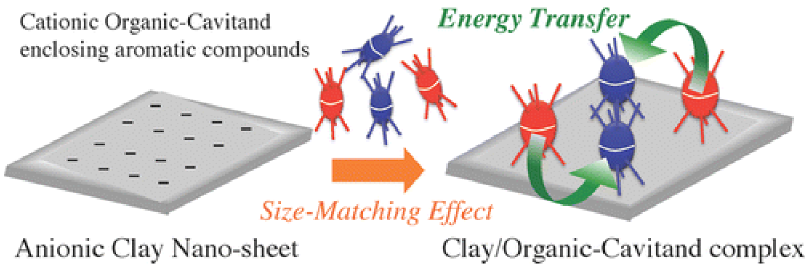
The fluoride anion has recently gained well deserved attention among the scientific community for its importance in many fields of human activities, but also for concerns on its effect on health and the environment. Although surprisingly overlooked in systematic studies in the past, fluoride has nowadays become a topical target in the field of anion recognition. A multitude of scientific reports are published every year where the establishment of efficient and specific interaction with fluoride is sought in polar and aqueous media. Here, the emphasis is directed to a detailed description of the most interesting contemporary studies in the field, with a particular focus given to those published in the last few years.

- π-Extended isomeric and expanded porphyrins
  Roznyatovskiy, V. V.; Lee, C.-H.; Sessler, J. L. *Chem. Soc. Rev.* **2013**, *42*, 1921-1933.
  Abstract:



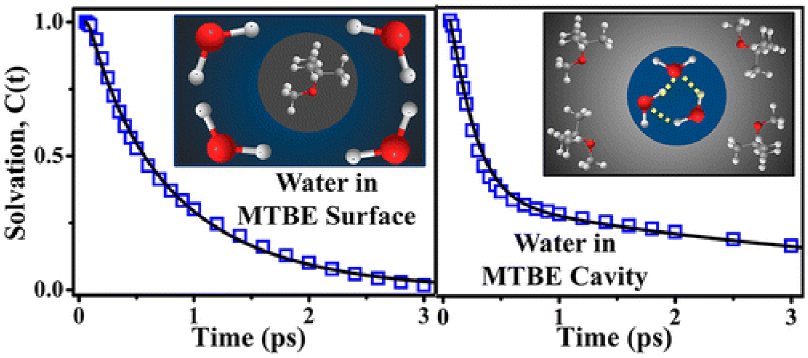
The phenomenon of π-extension has been widely applied to, and exploited within, the field porphyrin chemistry. The development of reliable synthetic routes to various useful starting materials has facilitated the underlying preparative work. The chemical resemblance between porphyrins and expanded and isomeric porphyrins, as well as the increasing accessibility of the requisite starting materials is giving birth to the hybrid field of π-extended expanded and isomeric porphyrins. This tutorial review is intended to provide an overview of up-to-date published synthetic efforts and to summarize the effect of annulation on the properties of expanded and isomeric porphyrins.

- Efficient Singlet–Singlet Energy Transfer in a Novel Host–Guest Assembly Composed of an Organic Cavitand, Aromatic Molecules, and a Clay Nanosheet
  Ishida, Y.; Kulasekharan, R.; Shimada, T.; Takagi, S.; Ramamurthy, V. *Langmuir* **2013**, *29*, 1748–1753.
  Abstract:



A supramolecular host–guest assembly composed of a cationic organic cavitand (host), neutral aromatic molecules (guests), and an anionic clay nanosheet has been prepared and demonstrated that in this arrangement efficient singlet–singlet energy transfer could take place. The novelty of this system is the use of a cationic organic cavitand that enabled neutral organic molecules to be placed on an anionic saponite nanosheet. Efficient singlet–singlet energy transfer between neutral pyrene and 2-acetylanthracene enclosed within a cationic organic cavitand (octa amine) arranged on a saponite nanosheet was demonstrated through steady-state and time-resolved emission studies. The high efficiency was realized from the suppression of aggregation, segregation, and self-fluorescence quenching. We believe that the studies presented here using a novel supramolecular assembly have expanded the types of molecules that could serve as candidates for efficient energy-transfer systems, such as in an artificial light-harvesting system.

- Effect of Hydrophobic Interaction on Structure, Dynamics, and Reactivity of Water
  Rakshit, S.; Saha, R.; Chakraborty, Z.; Pal, S. K. *Langmuir* **2013**, *29*, 1808–1817.
  Abstract:



The effect of hydrophobic interaction on water is still controversial and requires more detailed experimental and theoretical investigation. The interaction between organic–water molecular complexes might be indicative of the perturbation of hydrogen-bond network in the tetrahedral structure of bulk waters, due to hydrophobic effect. In this contribution, femto/picosecond-resolved solvation dynamics techniques have been adopted to explore the dynamical modification of water clusters in hydrophobic solvent methyl tert-butyl ether (MTBE). The dynamical evolution of water molecules at the surface of micelle-like MTBE has also been studied. Dynamic light scattering techniques have been employed to determine the size of the molecular clusters being formed in respective solvents. Fourier transform infrared (FTIR) spectroscopy well measures the changes in O–H vibration frequency of water induced by MTBE. We have also monitored temperature dependent picosecond-resolved solvation dynamics in order to explore the energetics associated with water solvation in bulk MTBE. Using detailed ab initio calculations at the MP2 level, our study attempts to predict the possible structures, energies, and thermochemical parameters of corresponding MTBE–water molecular complexes in more detail. The chemical reactivity of water further confirms the effect of the hydrophobic interaction on water molecules. The results impart an understanding on hydrophobic interaction imposed by a biomolecule on the structure and reactivity of water, significant for the in vivo cellular condition.