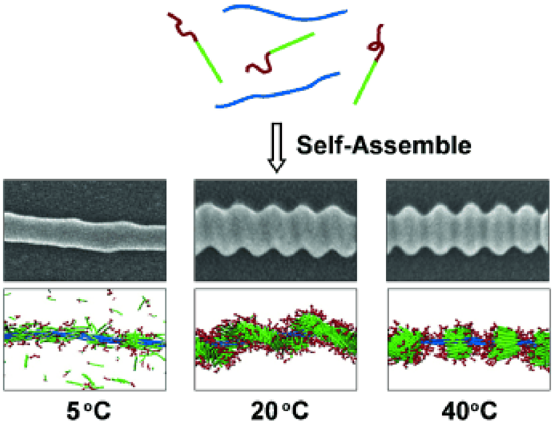
- Self-Assembly of a Supramolecular, Three-Dimensional, Spoked, Bicycle-like Wheel
  Lu, X.; Li, X.; Cao, Y.; Schultz, A.; Wang, J.-L.; Moorefield, C. N.; Wesdemiotis, C.; Cheng, S. Z. D.; Newkome, G. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 7728–7731.
  Abstract:

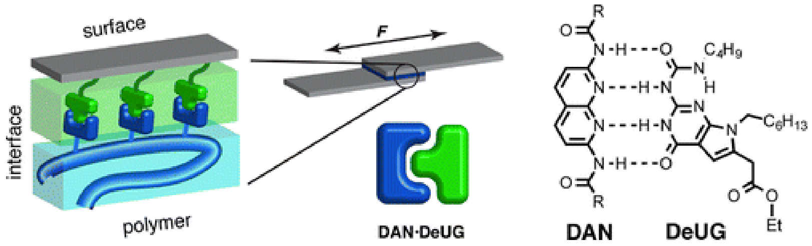
Where there's a wheel, there's a way: The terpyridine-based title system has been synthesized through a facile self-assembly process. Two tris(terpyridine) ligands possessing angles of either 120° or 60° between adjacent tpy units were mixed with a stoichiometric amount of Zn^{2+} (2:6:12) to generate the desired coordination-driven bicycle-like wheel (90 % yield).

- Simulation-Assisted Self-Assembly of Multicomponent Polymers into Hierarchical Assemblies with Varied Morphologies
  Cai, C.; Li, Y.; Lin, J.; Wang, L.; Lin, S.; Wang, X.-S.; Jiang, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 7732–7736.
  Abstract:



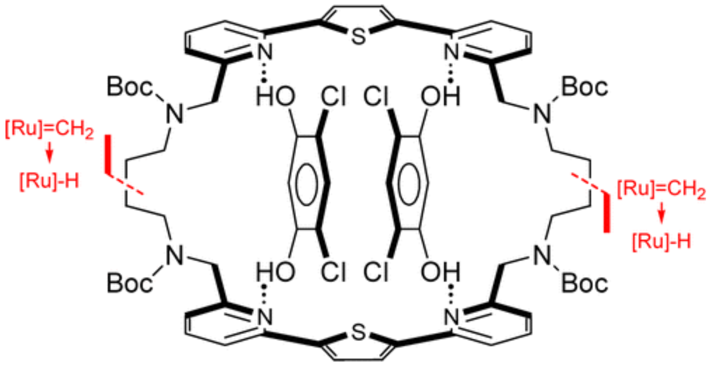
As you like it: The synthesis of supramolecular hierarchical nanostructures with designed morphologies has been realized through computer-simulation-guided multicomponent assembly of polypeptide-based block copolymers and homopolymers. By adjusting the attraction between hydrophobic polypeptide rods, as well as other parameters such as the molar ratio of copolymers and the rigidity of polymers, a variety of morphologies were obtained.

- Quadruply Hydrogen Bonding Modules as Highly Selective Nanoscale Adhesive Agents
  Zhang, Y.; Anderson, C. A.; Zimmerman, S. C. *Org. Lett.* **2013***, 15,* 3506-3509.
  Abstract:



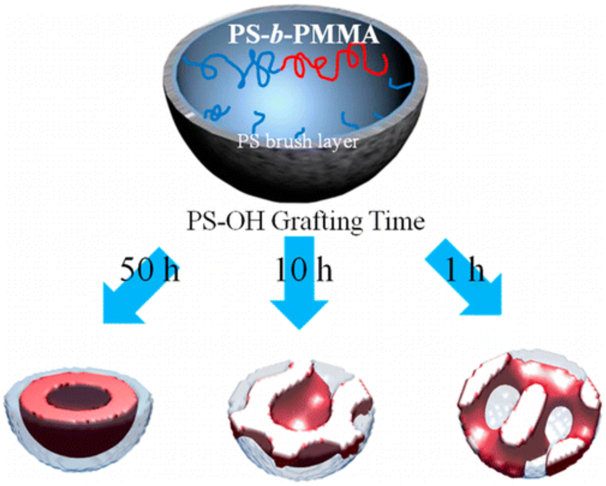
Covalently linking DNA base analogues DAN, DeUG, or UPy to glass slides led to functional surfaces that could be glued together using a functionalized polystyrene displaying the complementary recognition unit. Nonspecific adhesion was minimized with fluorinated alkane (Teflon-like or Scotchgard-like) surfaces.

- Hydrogen Bond Templated 1:1 Macrocyclization through an Olefin Metathesis/Hydrogenation Sequence
  Trita, A. S.; Roisnel, T.; Mongin, F.; Chevallier, F. *Org. Lett.* **2013**, *15,* 3798–3801.
  Abstract:



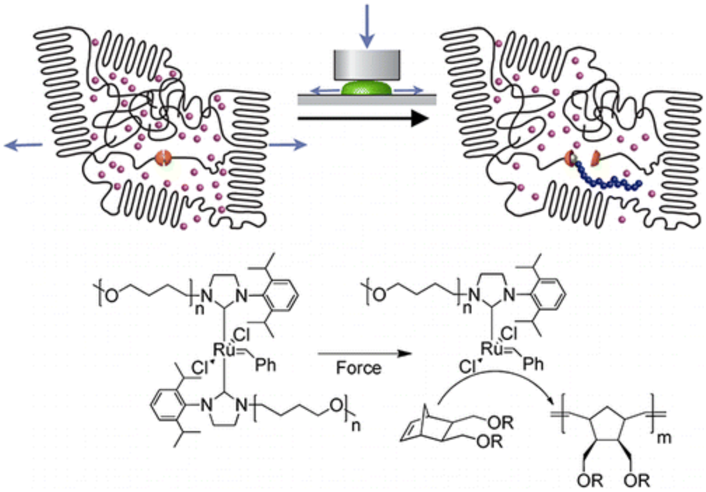
The construction of pyridine-containing macrocyclic architectures using a nonmetallic template is described. 4,6-Dichlororesorcinol was used as an exotemplate to self-organize two aza-heterocyclic units by OH···N hydrogen bonds. Subsequent sequential double olefin metathesis/hydrogenation reactions employing a single rutheniumalkylidene precatalyst open access to macrocyclic molecules.

- Arrangement of Block Copolymer Microdomains Confined inside Hemispherical Cavities
  Bae, D.; Jeon, G.; Jinnai, H.; Huh, J.; Kim, J. K. *Macromolecules* **2013**, *46*, 5301-5307.
  Abstract:



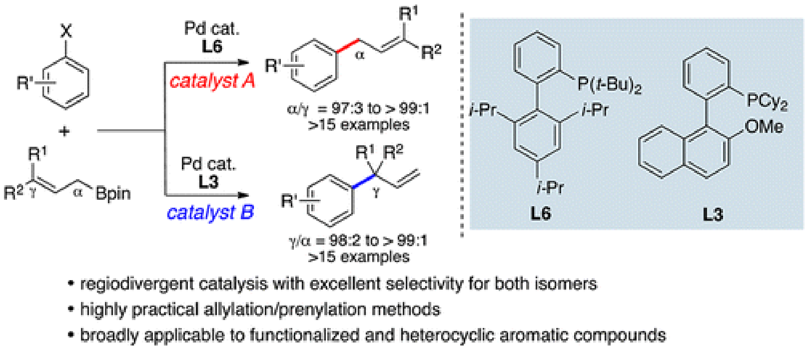
We investigated, via scanning and transmission electron microscopy, the arrangement of the microdomains of symmetric polystyrene-*block*-poly(methyl methacrylate) copolymer (PS-*b*-PMMA) confined in hemispherical cavities. The hemispherical cavities were prepared by using anodic aluminum oxide (AAO) template, where the inner surface of the cavities was modified by thin brush layers of PS, PMMA, and PS-*ran*-PMMA copolymer. When the inner surface of the cavity is strongly selective to PS chains, concentric rings consisting of PS and PMMA microdomains are formed, replicating the confined geometry of hemisphere. However, as the selectivity of a brush to PS chains becomes weaker, various interesting morphologies are formed that have not been reported in the literature. The experimentally observed microdomain arrangement confined inside the hemispherical cavities was compared with the simulation results based on the dynamic Metropolis Monte Carlo method.

- Mechanocatalytic Polymerization and Cross-Linking in a Polymeric Matrix
  Jakobs, R. T. M.; Ma, S.; Sijbesma, R. P. *ACS Macro Lett.* **2013**, *2*, 613-616.
  Abstract:



A latent olefin metathesis catalyst, bearing two polymeric NHC ligands, was embedded in a semicrystalline polymer matrix containing cyclic olefins. The catalyst was activated by straining the solid material under compression, resulting in polymerization and cross-linking reactions of the monomers in situ. Catalyst activation in the solid state may be employed in new self-healing materials.

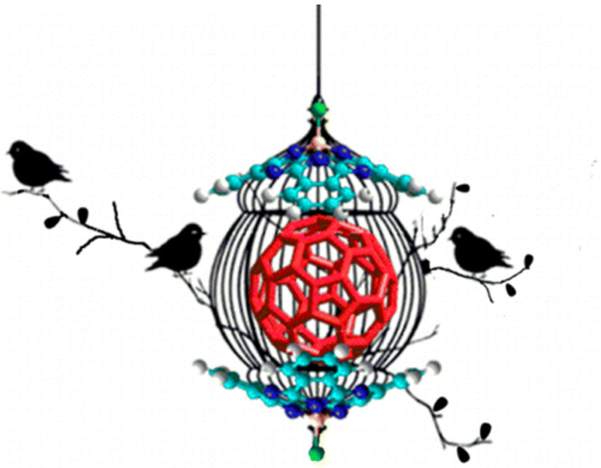
- Ligand-Controlled Palladium-Catalyzed Regiodivergent Suzuki–Miyaura Cross-Coupling of Allylboronates and Aryl Halides
  Yang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2013***, 135*, 10642-10645.
  Abstract:



An orthogonal set of catalyst systems has been developed for the Suzuki–Miyaura coupling of 3,3-

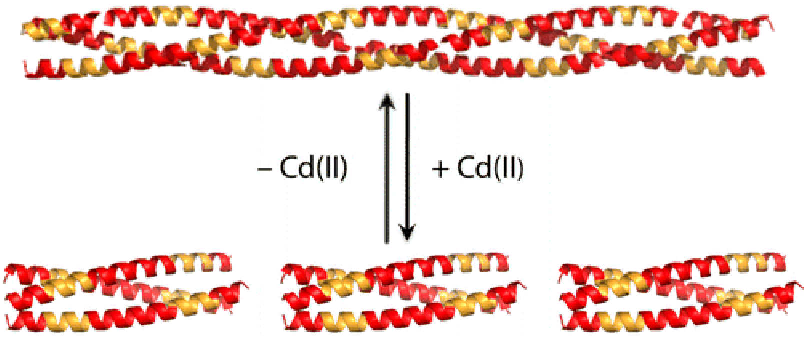
disubstituted and 3-monosubstituted allylboronates with (hetero)aryl halides. These methods allow for the highly selective preparation of either the α- or the γ-isomeric coupling product.

- Self-Assembly, Host–Guest Chemistry, and Photophysical Properties of Subphthalocyanine-Based Metallosupramolecular Capsules
  Sánchez-Molina, I.; Grimm, B.; Krick Calderon, R. M.; Claessens, C. G.; Guldi, D. M.; Torres, T. *J. Am. Chem. Soc.* **2013**, *135*, 10503–10511.
  Abstract:



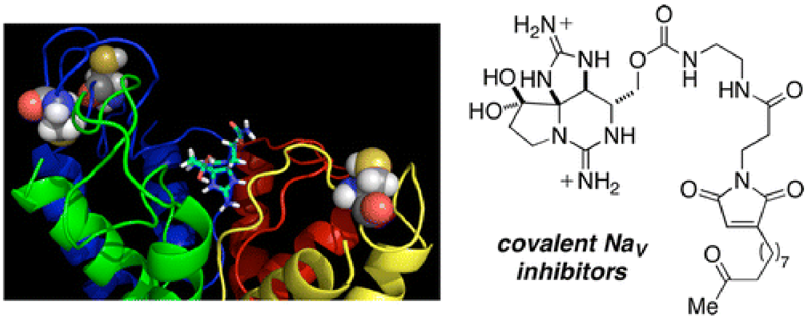
Four new subphthalocyanine-based capsules have been synthesized and characterized. These supramolecular systems have been successfully employed for the encapsulation of fullerenes and probed by a wide range of characterization methods, including NMR, UV–vis and fluorescence spectroscopy, electrospray ionization mass spectrometry, and electrochemistry. Furthermore, the binding constants of the host guest complexes were estimated. Finally, the photophysical properties revealed that the subphthalocyanines undergo a transduction of singlet excited-state energy to the fullerene inside the cavity upon photoexcitation.

- Controlling Self-Assembly of a Peptide-Based Material via Metal-Ion Induced Registry Shift
  Anzini, P.; Xu, C.; Hughes, S.; Magnotti, E.; Jiang, T.; Hemmingsen, L.; Demeler, B.; Conticello, V. P. *J. Am. Chem. Soc.* **2013**, *135*, 10278–10281.
  Abstract:



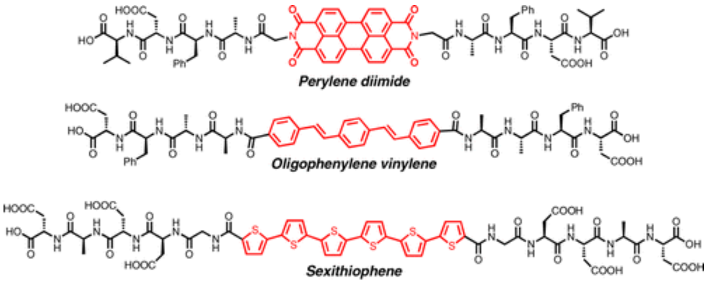
Peptide TZ1C2 can populate two distinct orientations: a staggered (out-of-register) fibril and an aligned (in-register) coiled-coil trimer. The coordination of two cadmium ions induces a registry shift that results in a reversible transition between these structural forms. This process recapitulates the self-assembly mechanism of native protein fibrils in which a ligand binding event gates a reversible conformational transition between alternate forms of a folded peptide structure.

- Maleimide Conjugates of Saxitoxin as Covalent Inhibitors of Voltage-Gated Sodium Channels
  Parsons, W. H.; Du Bois, J. *J. Am. Chem. Soc.* **2013**, *135,* 10582-10585.
  Abstract:



(+)-Saxitoxin, a naturally occurring guanidinium poison, functions as a potent, selective, and reversible inhibitor of voltage-gated sodium ion channels (Na_Vs). Modified forms of this toxin bearing cysteine-reactive maleimide groups are available through total synthesis and are found to irreversibly inhibit sodium ion conductance in recombinantly expressed wild-type sodium channels and in hippocampal nerve cells. Our findings support a mechanism for covalent protein modification in which toxin binding to the channel pore precedes maleimide alkylation of a nucleophilic amino acid. Second-generation maleimide-toxin conjugates, which include bioorthogonal reactive groups, are also found to block channel function irreversibly; such compounds have potential as reagents for selective labeling of Na_Vs for live cell imaging and/or proteomics experiments.

- Supramolecular Construction of Optoelectronic Biomaterials
  Tovar, J. D. *Acc. Chem. Res.* **2013**, *46*, 1527–1537.
  Abstract:



Peptide self-assembly is a powerful method to create functional nanoscale materials such as optoelectronically relevant organic nanostructures. The enormous potential that may come from bringing π-conjugated electronic function into biological environments is poised to impact cell and tissue engineering, biosensors, and related biomedical applications. However, very little synthetic guidance is available with respect to uniting these two different materials sets in a generally applicable manner.

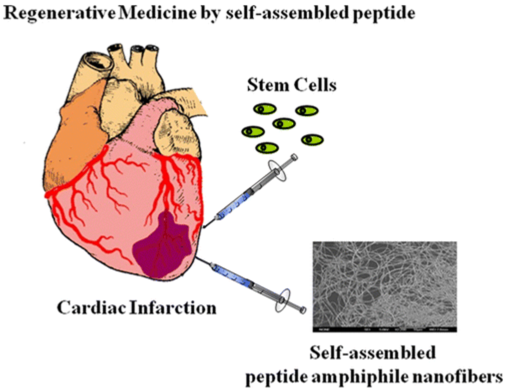
In this Account, I describe my group's work to synthesize and assemble peptidic nanostructures built around organic electronic elements. The Account begins with a very brief background to the area of supramolecular electronics, followed by a description of areas where these nanomaterials could be useful in biology. I then discuss the synthetic approaches that we utilized to embed a variety of π-electron units directly within peptide backbones. A key supramolecular challenge with respect to subsequent self-assembly of these new molecules is balancing electrostatic contributions within the resulting nanomaterials, because the suitable geometries for stabilizing peptide assemblies may not

necessarily correspond to those suitable for maximizing intermolecular π-electron interactions. Regardless of the respective magnitudes of these two major influences, the assembly paradigm is fairly robust. Variation of the π-electron units and the peptide sequences that make up the "peptide-π-peptide" triblock molecules consistently leads to fairly uniform tape-like nanostructures that maintain strong electronic coupling among the component π-electron units. We explored a diverse range of π-electron units spanning fluorescent oligo(phenylene vinylene)s, electron-accepting rylene diimides, and hole-transporting oligothiophenes.

I then describe the characterization of the nanomaterials that form after molecular self-assembly in order to understand their internal structures, electronic interactions, and morphologies as existing within self-supporting hydrogel matrices. I also describe how a facile shearing process provided globally aligned macroscopic collections of one-dimensional electronic fibrils in hydrogel matrices. These general assembly processes influence intermolecular π-stacking among the embedded chromophores, and the assemblies themselves can facilitate the covalent cross-linking and polymerization (for example, of reactive diyne units). The latter offers an exciting possibility to create peptidic nanostructures comprised of single polymer chains.

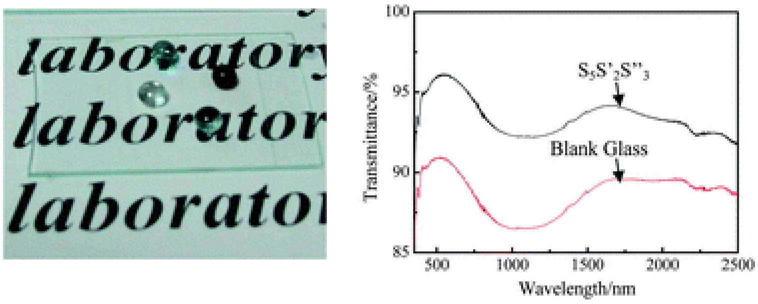
Finally, I discuss electronic properties as manifested in the interactions of transition dipoles within the nanomaterials and electrical properties resulting from field-effect gating. The ability to tune the observable electrical properties of the nanostructures externally will allow for their transition to in vitro or in vivo platforms as a powerful new approach to regulating biological interactions at the nanoscale.

- Self-Assembled Proteins and Peptides for Regenerative Medicine
  Hosseinkhani, H.; Hong, P.-D.; Yu, D.-S. *Chem. Rev.* **2013**, *113*, 4837–4861.
  Abstract:



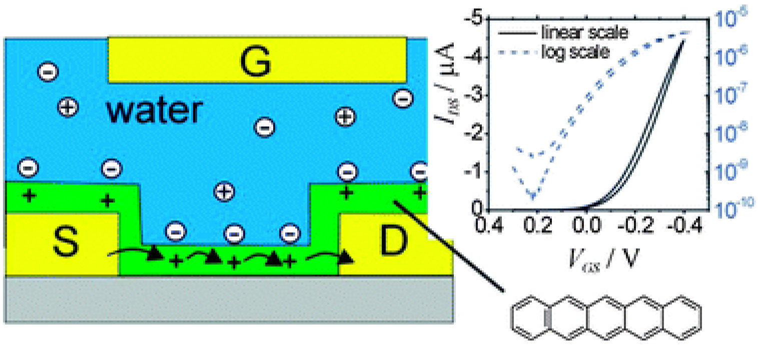
"Many diseases including cardiovascular disease, diabetes, osteoporosis, and cancers cannot be treated effectively with current clinical therapy because of a significant reduction in the level of tissue regeneration. Every day thousands of people of all ages are admitted to hospitals because of the malfunction of some vital organ. Because of the dearth of transplantable organs, many of these people will die. The evergrowing demand for donor organs to meet the needs of individuals on waiting lists will likely never be met. In short, the need for organs cannot be met by traditional methods of transplantation. Regenerative medicine may change that. Regenerative medicine is a new field of science that uses stem cells to regenerate biological tissues and improve tissue functions. Replacing these lost cells using stem cell-based therapies offers the possibility of exciting alternative treatments of current clinical medicine. Regenerative medicine will only be a topic of the future rather than the present and is based on combinational technology of materials science, stem cells technology, and reconstructive surgery that aim to regenerate natural tissues as well as create biological substitutes for defective or lost organs and tissues"……"This review will consider the self-assembled systems and recent developments for their potential applications in regenerative medicine. Self-assembling proteins and peptides for designing novel biomaterials and their potential applications in regenerative medicine and biomedical applications will be also discussed in detail from the viewpoint of their biological applications."

- Rational design and elaborate construction of surface nano-structures toward highly antireflective superamphiphobic coatings
  Geng, Z.; He, J.; Xu, L.; Yao, L. *J. Mater. Chem. A* **2013**, *1*, 8721-8724.
  Abstract:



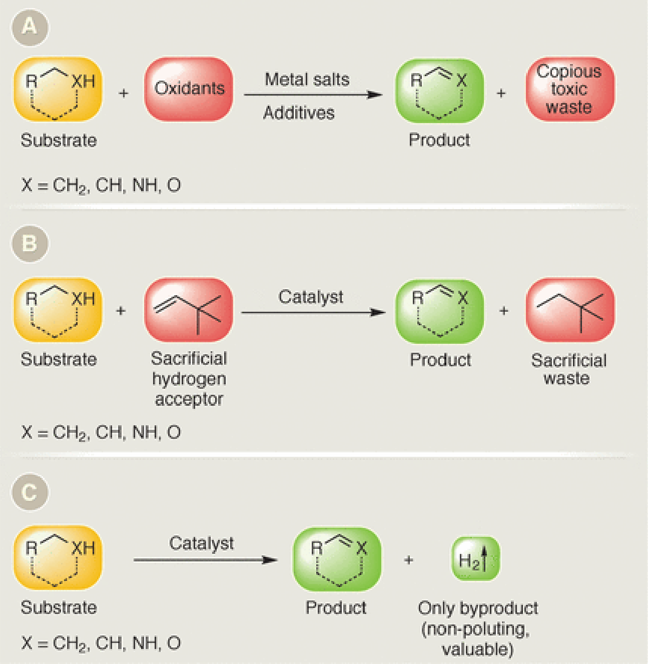
Three different nanostructures were assembled sequentially to build highly antireflective superamphiphobic coatings. A typical coating consisted of 5 layers of a 20 nm silica nanoparticle, 2 layers of an 80 nm hollow silica nanosphere and 3 layers of a mesoporous silica nanosheet deposited on a glass substrate. For this particular coating, the contact angle was 171° for water, 157° for diiodomethane and 156° for ethylene glycol. The maximum light transmittance obtained was as high as 96.1% at 530 nm, while only 91% was transmitted through a blank glass substrate.

- Water-gated organic field effect transistors – opportunities for biochemical sensing and extracellular signal transduction
  Cramer, T.; Campana, A.; Leonardi, F.; Casalini, S.; Kyndiah, A.; Murgia, M.; Biscarini, F. *J. Mater. Chem. B* **2013**, *1*, 3728-3741.
  Abstract:



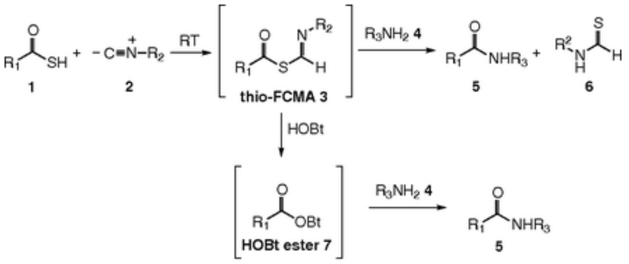
There is a quest for electronic biosensors operated in water for biomedical applications and environmental monitoring. Water is an aggressive medium for standard electronics materials and devices due to its strong polarizability and electrochemical activity. Thick dielectric encapsulation provides necessary stability while it damps the sensitivity of the device to sensing events occurring in the aqueous environment. Organic electronics provides materials that exhibit stable electronic conduction in direct contact with water combined with other desirable properties like mechanical softness, biocompatibility and processability onto flexible substrates. In this review, we introduce an emerging class of organic transistors, in which the current across the organic film is gated by the electric field of the Debye–Helmholtz layer. We discuss the device physics, the sensing mechanism and the relevant electrochemical processes. Applications of water-gated transistors range from the sensing of biologically relevant molecules like DNA, proteins or hormones to non-invasive recording and stimulation of electrical activity of neurons. Materials chemistry is crucial to control properties of electrically active films and to allow the introduction of specific chemical functionalities and receptors at sensing interfaces of the device.

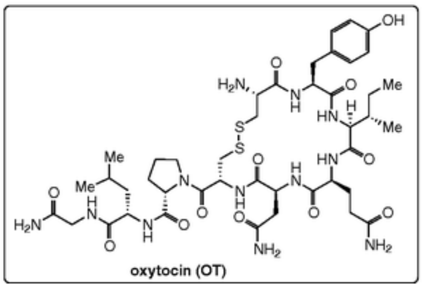
- Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis
  Gunanathan, C.; Milstein, D. *Science* **2013**, *341*, 1229712.
  <u>Abstract:</u>



Conventional oxidations of organic compounds formally transfer hydrogen atoms from the substrate to an acceptor molecule such as oxygen, a metal oxide, or a sacrificial olefin. In acceptorless dehydrogenation (AD) reactions, catalytic scission of C−H, N−H, and/or O−H bonds liberates hydrogen gas with no need for a stoichiometric oxidant, thereby providing efficient, nonpolluting activation of substrates. In addition, the hydrogen gas is valuable in itself as a high-energy, clean fuel. Here, we review AD reactions selectively catalyzed by transition metal complexes, as well as related transformations that rely on intermediates derived from reversible dehydrogenation. We delineate the methodologies evolving from this recent concept and highlight the effect of these reactions on chemical synthesis.

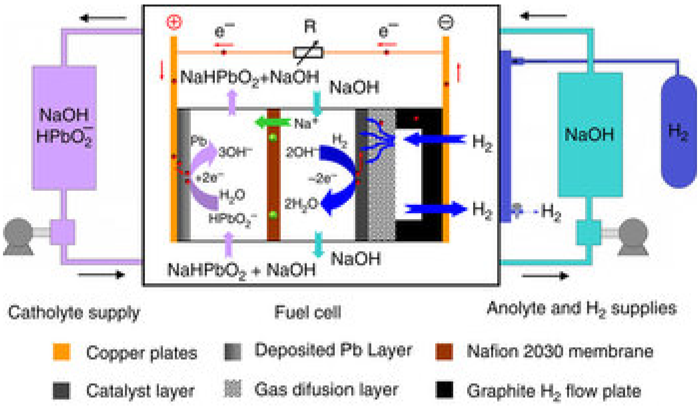
- Solid-phase peptide synthesis and solid-phase fragment coupling mediated by isonitriles
  Wang, T.; Danishefsky, S. J. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 11708-11713.
  <u>Abstract:</u>




oxytocin (OT)

The synthesis of polypeptides on solid phase via mediation by isonitriles is described. The acyl donor is a thioacid, which presumably reacts with the isonitrile to generate a thio-formimidate carboxylate mixed anhydride intermediate. Applications of this chemistry to reiterative solid-phase peptide synthesis as well as solid-phase fragment coupling are described.

- A green lead hydrometallurgical process based on a hydrogen-lead oxide fuel cell
  Pan, J.; Sun, Y.; Li, W.; Knight, J.; Manthiram, A. *Nature Commun.* **2013**, *4*, 2178.
  Abstract:

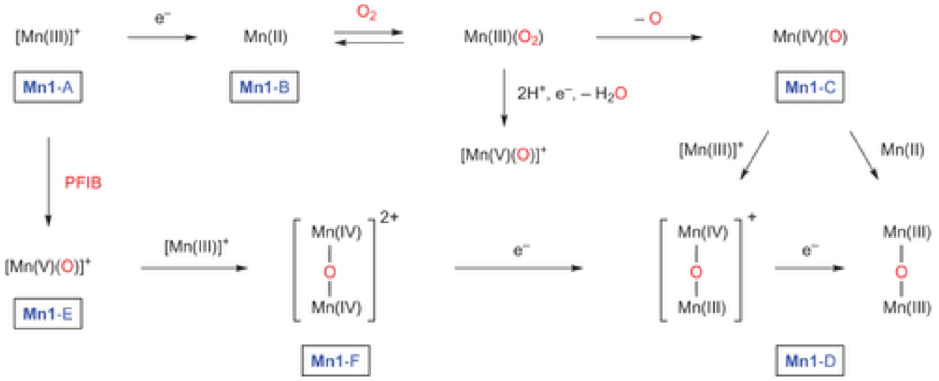


The automobile industry consumed 9 million metric tons of lead in 2012 for lead-acid batteries. Recycling lead from spent lead-acid batteries is not only related to the sustainable development of the lead industry, but also to the reduction of lead pollution in the environment. The existing lead pyrometallurgical processes have two main issues, toxic lead emission into the environment and high energy consumption; the developing hydrometallurgical processes have the disadvantages of high electricity consumption, use of toxic chemicals and severe corrosion of metallic components. Here we demonstrate a new green hydrometallurgical process to recover lead based on a hydrogen-lead oxide fuel cell. High-purity lead, along with electricity, is produced with only water as the by-product. It has a >99.5% lead yield, which is higher than that of the existing pyrometallurgical processes (95–97%). This greatly reduces lead pollution to the environment.

- Detection of different oxidation states of individual manganese porphyrins during their reaction with oxygen at a solid/liquid interface
  Den Boer, D.; Li, M.; Habets, T.; Iavicoli, P.; Rowan, A. E.; Nolte, R. J. M.; Speller, S.; Amabilino,

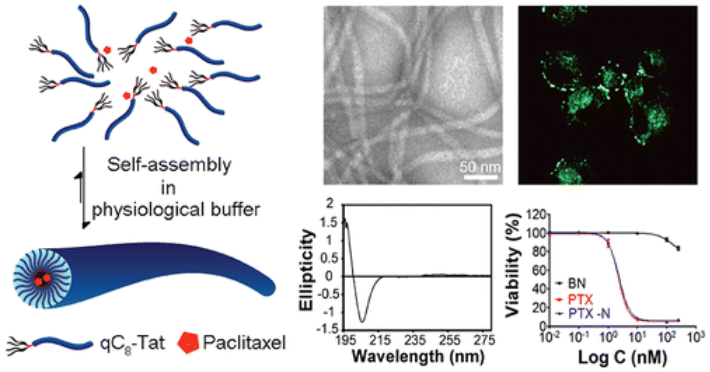
D. B.; De Feyter, S.; Elemans, J. A. A. W. *Nature Chem.* **2013**, *5*, 621–627.

Abstract:



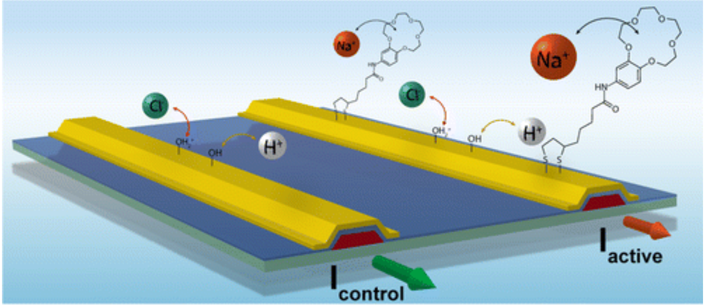
Manganese porphyrins have been extensively investigated as model systems for the natural enzyme cytochrome P450 and as synthetic oxidation catalysts. Here, we report single-molecule studies of the multistep reaction of manganese porphyrins with molecular oxygen at a solid/liquid interface, using a scanning tunnelling microscope (STM) under environmental control. The high lateral resolution of the STM, in combination with its sensitivity to subtle differences in the electronic properties of molecules, allowed the detection of at least four distinct reaction species. Real-space and real-time imaging of reaction dynamics enabled the observation of active sites, immobile on the experimental timescale. Conversions between the different species could be tuned by the composition of the atmosphere (argon, air or oxygen) and the surface bias voltage. By means of extensive comparison of the results to those obtained by analogous solution-based chemistry, we assigned the observed species to the starting compound, reaction intermediates and products.

- Self-assembled Tat nanofibers as effective drug carrier and transporter
  Zhang, P.; Cheetham, A. G.; Lin, Y.; Cui, H. *ACS Nano* **2013**, *7*, 5965-5977.
  Abstract:



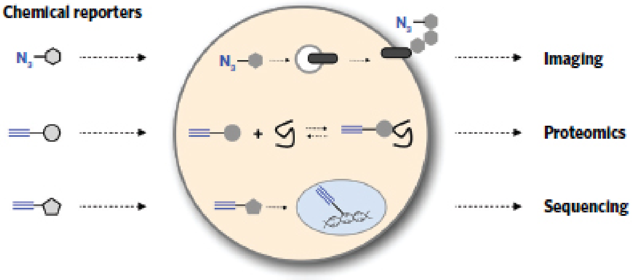
Cell penetrating peptides (CPPs) have been extensively explored as molecular vectors through covalent linkage to anticancer drugs to improve the drug's water solubility and to help overcome multidrug resistance. We report here the use of the Tat CPP as a molecular building unit to construct well-defined supramolecular nanofibers that can be utilized as a nanoscale vector to encapsulate the hydrophobic drug paclitaxel (PTX) (loading efficiency: 89.7 ± 5.0%) with a high loading capacity (6.8 ± 0.4%). Notably, our TEM imaging results reveal that nanofibers containing a higher PTX content tend to be more flexible than those with a lower PTX content. Fluorescence and confocal microscopy imaging show that the Tat nanofibers can effectively transport encapsulated molecules into the cells through an adsorptive-mediated endocytosis pathway. Cytotoxicity experiments and flow cytometry measurements demonstrate that PTX loaded in the nanofibers exerts its cytotoxicity against cancer cells by arresting the cells at the G2/M phase, the same working mechanism as free PTX.

- Selective sodium sensing with gold-coated silicon nanowire field-effect transistors in a differential setup
  Wipf, M.; Stoop, R. L.; Tarasov, A.; Bedner, K.; Fu, W.; Wright, I. A.; Martin, C. J.; Constable, E. C.; Calame, M.; Schönenberger, C. *ACS Nano* **2013**, *7*, 5978-5983.
  Abstract:



Ion-sensitive field-effect transistors based on silicon nanowires with high dielectric constant gate oxide layers (e.g., Al_2O_3 or HfO_2) display hydroxyl groups which are known to be sensitive to pH variations but also to other ions present in the electrolyte at high concentration. This intrinsically nonselective sensitivity of the oxide surface greatly complicates the selective sensing of ionic species other than protons. Here, we modify individual nanowires with thin gold films as a novel approach to surface functionalization for the detection of specific analytes. We demonstrate sodium ion (Na^+) sensing by a self-assembled monolayer (SAM) of thiol-modified crown ethers in a differential measurement setup. A selective Na^+ response of≈-44 mV per decade in a NaCl solution is achieved and tested in the presence of protons (H^+), potassium (K^+), and chloride (Cl^-) ions, by measuring the difference between a nanowire with a gold surface functionalized by the SAM (active) and a nanowire with a bare gold surface (control). We find that the functional SAM does not affect the unspecific response of gold to pH and background ionic species. This represents a clear advantage of gold compared to oxide surfaces and makes it an ideal candidate for differential measurements.

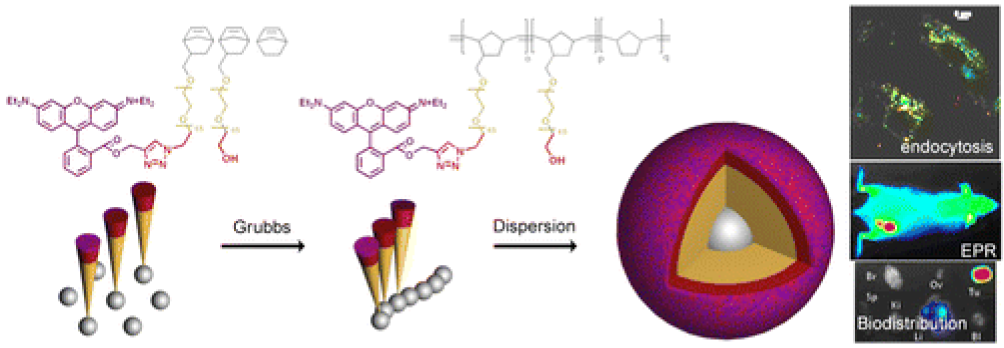
- Chemical reporters for biological discovery
  Grammel, M.; Hang, H. C. *Nature Chem. Biol.* **2013**, *9*, 475–484.
  Abstract:



Functional tools are needed to understand complex biological systems. Here we review how chemical reporters in conjunction with bioorthogonal labeling methods can be used to image and retrieve nucleic acids, proteins, glycans, lipids and other metabolites *in vitro*, in cells as well as in whole organisms. By tagging these biomolecules, researchers can now monitor their dynamics in living systems and discover specific substrates of cellular pathways. These advances in chemical biology are

thus providing important tools to characterize biological pathways and are poised to facilitate our understanding of human diseases.

- Nanoparticles Produced by Ring-Opening Metathesis Polymerization Using Norbornenyl-poly(ethylene oxide) as a Ligand-Free Generic Platform for Highly Selective In Vivo Tumor Targeting
  Gueugnon, F.; Denis, I.; Pouliquen, D.; Collette, F.; Delatouche, R.; Héroguez, V.; Grégoire, M.; Bertrand, P.; Blanquart, C. *Biomacromol.* **2013**, *14*, 2396-2402.
  <u>Abstract:</u>



We described a norbornenyl-poly(ethylene oxide) nanoparticles ligand-free generic platform, made fluorescent with straightforward preparation by ring-opening metathesis polymerization (ROMP). Our method allowed to easily obtain a drug delivery system (DDS) with facilitated functionalization by means of azide–alkyne click chemistry and with a high selectivity for the tumor in vivo, while cellular internalization is obtained without cell targeting strategy. We demonstrated that our nanoparticles are internalized by endocytosis and colocalized with acidic intracellular compartments in two models of aggressive tumoral cell lines with low prognostic and limited therapeutic treatments. Our nanoparticles could be of real interest to limit the toxicity and to increase the clinical benefit of drugs suffering rapid clearance and side effects and an alternative for cancers with poorly efficient therapeutic solutions by associating the drug delivery in the tumor tissue with an acid-sensitive release system.