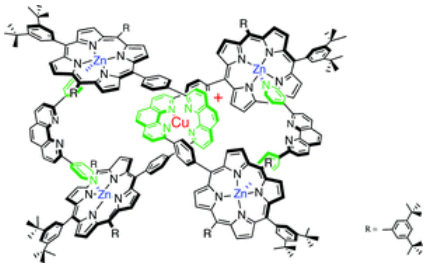
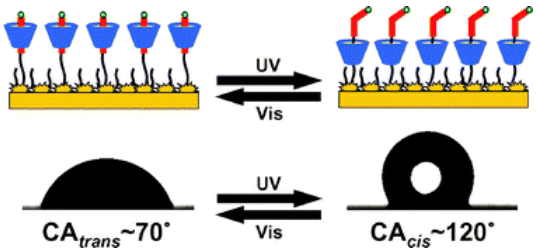
- Quantitative formation of a tetraporphyrin [2]catenane *via* copper and zinc coordination
  Beyler, M. ; Heitz, V.; Sauvage, J.-P. *Chem. Commun.* **2008**, 5396 – 5398.
  Abstract:



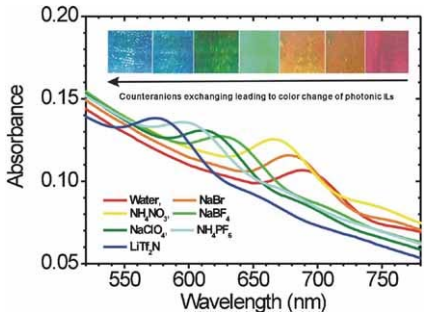
A [2]catenane is formed quantitatively by mixing substituted 1,10-phenanthroline-based chelates with copper(I) acting as central template, the ring-forming reaction being based on the coordination of pyridinic bidentate ligands onto the zinc atoms of the four porphyrins surrounding the core of the molecule.

- Tuning surface wettability through photocontrolled reversible molecular shuttle
  Wan, P.; Jiang, Y.; Wang, Y.; Wang, Z.; Zhang, X. *Chem. Commun.* **2008**, 5710 – 5712.
  Abstract:



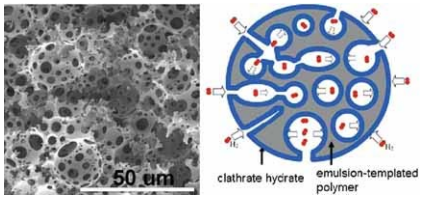
A photocontrolled molecular shuttle SAM based on an α-cyclodextrin (α-CD)/azobenzene inclusion complex on rough gold surfaces is fabricated, which can reversibly switch the surface wettability by transferring external energy (light) to molecular mechanical motion.

- Photonic Ionic Liquids Polymer for Naked-Eye Detection of Anions
  Hu, X.; Huang, J.; Zhang, W.; Li, M.; Tao, C.; Li, G. *Adv. Mater.* **2008**, *20*, 4074–4078.
  Abstract:



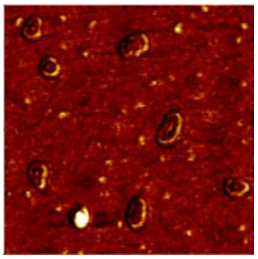
A new concept for anion detection in a handy, rapid, and sensitive way is described based on the combination of the unique properties of both ILs and photonic crystals. By simple counteranion exchanging of the pendant IL units, the 3D highly ordered IL porous structure can directly sense different anions and easily convert the anion detection events into readable optical signals with color changes.

- Rapid and Reversible Hydrogen Storage in Clathrate Hydrates Using Emulsion-Templated Polymers
  Su, F.; Bray, C. L.; Tan, B.; Cooper, A. I. *Adv. Mater.* **2008**, *20*, 2663–2666.
  Abstract:



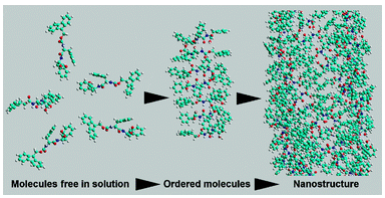
A method for greatly accelerating the storage of gases such as hydrogen in clathrates by supporting the clathrate phase on a highly macroporous emulsion-templated polymer is presented. The gravimetric penalty is low due to the low bulk density of the support, no mechanical mixing is required, and the system is fully recyclable over multiple charge/ discharge cycles.

- All-Conjugated Block Copolymers
  Scherf, U.; Gutacker, A.; Koenen, N. *Acc. Chem. Res.* **2008**, *41*, 1086-1097.
  Abstract:



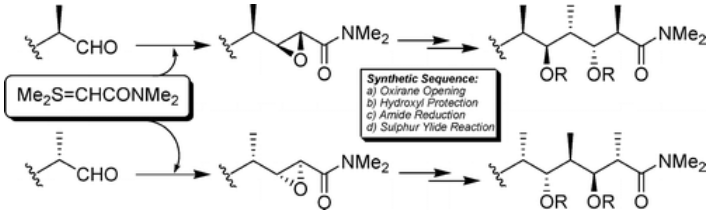
All-conjugated block copolymers of the rod-rod type came into the focus of interest because of their unique and attractive combination of nanostructure formation and electronic activity. Potential applications in a next generation of organic polymer materials for photovoltaic devices ("bulk heterojunction"-type solar cells) or (bio)-sensors have been proposed. Combining the fascinating self-assembly properties of block copolymers with the active electronic and/or optical function of conjugated polymers in all-conjugated block copolymers is, therefore, a very challenging goal of synthetic polymer chemistry.
First examples of such all-conjugated block copolymers from a couple of research groups all over the world demonstrate possible synthetic approaches and the rich application potential in electronic devices. A crucial point in such a development of novel polymer materials is a rational control over their nanostructure formation. All-conjugated di- or triblock copolymers may allow for an organization of the copolymer materials into large-area ordered arrays with a length scale of nanostructure formation of the order of the exciton diffusion length of organic semiconductors (typically ca. 10 nm). Especially for amphiphilic, all-conjugated copolymers the formation of well-defined supramolecular structures (vesicles) has been observed. However, intense further research is necessary toward tailor-made, all-conjugated block copolymers for specific applications. The search for optimized block copolymer materials should consider the electronic as well as the morphological (self-assembly) properties.

- Designing peptide based nanomaterials
  Ulijn, R. V.; Smith, A. M. *Chem. Soc. Rev.* **2008**, *37*, 664-675.
  Abstract:



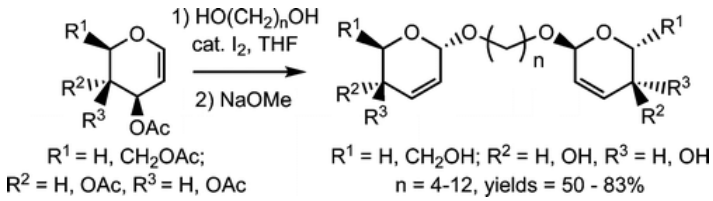
This *tutorial review* looks at the design rules that allow peptides to be exploited as building blocks for the assembly of nanomaterials. These design rules are either derived by copying nature (α-helix, β-sheet) or may exploit entirely new designs based on peptide derivatives (peptide amphiphiles, π-stacking systems). We will examine the features that can be introduced to allow self-assembly to be controlled and directed by application of an externally applied stimulus, such as pH, light or enzyme action. Lastly the applications of designed self-assembly peptide systems in biotechnology (3D cell culture, biosensing) and technology (nanoelectronics, templating) will be examined.

- Epoxyamide-Based Strategy for the Synthesis of Polypropionate-Type Frameworks
  Sarabia, F.; Martín-Gálvez, F.; García-Castro, M.; Chammaa, S.; Sánchez-Ruiz, A.; Tejón-Blanco, J. F. *J. Org. Chem.* **2008**, *73*, 8979-8986.
  Abstract:



A new approach to the stereoselective synthesis of polypropionate-type frameworks is reported utilizing reactions of amide-stabilized sulfur ylides with chiral aldehydes. To establish a new strategy for macrolide fragment synthesis, the stereoselectivity of these reactions in the construction of epoxy amides was the most important aspect of this study. In this aspect, we found a strong influence of the protecting groups employed in the starting aldehydes upon the stereochemical outcome of their reactions with the sulfur ylide **1**. Thus, numerous aldehydes showed remarkable stereofacial differentiation, providing a major diastereoisomer, in contrast to others that displayed a poor or no stereoselectivity. Despite the difficulties encountered for some cases with respect to their diastereomeric yields, we were able to prepare various stereotetrads and stereopentads, thus enhancing the synthetic value of this new methodology for the preparation of typical polypropionate frameworks found in many natural products, in particular the macrolide class of antibiotics.

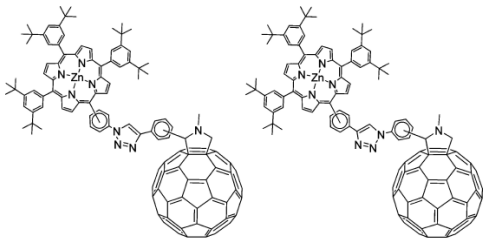
- Synthesis and Self-Assembly of Glycal-Based Bolaforms
  Bozell, J. J.; Tice, N. C.; Sanyal, N.; Thompson, D.; Kim, J.-M.; Vidal, S. *J. Org. Chem.* **2008**, *73*, 8763–8771.
  Abstract:



Glycal-based bolaforms serve as synthetically flexible components of molecular self-assembly. The compounds are prepared in good yield by a Ferrier reaction between triacetylglucal or -galactal or

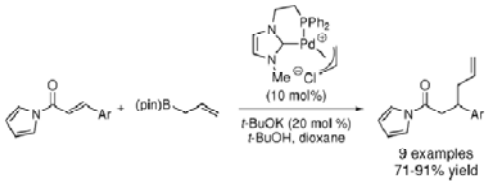
diacetylxylal and a long chain α,ω-diol, followed by deacetylation under Zemplén conditions. The reactions are stereoselective and preferentially afford the α-diastereomer. The bolaforms undergo self-assembly in water or water/dioxane solution to give a variety of nanostructures. In solution, bolaforms with C8 or C10 chains between glucal headgroups form nanoscale vesicles. In contrast, bolaforms with C12 chains exhibit lower solubility and a dynamic self-assembly, forming several different nanoscale structures. However, the solid-state structures of C12 bolaform isomers adopt shapes very similar to those of bolaforms possessing more extensive hydrogen-bonding networks, indicating that multiple hydrogen bonds in solution are important to formation of stable, discrete nanostructures but that only a few key intermolecular interactions between bolaform headgroups are necessary to determine the structure in the solid state. The diversity and differentiation of the functional groups present in glycal-based bolaforms suggest that they could be useful probes of the various noncovalent forces controlling the structure of new nanomaterials.

- First Triazole-Linked Porphyrin−Fullerene Dyads
  Fazio, M. A.; Lee, O. P.; Schuster, D. I. *Org. Lett.* **2008**, *10*, 4979–4982.
  Abstract:



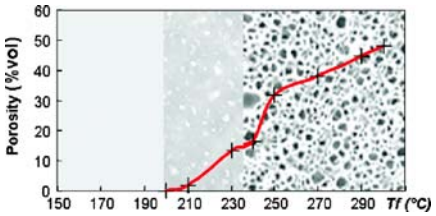
A general procedure for the synthesis of 1,2,3-triazole-linked porphyrin-fullerene dyads is described. Four of these compounds have been prepared and characterized.

- Palladium-Catalyzed Conjugate Allylation Reactions of α,β-Unsaturated *N*-Acylpyrroles
  Shaghafi, M. B.; Kohn, B. L.; Jarvo, E. R. *Org. Lett.* **2008**, *10*, 4743–4746.
  Abstract:



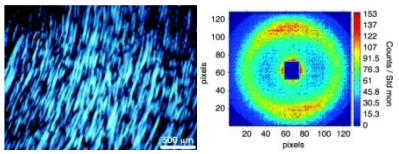
Conjugate allylation reactions of α,β-unsaturated *N*-acylpyrroles using allylboronic ester are catalyzed by a palladium complex that is ligated by a bidentate N-heterocyclic carbene. A variety of functional groups are tolerated, and substrates functionalized with electron-withdrawing groups react to afford the highest yields of products. Regioselectivity for 1,4-allylation over 1,2-allylation is demonstrated, and mechanistic experiments are consistent with formation of nucleophilic allylpalladium intermediates.

- "Self-Foaming" Poly(phenylquinoxaline)s for the Designing of Macro and Nanoporous Materials
  Merlet, S.; Marestin, C.; Romeyer, O.; Mercier, R. *Macromolecules*, **2008**, *41*, 4205–4215.
  Abstract:



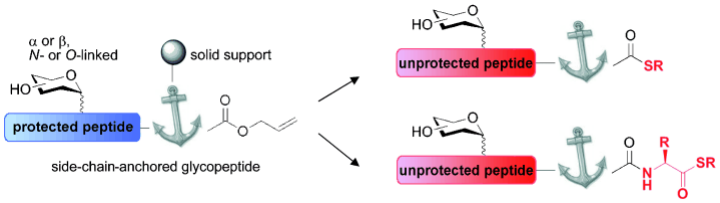
This work concerns the investigation of porous poly(phenylquinoxaline)s (PPQ) films. The approach described relies on the *in situ* generation of foaming agents during the thermal curing of dense thin films of PPQ-containing thermolabile groups. For this purpose, a series of phenol-containing PPQ has been previously synthesized and then modified by grafting thermolabile *tert*-butyl carbonate groups (Boc) via a reaction involving the phenol groups. Thin dense films obtained by a solution casting method were thermally treated at different temperatures. The morphology of the resulting porous materials, characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), is discussed in relation with the chemical structure of the polymers and to the thermal treatment conditions as well.

- Organization of Self-Assembled Peptide–Polymer Nanofibers in Solution
  Börner, H. G.; Smarsly, B. M.; Hentschel, J.; Rank, A.; Schubert, R.; Geng, Y.; Discher, D. E.; Hellweg, T.; Brandt, A. *Macromolecules*, **2008**, *41*, 1430–1437.
  Abstract:



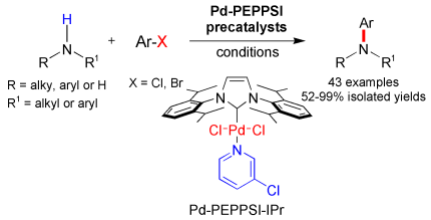
The solution structure and the aggregation behavior of stiff polymer–peptide nanofibers, self-assembled from well-defined poly(ethylene oxide)–peptide conjugates are described. Aqueous solutions at different concentrations of core–shell nanofibers were investigated by cryo-fixation transmission electron microscopy (*cryo*TEM) and small-angle neutron scattering (SANS). Both methods show the presence of stiff, extended nanofibers in dilute solution, providing nanodimensions for the fiber cross section, which are in good agreement with previously shown investigations on dried and deposited fibers. Moreover the previously suggested core–shell character of the fiber cross section could be verified by SANS density profiles. In concentrated solutions exceeding 2 mg/mL, the nanofibers tended to further organize into nematic “bundles”. Polarized optical microscopy (POM) indeed shows birefringence of the solutions and typical Schlieren textures in shear oriented films, consistent with high aspect ratio nanofibers. The results of this investigation are discussed in the context of the Flory theory of rigid rods.

- Solid-Phase Synthesis of Peptide and Glycopeptide Thioesters through Side-Chain-Anchoring Strategies
  Ficht, S.; Payne, R. J.; Guy, R. T.; Wong, C.-H. *Chem. Eur. J.* **2008**, *14*, 3620-3629.
  Abstract:



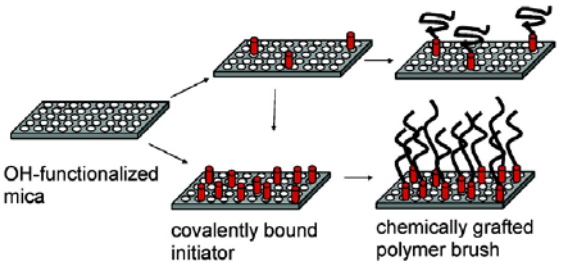
An efficient new strategy for the synthesis of peptide and glycopeptide thioesters is described. The method relies on the side-chain immobilization of a variety of Fmoc-amino acids, protected at their C-termini, on solid supports. Once anchored, peptides were constructed using solid-phase peptide synthesis according to the Fmoc protocol. After unmasking the C-terminal carboxylate, either thiols or amino acid thioesters were coupled to afford, after cleavage, peptide and glycopeptide thioesters in high yields. Using this method a significant proportion of the proteinogenic amino acids could be incorporated as C-terminal amino acid residues, therefore providing access to a large number of potential targets that can serve as acyl donors in subsequent ligation reactions. The utility of this methodology was exemplified in the synthesis of a 28 amino acid glycopeptide thioester, which was further elaborated to an N-terminal fragment of the glycoprotein erythropoietin (EPO) by native chemical ligation.

- Pd-Catalyzed Aryl Amination Mediated by Well Defined, N-Heterocyclic Carbene (NHC)-Pd Precatalysts, PEPPSI
  Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Sayah**,** M.; Valente, C. *Chem. Eur. J.* **2008**, *14*, 2443-2452.
  Abstract:



Pd-N-heterocyclic carbene (NHC)-catalyzed Buchwald-Hartwig amination protocols mediated by Pd-PEPPSI precatalysts is described. These protocols provide access to a range of hindered and functionalized drug-like aryl amines in high yield with both electron-deficient and electron-rich aryl- and heteroaryl chlorides and bromides. Variations in solvent polarity, base and temperature are tolerated, enhancing the scope and utility of this protocol. A mechanistic rationalization for base strength (pK_b) requirements is also provided.

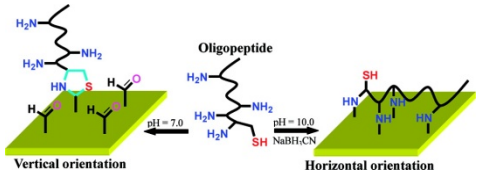
- Unprecedented Covalently Attached ATRP Initiator onto OH-Functionalized Mica Surfaces
  Lego, B.; Skene, W. G.; Giasson, S. *Langmuir* **2008**, *24*, 379-382.
  Abstract:



Mica substrates were activated by a plasma method leading to OH-functionalized surfaces to which an atom transfer radical polymerization (ATRP) radical initiator was covalently bound using standard siloxane protocols. The unprecedented covalently immobilized initiator underwent radical polymerization with *tert*-butyl acrylate, yielding for the first time end-grafted polymer brushes that are covalently linked to mica. The initiator grafting on the mica substrate was confirmed by time-of-flight secondary ion mass spectrometry (TOF-SIMS), while the change in the water contact angle of

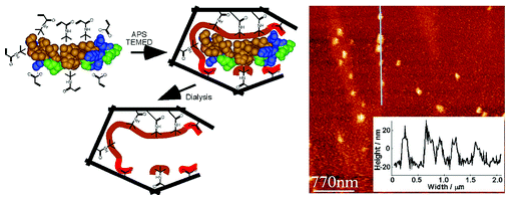
the OH-activated mica surface was used to follow the change in surface coverage of the initiator on the surface. The polymer brush and initiator film thicknesses relative to the virgin mica were confirmed by atomic force microscopy (AFM). This was done by comparing the atomic step-height difference between a protected area of freshly cleaved mica and a zone exposed to plasma activation, initiator immobilization, and then ATRP.

- Controlling Orientations of Immobilized Oligopeptides Using N-Terminal Cysteine Labels
  Bi, X.; Hartono, D.; Yang, K.-L. *Langmuir* **2008**, *24*, 5238-5240.
  Abstract:



This letter reports a strategy of using N-terminal cysteine labels for controlling the immobilization of oligopeptides on aldehyde-terminated surfaces through the formation of stable thiazolidine rings. We also study the effect of cysteine position (either N-terminal or C-terminal) and lysine residue on the immobilization of oligopeptides. On the basis of our ellipsometry and quartz crystal microbalance (QCM) results, we conclude that the proposed immobilization strategy is highly site-specific. It works only when cysteine is in the N-terminal position, and the formation of thiazolidine is much faster than the formation of imines between lysine residues and aldehydes, even in the presence of a reducing agent such as NaBH3CN. By labeling an oligopeptide CSNKTRIDEANNKATKML with an N-terminal cysteine, we immobilize this oligopeptide on an aldehyde-terminated surface and investigate the enzymatic activity of trypsin acting on the oligopeptide. It is found that trypsin is able to cleave the immobilized oligopeptide having a single anchoring point at the N-terminal cysteine. No cleavage is observed when the oligopeptide is immobilized through multiple anchoring points at lysine residues.

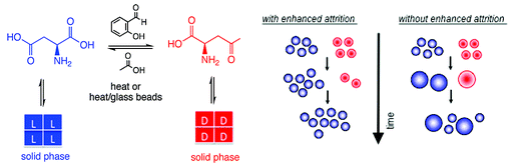
- Peptide Imprinted Polymer Nanoparticles: A Plastic Antibody
  Hoshino, Y.; Kodama, T.; Okahata, Y.; Shea, K. J. *J. Am. Chem. Soc.* **2008**, *130*, 15242–15243.
  Abstract:



A novel method for preparation of biomacromolecular imprinted nanoparticles is described. Combinations of functional monomers were polymerized in the presence of the imprinting peptide melittin in aqueous solution at room temperature to produce a small library of polymer nanoparticles. The template peptide and unreacted monomers are subsequently removed by dialysis. Nanoparticles (NPs) from the library were evaluated for their binding to melittin by 27 MHz QCM analysis. NPs prepared with optimized functional monomer combinations bind strongly to the target molecule. Nanoparticles that were polymerized in the absence of template peptide were found to have little affinity to the peptide. Binding affinity and the size of imprinted particles are comparable to those of natural antibodies. They interact specifically with the target peptide and show little affinity for other proteins. These NPs are of interest as inert and stable substitutes for

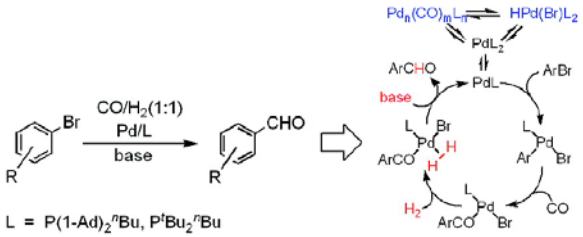
antibodies. Extension of this approach to other targets of biological importance and the applications of these materials are currently being evaluated.

- Evolution of Solid Phase Homochirality for a Proteinogenic Amino Acid
  Viedma, C.; Ortiz, J. E.; de Torres, T.; Izumi, T.; Blackmond, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 15274–15275.
  Abstract:



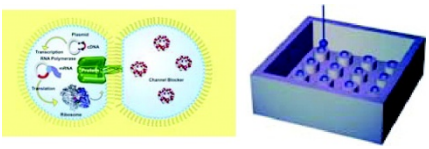
The inexorable evolution of solid-phase single chirality is demonstrated for the first time for a proteinogenic amino acid. Enantioenrichment is observed both under attrition-enhanced conditions and without the aid of particle grinding. Differences in the form of the conversion profiles for the process under the two sets of conditions provide suggestions concerning the mechanism of the transformation.

- Palladium-Catalyzed Formylation of Aryl Bromides: Elucidation of the Catalytic Cycle of an Industrially Applied Coupling Reaction
  Sergeev, A. G.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2008**, *130*, 15549–15563.
  Abstract:



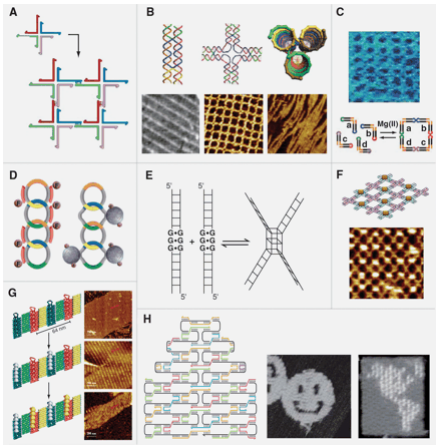
The first comprehensive study of the catalytic cycle of the palladium-catalyzed formylation of aryl bromides with synthesis gas (CO/H_2, 1:1) is presented. The formylation in the presence of efficient (Pd/PR_2^nBu, R = 1-Ad, ^tBu) and nonefficient (Pd/P^tBu_3) catalysts was investigated. The main organometallic complexes involved in the catalytic cycle were synthesized and characterized, and their solution chemistry was studied in detail. Comparison of stoichiometric and catalytic reactions using $P(1\text{-}Ad)_2{}^nBu$, the most efficient ligand known for the formylation of aryl halides, led to two pivotal results: (1) The corresponding carbonylpalladium(0) complex $[Pd_n(CO)_mL_n]$ and the respective hydrobromide complex $[Pd(Br)(H)L_2]$ are resting states of the active catalyst, and they are not directly involved in the catalytic cycle. These complexes maintain the concentration of most active [PdL] species at a low level throughout the reaction, making oxidative addition the rate-determining step, and provide high catalyst longevity. (2) The product-forming step proceeds via base-mediated hydrogenolysis of the corresponding acyl complex, e.g., $[Pd(Br)(p\text{-}CF_3C_6H_4CO)\{P(1\text{-}Ad)_2{}^nBu\}]_2$ (**8**), under mild conditions (25−50 °C, 5 bar). Stoichiometric studies using the less efficient Pd/P^tBu_3 catalyst resulted in the isolation and characterization of the first stable three-coordinated neutral acylpalladium complex, $[Pd(Br)(p\text{-}CF_3C_6H_4CO)(P^tBu_3)]$ (**10**). Hydrogenolysis of **10** needed significantly more drastic conditions compared to that of dimeric **8**. In the presence of amine base, complex **10** gave a catalytically inactive diamino acyl complex, which explains the low activity of the Pd/P^tBu_3 catalyst formylation of aryl bromides.

- Screening Blockers Against a Potassium Channel with a Droplet Interface Bilayer Array
  Syeda, R.; Holden, M. A.; Hwang, W. L.; Bayley, H. *J. Am. Chem. Soc.* **2008**, *130*, 15543–15548.
  Abstract:



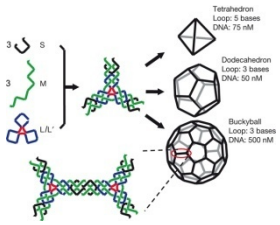
Droplet interface bilayers (DIBs) form between two lipid monolayer-encased aqueous droplets submerged in oil. Both major structural classes of membrane proteins, α-helix bundles and β barrels, represented by channels and pores, respectively, spontaneously insert into DIBs when freshly expressed by cell-free transcription and translation. Electrodes embedded within the droplets allow the measurement of transmembrane ionic currents carried by individual channels and pores. On the basis of these findings, we have devised a chip-based approach for the rapid screening of blockers against ion channels. The technique is demonstrated here with the viral potassium channel, Kcv.

- Assembling Materials with DNA as the Guide
  Aldaye, F. A.; Palmer, A. L.; Sleiman, H. F. *Science* **2008**, *321*, 1795 – 1799.
  Abstract:



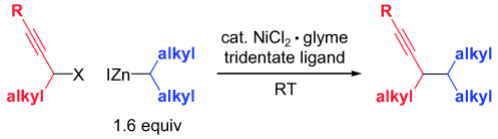
DNA's remarkable molecular recognition properties and structural features make it one of the most promising templates to pattern materials with nanoscale precision. The emerging field of DNA nanotechnology strips this molecule from any preconceived biological role and exploits its simple code to generate addressable nanostructures in one, two, and three dimensions. These structures have been used to precisely position proteins, nanoparticles, transition metals, and other functional components into deliberately designed patterns. They can also act as templates for the growth of nanowires, aid in the structural determination of proteins, and provide new platforms for genomics applications. The field of DNA nanotechnology is growing in a number of directions, carrying with it the promise to substantially affect materials science and biology.

- Hierarchical self-assembly of DNA into symmetric supramolecular polyhedral
  He, Y.; Ye, T.; Su, M.; Zhang, C.; Ribbe, A. E.; Jiang, W.; Mao, C. *Nature* **2008**, *452*, 198-201.
  Abstract:



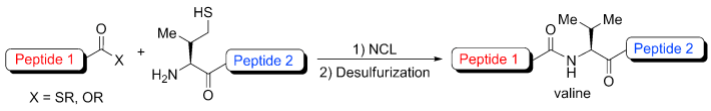
DNA is renowned for its double helix structure and the base pairing that enables the recognition and highly selective binding of complementary DNA strands. These features, and the ability to create DNA strands with any desired sequence of bases, have led to the use of DNA rationally to design various nanostructures and even execute molecular computations. Of the wide range of self-assembled DNA nanostructures reported, most are one- or two-dimensional. Examples of three-dimensional DNA structures include cubes, truncated octahedra, octohedra and tetrahedra, which are all comprised of many different DNA strands with unique sequences. When aiming for large structures, the need to synthesize large numbers (hundreds) of unique DNA strands poses a challenging design problem. Here, we demonstrate a simple solution to this problem: the design of basic DNA building units in such a way that many copies of identical units assemble into larger three-dimensional structures. We test this hierarchical self-assembly concept with DNA molecules that form three-point-star motifs, or tiles. By controlling the flexibility and concentration of the tiles, the one-pot assembly yields tetrahedra, dodecahedra or buckyballs that are tens of nanometres in size and comprised of four, twenty or sixty individual tiles, respectively. We expect that our assembly strategy can be adapted to allow the fabrication of a range of relatively complex three-dimensional structures.

- Nickel-Catalyzed Negishi Cross-Couplings of Secondary Nucleophiles with Secondary Propargylic Electrophiles at Room Temperature
  Smith, S. W.; Fu, G. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 9334 –9336.
  Abstract:



Mild thing: The first nickel-based catalysts for cross-couplings of secondary organometallic nucleophiles with secondary alkyl electrophiles have been developed. Thus, Negishi reactions proceed under mild conditions (at room temperature with no basic activators) in the presence of $NiCl_2$·glyme and a tridentate ligand.

- Native Chemical Ligation at Valine: A Contribution to Peptide and Glycopeptide Synthesis
  Chen, J.; Wan, Q.; Yuan, Y.; Zhu, J.; Danishefsky, S. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 8521 – 8524.
  Abstract:



A Val-uable link: The title transformation is achieved by a two-step ligation, radical-based desulfurization strategy (see scheme; NCL=native chemical ligation). After S⟶N acyl transfer, in which the acyl acceptor is a γ-thiol valine derivative, and site-specific dethiolation, a valine residue appears at the site of ligation. This method accomplishes ligations at Thr-Val and Pro-Val sites, and allows successful ligation of glycopeptide fragments.