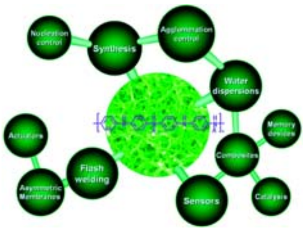
- Polyaniline Nanofibers: A Unique Polymer Nanostructure for Versatile Applications
  Li, D.; Huang, J.; Kaner, R. B. *Acc. Chem. Res.* **2009**, *42*, 135-145.
  Abstract:

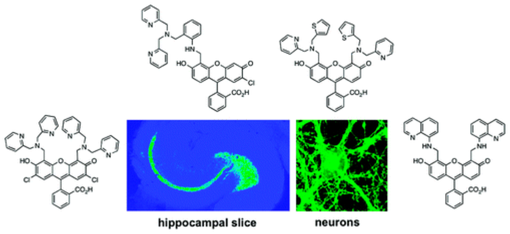


Known for more than 150 years, polyaniline is the oldest and potentially one of the most useful conducting polymers because of its facile synthesis, environmental stability, and simple acid/base doping/dedoping chemistry. Because a nanoform of this polymer could offer new properties or enhanced performance, nanostructured polyaniline has attracted a great deal of interest during the past few years. This Account summarizes our recent research on the syntheses, processing, properties, and applications of polyaniline nanofibers.

By monitoring the nucleation behavior of polyaniline, we demonstrate that high-quality nanofibers can be readily produced in bulk quantity using the conventional chemical oxidative polymerization of aniline. The polyaniline nanostructures formed using this simple method have led to a number of exciting discoveries. For example, we can readily prepare aqueous polyaniline colloids by purifying polyaniline nanofibers and controlling the pH. The colloids formed are self-stabilized via electrostatic repulsions without the need for any chemical modification or steric stabilizer, thus providing a simple and environmentally friendly way to process this polymer. An unusual nanoscale photothermal effect called “flash welding”, which we discovered with polyaniline nanofibers, has led to the development of new techniques for making asymmetric polymer membranes and patterned nanofiber films and creating polymer-based nanocomposites. We also demonstrate the use of flash-welded polyaniline films for monolithic actuators. Taking advantage of the unique reduction/oxidation chemistry of polyaniline, we can decorate polyaniline nanofibers with metal nanoparticles through in situ reduction of selected metal salts. The resulting polyaniline/metal nanoparticle composites show promise for use in ultrafast nonvolatile memory devices and for chemical catalysis. In addition, the use of polyaniline nanofibers or their composites can significantly enhance the sensitivity, selectivity, and response time of polyaniline-based chemical sensors.

By combining straightforward synthesis and composite formation with exceptional solution processability, we have developed a range of new useful functionalities. Further research on nanostructured conjugated polymers holds promise for even more exciting discoveries and intriguing applications.

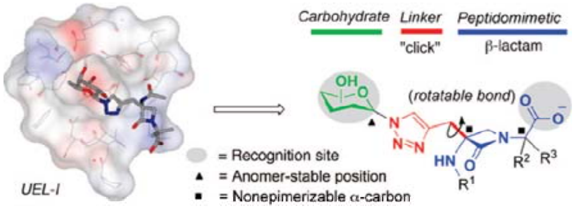
- Small-Molecule Fluorescent Sensors for Investigating Zinc Metalloneurochemistry
  Nolan, E. M.; Lippard, S. J. *Acc. Chem. Res.* **2009**, *42*, 193-203.
  Abstract:



The metalloneurochemistry of Zn(II) is of substantial current interest. Zinc is the second most abundant d-block metal ion in the human brain, and its distribution varies with relatively high concentrations found in the hippocampus. Brain zinc is generally divided into two types, protein-bound and loosely bound, the latter also being termed histochemically observable, chelatable, labile, or mobile zinc. The neurophysiological and neuropathological significance of mobile Zn(II) remains enigmatic. Studies of Zn(II) distribution, translocation, and function in vivo require tools for its detection. Because Zn(II) has a closed-shell $d^{10}$ configuration and no convenient spectroscopic signature, fluorescence is a well-suited method for monitoring Zn(II) in biological contexts.

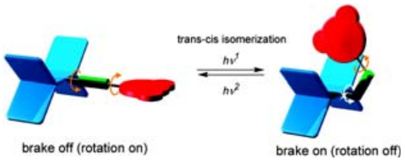
This Account summarizes work by our laboratory addressing the design, preparation, characterization, and use of small-molecule fluorescent sensors for imaging Zn(II) in living cells and samples of brain tissue. These sensors provide "turn-on" or ratiometric Zn(II) detection in aqueous solution at neutral pH. By making alterations to the Zn(II)-binding unit and fluorophore platform, we have devised sensors with varied photophysical and metal-binding properties. Several of these probes have been applied to image Zn(II) distribution, uptake, and mobilization in a variety of cell types, including neuronal cultures.

- "Click" Saccharide/$\beta$-Lactam Hybrids for Lectin Inhibition
  Palomo C.; Aizpurua J. M.; Balentova E.; Azcune I.; Santos J. I.; Jiménez-Barbero J.; Cañada J.; Miranda J. I. *Org. Lett.* **2008**, *10*, 2227-2230.
  Abstract:



Hybrid glycopeptide $\beta$-lactam mimetics designed to bind lectins or carbohydrate recognition domains in selectins have been prepared according to a "shape-modulating linker" design. This approach was implemented using the azide-alkyne "click" cycloaddition reaction, and as shown by NMR/MD experiments, binding of the resulting mimetics to *Ulex Europaeus Lectin-1* (UEL-1) occurred after a "bent-to-extended" conformational change around a partially rotatable triazolylmethylene moiety.

- A Pentiptycene-Derived Light-Driven Molecular Brake
  Yang J.-S.; Huang Y.-T.; Ho J.-H.; Sun W.-T.; Huang H.-H.; Lin Y.-C.; Huang S.-J.; Huang S.-L.; Lu H.-F.; Chao I. *Org. Lett.* **2008**, *10*, 2279-2282.
  Abstract:



A room-temperature light-driven molecular brake (1), consisting of a pentiptycene rotator, a 3,5-dinitrophenyl brake, and a photoisomerizable ethenyl spacer, is reported. The rotation rates of the rotator differ by about 9 orders of magnitude between the brake-on (*cis*-1) and brake-off (*trans*-1) states.

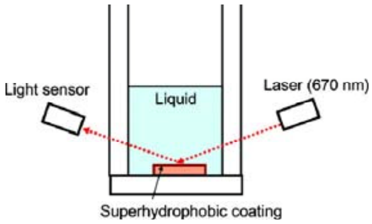
- Layer-by-Layer Deposition of Polyelectrolytes. Dipping versus Spraying

Kolasinska, M.; Krastev, R.; Gutberlet, T.; Warszynski, P. *Langmuir* **2009**, *25*, 1224-1232.

<u>Abstract:</u>

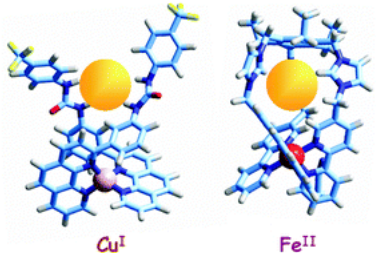
We studied the properties of polyelectrolyte multilayer films prepared using the technique of polyelectrolyte deposition from solution (dipping) or supplying the solutions to the surface by spraying. The quality of films obtained by those two techniques was compared to find out whether the well-established dipping procedure can be replaced with the spraying technique. Neutron and X-ray reflectometric studies were performed on the samples of interest. We found that multilayers prepared by dipping are thicker, denser and less rough than films having the same number of layers, i.e., having the same number of deposition cycles, obtained by spraying.

- Effect of Surface Structure on the Sustainability of an Air Layer on Superhydrophobic Coatings in a Water-Ethanol Mixture
  Sakai, M.; Yanagisawa, T.; Nakajima, A.; Kameshima, Y.; Okada, K. *Langmuir* **2009**, *25*, 13-16.
  <u>Abstract:</u>



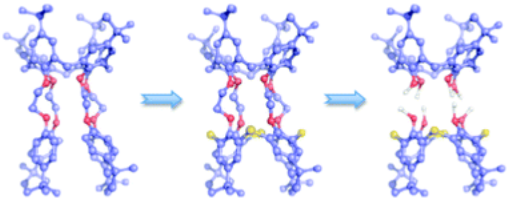
Using a laser beam and its reflection, we evaluated surface air layers on two superhydrophobic coatings with different roughnesses (*Ra* ) 1900 and 74 nm) in a water-ethanol mixture. The reflected laser intensity decreased by increasing the ethanol concentration for the superhydrophobic coating with large roughness because of increased scattering by the surface structure of the solid. However, it was almost constant and slightly increased for the coating with small roughness, probably because the liquid-air interface becomes flatter as the liquid intrudes into the surface structure. Results demonstrated that the difference in surface structure provides different sustainability of the surface air layer.

- Anion receptors that contain metals as structural units
  Amendola, V.; Fabbrizzi, L. *Chem. Commun.* **2009**, 513 – 531.
  <u>Abstract:</u>



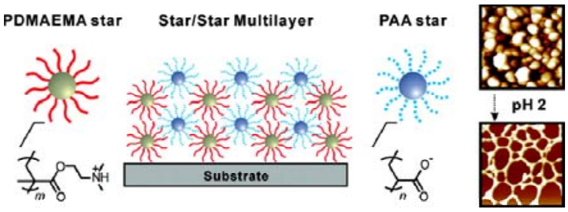
Transition metals can be used as structural elements to build up anion receptors, enhancing H-bond donor tendencies, favouring the assembling of the molecular framework, inducing the formation of a cage. The versatile spectroscopic and electrochemical properties of the metal ion can provide a convenient signalling mechanism to communicate the occurrence of anion recognition.

- Casting heteracalixarenes from calixarene templates: a unique synthetic strategy
  Patel, M. H.; Shrivastav, P. S. *Chem. Commun.* **2009**, 586 – 588.
  <u>Abstract:</u>



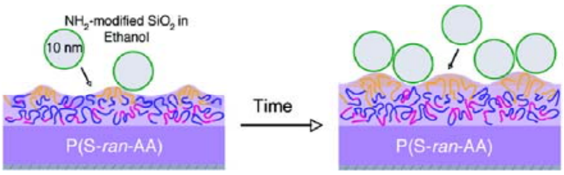
A simple, intuitive and modular strategy to synthesize higher heteracalixarene (in particular thiacalixarene) homologs using respective calixarene templates has been developed and demonstrated.

- All-Star Polymer Multilayers as pH-Responsive Nanofilms
  Kim, B.-S.; Gao, H.; Argun, A. A.; Matyjaszewski, K.; Hammond, P. T. *Macromolecules* **2009**, *42*, 368-375.
  <u>Abstract:</u>



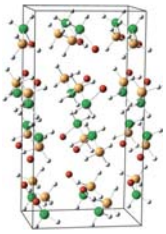
Star polymers with globular architecture and multiple arms are among the simplest forms of polymers with branched topologies. The combination of their unique architecture and high local densities of active functional groups makes star polymers unique candidates for a diverse range of applications. In this article, we describe the synthesis of star polymers with precisely controlled structures via atom transfer radical polymerization (ATRP) using the one-pot arm-first method. Specifically, two types of highly defined, high charge density star polymers with oppositely charged arm structures were prepared: poly[2-(dimethylamino)ethylmethacrylate] (PDMAEMA) star and poly(acrylic acid) (PAA) star polymers with cross-linked cores. By exploiting the electrostatic interactions between the polyelectrolyte arms, we have integrated the PDMAEMA star and PAA star polymers within alternating multilayer thin films using layer-by-layer (LbL) assembly to generate all-star polyelectrolyte LbL films. The prepared star/star multilayer films illustrate nonuniform and nanoporous structures, which result from the characteristic architecture of star polymers. The thickness, porosity, and refractive index of star/star multilayer films are precisely tunable by assembly pH conditions. Furthermore, as-assembled star/star multilayer films exhibit distinct morphological changes by undergoing extensive structural reorganization upon post-treatment under different pH conditions that do not lead to any changes with their linear compositional counterparts; it is hypothesized that these differences are due to the star polyelectrolyte's compact structure and decreased extent of entanglement and interpenetration, which lead to a low degree of ionic cross-linking compared to their linear counterparts. The pH-responsive structural changes of the films are characterized by AFM, SEM, and FTIR. Finally, we have observed an enhanced ionic (proton) conductivity of star/star multilayers following.

- Covalent Nanoparticle Assembly onto Random Copolymer Films
  McConnell, M. D.; Yang, S.; Composto, R. J. *Macromolecules* **2009**, *42*, 517-523.
  Abstract:



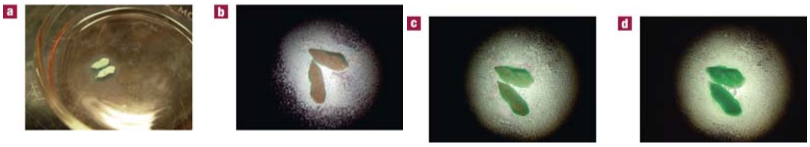
We present a novel class of nanoparticle-decorated surfaces: amine-functionalized silica nanoparticles covalently attached to poly(styrene-*random*-acrylic acid) films and carboxylic acid-terminated selfassembled monolayers (SAMs). The dependence of the particle attachment kinetics on the concentration of particles in solution and acrylic acid moieties in the polymer backbone was investigated and was compared to the observed kinetics with SAM substrates. The kinetics on the polymer films included three distinct stages, which were governed by the acrylic acid concentration-dependent morphological changes of the films under the reaction conditions. The first stage was an induction period with little change in the particle coverage with time, followed by a rapid rise in the coverage, and finally a plateau. The maximum coverage achieved for the polymer films, 70%, was nearly twice that of the SAM substrates, which followed diffusion-limited coverage kinetics prior to reaching saturation. This enhanced coverage is attributed to the swelling of the acrylic acid groups at the film surface in the reaction solvent, which increases the surface area and roughness of the substrate. This approach is a reproducible way of preparing nanoparticle-decorated, chemically robust surfaces with controlled coverages and have potential applications for controlling surface wettability, optical properties, and cellular adhesion.

- High-capacity hydrogen storage in lithium and sodium amidoboranes
  Xiong, Z.; Yong, C. K.; Wu, G.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F. *Nature Materials* **2008**, *7*, 138-141.
  Abstract:



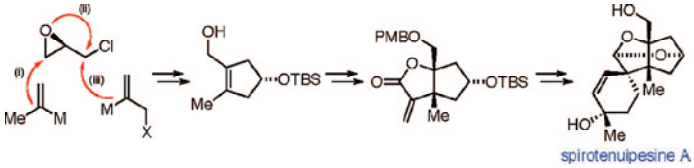
The safe and efficient storage of hydrogen is widely recognized as one of the key technological challenges in the transition towards a hydrogen-based energy economy. Whereas hydrogen for transportation applications is currently stored using cryogenics or high pressure, there is substantial research and development activity in the use of novel condensed-phase hydride materials. However, the multiple-target criteria accepted as necessary for the successful implementation of such stores have not yet been met by any single material. Ammonia borane, $NH_3BH_3$, is one of a number of condensed-phase compounds that have received significant attention because of its reported release of ~12 wt% hydrogen at moderate temperatures (~150 °C). However, the hydrogen purity suffers from the release of trace quantities of borazine. Here, we report that the related alkali-metal amidoboranes, $LiNH_2BH_3$ and $NaNH_2BH_3$, release ~10.9 wt% and ~7.5 wt% hydrogen, respectively, at significantly lower temperatures (~90 °C) with no borazine emission. The low-temperature release of a large amount of hydrogen is significant and provides the potential to fulfil many of the principal criteria required for an on-board hydrogen store.

- Mechanical gas capture and release in a network solid via multiple single-crystalline transformations
  Chandler, B. D.; Enright, G. D.; Udachin, K. A.; Pawsey, S.; Ripmeester, J. A.; Cramb D. T.; Shimizu, G. K. H. *Nature Materials* **2008**, *7*, 229-235.
  Abstract:



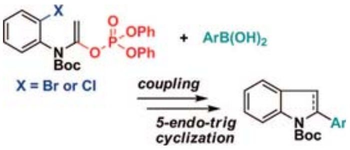
Metal–organic frameworks have demonstrated functionality stemming from both robustness and pliancy and as such, offer promise for a broad range of new materials. The flexible aspect of some of these solids is intriguing for so-called 'smart' materials in that they could structurally respond to an external stimulus. Herein, we present an open-channel metal–organic framework that, on dehydration, shifts structure to form closed pores in the solid. This occurs through multiple single-crystal-to-single-crystal transformations such that snapshots of the mechanism of solid-state conversion can be obtained. Notably, the gas composing the atmosphere during dehydration becomes trapped in the closed pores. On rehydration, the pores open to release the trapped gas. Thus, this new material represents a thermally robust and porous material that is also capable of dynamically capturing and releasing gas in a controlled manner.

- Total Synthesis of Spirotenuipesines A and B
  Dai, M.; Krauss I. J.; and Danishefsky, S. J. *J. Org. Chem.* **2008**, *73*, 9576–9583.
  Abstract:



Spirotenuipesines A and B, isolated from the entomopathogenic fungus *Paecilomyces tenuipes* by Oshima and co-workers, have been synthesized. The synthesis features the highly stereoselective construction of two vicinal all-carbon quaternary centers (C5 and C6) via an intramolecular cyclopropanation/radical initiated fragmentation sequence and a diastereoselective intermolecular Diels-Alder reaction between R-methylenelactone dienophile **20** and synergistic diene **6a**. Installation of the C9 tertiary alcohol occurred via nucleophilic methylation. An RCM reaction to produce a tetrasubstituted double bond in the presence of free allylic alcohol and homoallylic oxygenated functional group is also described. This route shortened the synthesis of **11** from 9 steps to 3 steps. We have further developed a strategy to gain access to optically active spirotenuipesines A and B through the synthesis of enantioenriched **10** from commercially available *R*-(-)-epichlorohydrin.

- Synthesis of 2-Substituted Indoles and Indolines via Suzuki-Miyaura Coupling/5-*endo-trig* Cyclization Strategies
  Fuwa, H.; Sasaki, M. *J. Org. Chem.* **2009**, *74*, 212–221.
  Abstract:

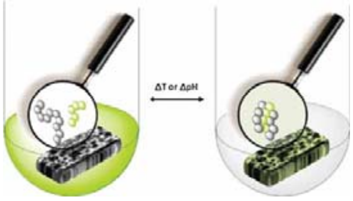


New strategies for the synthesis of 2-substituted indoles and indolines using acyclic, imide-derived enol phosphates, which were readily prepared from *o*-haloanilides, have been developed based on Suzuki-Miyaura coupling-cyclization sequences. A highly chemoselective cross-coupling of imide-derived enol phosphates with boron nucleophiles under Suzuki-Miyaura conditions allowed for the efficient preparation of various *N*-(*o*-halophenyl)enecarbamates that served as useful precursors for subsequent 5-*endo-trig* Heck or 5-*endotrig* aryl radical cyclizations to furnish 2-substituted indoles or indolines, respectively. Furthermore, a one-pot Suzuki-Miyaura coupling-cyclization cascade starting from enol phosphates has been developed, which was successfully applied to the efficient synthesis of an indol-2-yl-1*H*-quinolin-2-one KDR inhibitor.

- Silk as a Biomimetic Ideal for Structural Polymers
  Porter, D.; Vollrath, F. *Adv. Mater*. **2009**, *21*, 487-492.
  Abstract:

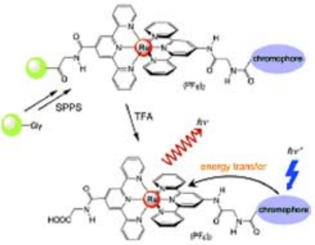
Two factors are critical for understanding silks: the nanoscale semicrystalline folding structure, which gives high strength and toughness, and the degree of hydration of the disordered fraction, which modifies these material properties. The combination of these two factors allows for a massive range of mechanical properties. Understanding and controlling these two factors are the key to the functionality of protein elastomers.

- Reversible Immobilization onto PEG-based Emulsion-templated Porous Polymers by Co-assembly of Stimuli Responsive Polymers.
  Fernández-Trillo, F.; van Hest, J. C. M.; Thies, J. C.; Michon, T.; Weberskirch, R.; Cameron, N. R. *Adv. Mater*. **2009**, *21*, 55-59.
  Abstract:



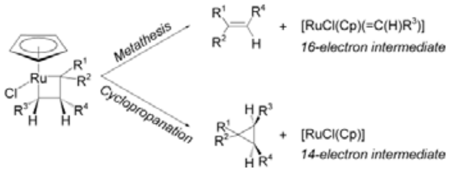
Reversible immobilization onto the surface of highly porous polymers through the co-assembly of stimuli-responsive polymers is explored (see figure). Elastin-based side-chain polymers (EBPs) are prepared by RAFT and attached to the surface of PEG-based emulsion-templated porous polymers, leading to a responsive surface capable of pH-controlled reversible immobilization.

- Solid-Phase Synthesis of Peptide Libraries Combining α-Amino Acids with Inorganic and Organic Chromophores
  Heinze, K.; Hempel, K. *Chem. Eur. J.* **2009**, *15*, 1346-1358.
  Abstract:



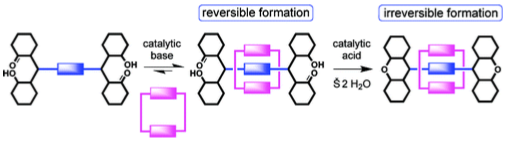
The synthesis of two series of peptidic chains composed of bis(terpyridine)ruthenium(II) acceptor units and organic chromophores (coumarin, naphthalene, anthracene, fluorene) by stepwise solid-phase peptide synthesis (SPPS) techniques is described. The first series of dyads comprises directly amide linked chromophores, while the second one possesses a glycine spacer between the two chromophores. All dyads were studied by UV/Vis and NMR spectroscopy, steady-state luminescence, luminescence decay and electrochemistry, as well as by DFT calculations. The results of these studies indicate weak electronic coupling of the chromophores in the ground state. Absorpion spectra of all dyads are dominated by metal-to-ligand charge-transfer (MLCT) bands around 500 nm. The bichromophoric systems, especially with coumarin as organic chromophore, display additional strong absorptions in the visible spectral region. All complexes are luminescent at room temperature ($^3$MLCT). Efficient quenching of the fluorescence of the organic chromophore by the attached ruthenium complex is observed in all dyads. Excitation spectra indicate energy transfer from the organic dye to the ruthenium chromophore.

- Reactions of Diazo Compounds with Alkenes Catalysed by [RuCl(cod)(Cp)]: Effect of the Substituents in the Formation of Cyclopropanation or Metathesis Products
  Basato, M.; Tubaro, C.; Biffis, A.; Bonato, M.; Buscemi, G.; Lighezzolo, F.; Lunardi, P.; Vianini, C.; Benetollo, F.; Del Zotto, A. *Chem. Eur. J.* **2009**, *15*, 1516-1526.
  Abstract:



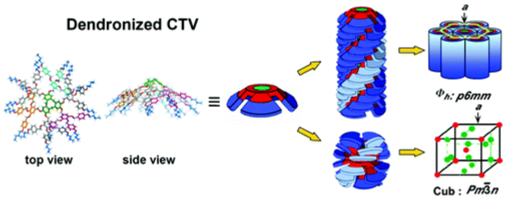
The reaction of diazo compounds with alkenes catalysed by complex [RuCl(cod)(Cp)] (cod=1,5-cyclooctadiene, Cp=cyclopentadienyl) has been studied. The catalytic cycle involves in the first step the decomposition of the diazo derivative to afford the reactive [RuCl(Cp){$=$C(R$^1$)R$^2$}] intermediate and a mechanism is proposed for this step based on a kinetic study of the simple coupling reaction of ethyl diazoacetate. The evolution of the Ru-carbene intermediate in the presence of alkenes depends on the nature of the substituents at both the diazo $N_2{=}C(R^1)R^2$ (R$^1$, R$^2$=Ph, H; Ph, $CO_2Me$; Ph, Ph; C(R$^1$)R$^2$=fluorene) and the olefin substrates $R^3(H)C{=}C(H)R^4$ (R$^3$, R$^4$=$CO_2Et$, $CO_2Et$; Ph, Ph; Ph, Me; Ph, H; Me, Br; Me, CN; Ph, CN; H, CN; CN, CN). A remarkable reactivity of the complex was recorded, especially towards unstable aryldiazo compounds and electron-poor olefins. The results obtained indicate that either cyclopropanation or metathesis products can be formed: the first products are favoured by the presence of a cyano substituent at the double bond and the second ones by a phenyl.

- An Approach to Thermodynamically Controlled Supramolecular Assembly Possessing an Integral Locking Mechanism
  Cagulada, A. M.; Hamilton, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 902–903.
  Abstract:



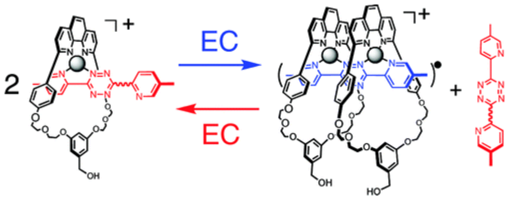
A general approach for thermodynamically controlled molecular assembly employing carbonyl addition chemistry is exemplified with a prototypical rotaxane synthesis. Recognition−driven assembly of the rotaxane proceeds under conditions of mild base catalysis, while subsequent treatment with catalytic acid triggers a dehydrative locking mechanism and fixes the evolved molecular architecture in place.

- Self-Assembly of Dendritic Crowns into Chiral Supramolecular Spheres
  Percec, V.; Imam, M. R.; Peterca, M.; Wilson, A.; Heiney, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 1294–1304.
  Abstract:



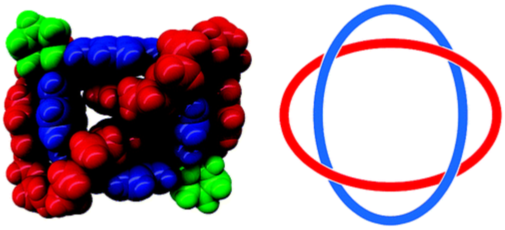
The synthesis and structural and retrostructural analysis of a library of dendronized cyclotriveratrylene containing seven nonchiral and seven chiral self-assembling dendrons is reported. These dendronized cyclotriveratrylenes exhibit a crown conformation that we named dendritic crown. Selected examples of dendritic crowns self-assemble into helical pyramidal columns that self-organize into columnar crystals or into 2-D columnar hexagonal lattices with intracolumnar order. A second group of dendritic crowns self-assembles into helical pyramidal columns and spherical supramolecular dendrimers that self-organize into cubic and tetragonal lattices. A third group of dendritic crowns self-assembles only in spherical supramolecular dendrimers. The helical pyramidal columns and spherical supramolecular dendrimers assembled from dendronized cyclotriveratrylene containing nonchiral dendrons are chiral but racemic while those generated from chiral dendrons exhibit amplified chirality. Structural analysis by a combination of X-ray diffraction methods and CD experiments demonstrated a new mechanism for the assembly of chiral supramolecular spheres that involves an intramolecular structure containing short fragments of helical pyramidal columns.

- Reduction of a Redox-Active Ligand Drives Switching in a Cu(I) Pseudorotaxane by a Bimolecular Mechanism
  McNitt, K. A.; Parimal, K.; Share, A. I.; Fahrenbach, A. C.; Witlicki, E. H.; Pink, M.; Bediako, D. K.; Plaisier, C. L.; Le, N.; Heeringa, L. P.; Vander Griend, D. A.; Flood, A. H. *J. Am. Chem. Soc.* 2009, *131*, 1305–1313.
  Abstract:



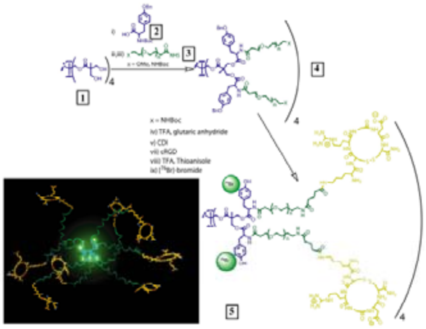
The reduction of a redox-active ligand is shown to drive reversible switching of a Cu(I) [2]pseudorotaxane (**[2]PR**$^{+}$) into the reduced [3]pseudorotaxane (**[3]PR**$^{+}$) by a bimolecular mechanism. The unreduced pseudorotaxanes **[2]PR**$^{+}$ and **[3]PR**$^{2+}$ are initially self-assembled from the binucleating ligand, 3,6-bis(5-methyl-2-pyridine)-1,2,4,5-tetrazine (**Me$_2$BPTZ**), and a preformed copper-macrocycle moiety (Cu-**M**$^{+}$) based on 1,10-phenanthroline. X-ray crystallography revealed a *syn* geometry of the **[3]PR**$^{2+}$. The UV−vis−NIR spectra show low-energy metal-to-ligand charge-transfer transitions that red shift from 808 nm for **[2]PR**$^{+}$ to 1088 nm for **[3]PR**$^{2+}$. Quantitative analysis of the UV−vis−NIR titration shows the stepwise formation constants to be $K_1 = 8.9 \times 10^8$ M$^{-1}$ and $K_2 = 3.1 \times 10^6$ M$^{-1}$, indicative of negative cooperativity. The cyclic voltammetry (CV) and coulometry of **Me$_2$BPTZ**, **[2]PR**$^{+}$, and **[3]PR**$^{2+}$ shows the one-electron reductions at $E_{1/2} = -0.96, -0.65$, and $-0.285$ V, respectively, to be stabilized in a stepwise manner by each Cu$^{+}$ ion. CVs of **[2]PR**$^{+}$ show changes with scan rate consistent with an EC mechanism of supramolecular disproportionation after reduction: **[2]PR**$^{0}$ + **[2]PR**$^{+}$ = **[3]PR**$^{+}$ + **Me$_2$BPTZ**$^{0}$ ($K_D$*, $k_d$). UV−vis−NIR spectroelectrochemistry was used to confirm the 1:1 product stoichiometry for **[3]PR**$^{+}$:**Me$_2$BPTZ**. The driving force ($\Delta G_D$* = −5.1 kcal mol$^{-1}$) for the reaction is based on the enhanced stability of the reduced **[3]PR**$^{+}$ over reduced **[2]PR**$^{0}$ by 365 mV (8.4 kcal mol$^{-1}$). Digital simulations of the CVs are consistent with a bimolecular pathway ($k_d$ = 12⍰000 s$^{-1}$ M$^{-1}$). Confirmation of the mechanism provides a basis to extend this new switching modality to molecular machines.

- A New Doubly Interlocked [2]Catenane
  Peinador, C.; Blanco, V.; Quintela, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 920–921.
  Abstract:



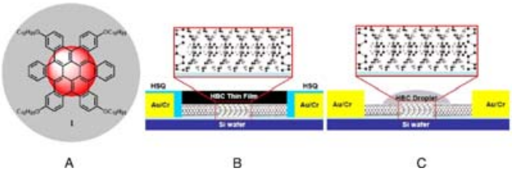
The synthesis and the crystal structure of a doubly braided [2]catenane, a new molecular Solomon link, obtained by a 5-component-self-assembly process based on coordinative bonds, π-donor/π-acceptor interactions, and hydrogen bonding is reported.

- Biodegradable dendritic positron-emitting nanoprobes for the noninvasive imaging of angiogenesis
  Almutairi, A.; Rossin, R.; Shokeen, M.; Hagooly, A.; Ananth, A.; Capoccia, B.; Guillaudeu, S.; Abendschein, D.; Anderson, C. J.; Welch, M. J.; Fréchet, J. M. J. *Proc. Nat. Acad. Sci.* **2009**, *106*, 685–690.
  Abstract:



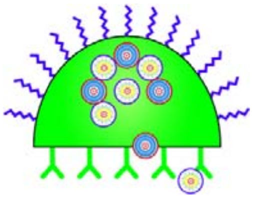
A biodegradable positron-emitting dendritic nanoprobe targeted at $\alpha_v\beta_3$ integrin, a biological marker known to modulate angiogenesis, was developed for the noninvasive imaging of angiogenesis. The nanoprobe has a modular multivalent core-shell architecture consisting of a biodegradable heterobifunctional dendritic core chemoselectively functionalized with heterobifunctional polyethylene oxide (PEO) chains that form a protective shell, which imparts biological stealth and dictates the pharmacokinetics. Each of the 8 branches of the dendritic core was functionalized for labeling with radiohalogens. Placement of radioactive moieties at the core was designed to prevent in vivo dehalogenation, a potential problem for radiohalogens in imaging and therapy. Targeting peptides of cyclic arginine–glycine–aspartic acid (RGD) motifs were installed at the terminal ends of the PEO chains to enhance their accessibility to $\alpha_v\beta_3$ integrin receptors. This nanoscale design enabled a 50-fold enhancement of the binding affinity to $\alpha_v\beta_3$ integrin receptors with respect to the monovalent RGD peptide alone, from 10.40 nM to 0.18 nM $IC_{50}$. Cell-based assays of the $^{125}$I-labeled dendritic nanoprobes using $\alpha_v\beta_3$-positive cells showed a 6-fold increase in $\alpha_v\beta_3$ receptor-mediated endocytosis of the targeted nanoprobe compared with the nontargeted nanoprobe, whereas $\alpha_v\beta_3$-negative cells showed no enhancement of cell uptake over time. In vivo biodistribution studies of $^{76}$Br-labeled dendritic nanoprobes showed excellent bioavailability for the targeted and nontargeted nanoprobes. In vivo studies in a murine hindlimb ischemia model for angiogenesis revealed high specific accumulation of $^{76}$Br-labeled dendritic nanoprobes targeted at $\alpha_v\beta_3$ integrins in angiogenic muscles, allowing highly selective imaging of this critically important process.

- Photoresponsive nanoscale columnar transistors
  Guo, X.; Xiao, S.; Myers, M.; Miao, Q.; Steigerwald, M. L.; Nuckolls, C. *Proc. Nat. Acad. Sci.* **2009**, *106*, 691–696.
  Abstract:



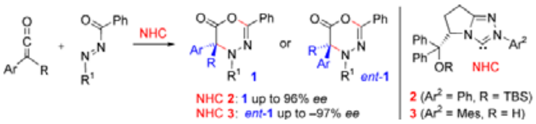
This study reports a general methodology for making stable high-performance photosensitive field effect transistors (FET) from self-assembled columns of polycyclic aromatic hydrocarbons by using single-walled carbon nanotubes (SWNTs) as point contacts. In particular, the molecules used in this work are liquid crystalline materials of tetra(dodecyloxy)hexabenzocoronenes (HBCs) that are able to self-organize into columnar nanostructures with a diameter similar to that of SWNTs and then form nanoscale columnar transistors. To rule out potential artifacts, 2 different structural approaches were used to construct devices. One approach is to coat thin films of HBCs onto the devices with the SWNT–metal junctions protected by hydrogensilsesquioxane resin (HSQ), and the other is to place a droplet of HBC exactly on the nanogaps of SWNT electrodes. Both types of devices showed typical FET behaviors, indicating that SWNT–molecule–SWNT nanojunctions are responsible for the electrical characteristics of the devices. After thermally annealing the devices, HBC molecules assembled into columnar structures and formed more efficacious transistors with increased current modulation and higher gate efficiency. More interestingly, when the devices were exposed to visible light, photocurrents with an on/off ratio of >3 orders of magnitude were observed. This study demonstrates that stimuli-responsive nanoscale transistors have the potential applications in ultrasensitive devices for environmental sensing and solar energy harvesting.

- Nanomedicine - Challenge and Perspectives
  Riehemann, K.; Schneider, S. W.; Luger, T. A.; Godin, B.; Ferrari, M.; Fuchs, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 872 – 897.
  Abstract:



**Future of nanomedicine**: Multiple functions can be integrated into nanoparticle systems for drug delivery. The schematic representation of a third-generation nanovector illustrates this: On the outside are recognition units to interact with target cells and biological barriers, while inside are drug-loaded nanoparticles, which leave the vector at the correct moment and release their load.

- [4+2] Cycloaddition of Ketenes with N-Benzoyldiazenes Catalyzed by N-Heterocyclic Carbenes
  Huang, X.-L.; He, L.; Shao, P.-L.; Ye, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 192 –195.
  Abstract:



**Enantioselectivity switch**: A catalytic enantioselective [4+2] cycloaddition reaction of alkylarylketenes with *N*-aryl-*N*′-benzoyldiazenes or *N*,*N*′-dibenzoyldiazenes to give 1,3,4-oxadiazin-6-ones **1** was developed by employing N-heterocyclic carbene (NHC) catalysts. The enantioselectivities could be switched for most reactions by changing the substituents on the NHC catalyst. TBS=*tert*-butyldimethylsilyl, Mes=2,4,6-trimethylphenyl