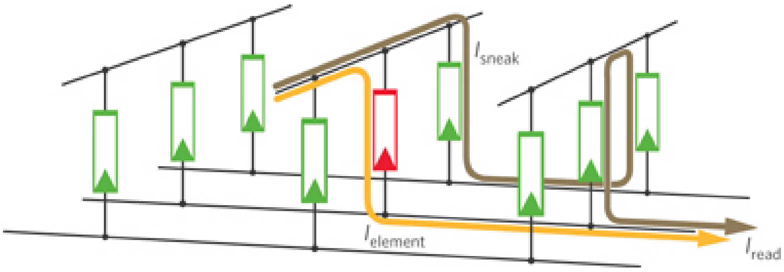
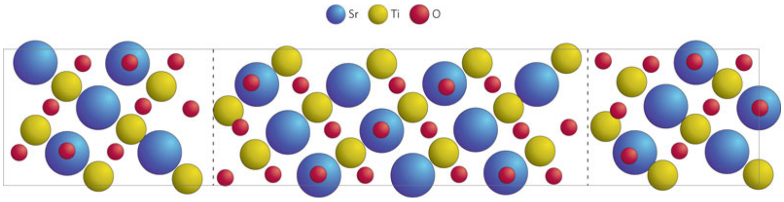
- Complementary resistive switches for passive nanocrossbar memories
  Linn, E.; Rosezin, R.; Kügeler, C.; Waser, R. *Nature Materials* **2010**, *9*, 403-406.
  Abstract:



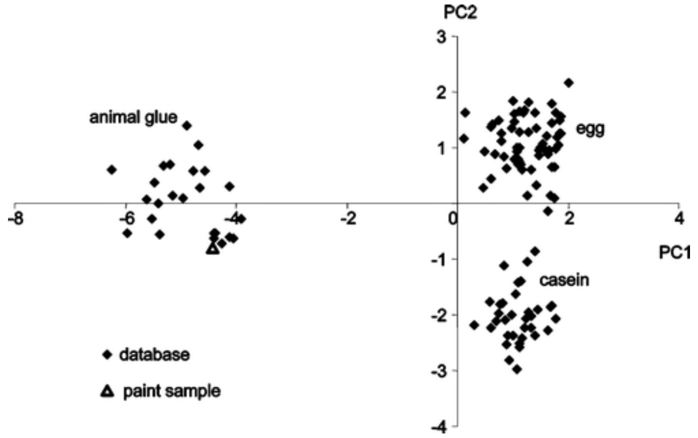
On the road towards higher memory density and computer performance, a significant improvement in energy efficiency constitutes the dominant goal in future information technology. Passive crossbar arrays of memristive elements were suggested a decade ago as non-volatile random access memories (RAM) and can also be used for reconfigurable logic circuits. As such they represent an interesting alternative to the conventional von Neumann based computer chip architectures. Crossbar architectures hold the promise of a significant reduction in energy consumption because of their ultimate scaling potential and because they allow for a local fusion of logic and memory, thus avoiding energy consumption by data transfer on the chip. However, the expected paradigm change has not yet taken place because the general problem of selecting a designated cell within a passive crossbar array without interference from sneak-path currents through neighbouring cells has not yet been solved satisfactorily. Here we introduce a complementary resistive switch. It consists of two antiserial memristive elements and allows for the construction of large passive crossbar arrays by solving the sneak path problem in combination with a drastic reduction of the power consumption.

- Structure Predictions: The genetics of grain boundaries
  Carter, W. C. *Nature Materials* 2010, 9, 383-385.
  Abstract:



The prediction of interface structures is an uncertain and time-consuming task. A technique merging ab initio calculations with a genetic algorithm simplifies the process and provides suitable solutions of the atomic structures that would be hard to envisage a priori.

- Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography/Mass Spectrometry
  Colombini, M. P.; Andreotti, A.; Bonaduce, I.; Modugno, F.; Ribechini, E. *Acc. Chem. Res.* **2010**, *43*, 715–727.
  Abstract:



Throughout history, artists have experimented with a variety of organic-based natural materials, using them as paint binders, varnishes, and ingredients for mordants in gildings. Artists often use many layers of paint to produce particular effects. How we see a painting is thus the final result of how this complex, highly heterogeneous, multimaterial, and multilayered structure interacts with light.

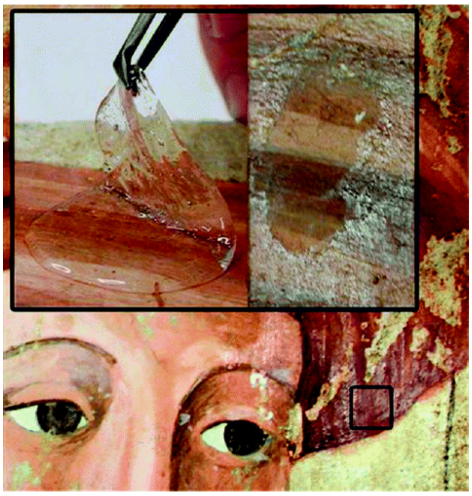
The chemical characterization of the organic substances in paint materials is of great importance for artwork conservation because the organic components of the paint layers are particularly subject to degradation. In addition, understanding the organic content and makeup of paint materials allows us to differentiate between the painting techniques that have been used over history.

Applying gas chromatography/mass spectrometry (GC/MS) analysis to microsamples of paint layers is widely recognized as the best approach for identifying organic materials, such as proteins, drying oils, waxes, terpenic resins, and polysaccharide gums. The method provides essential information for reconstructing artistic techniques, assessing the best conditions for long-term preservation, and planning restoration.

In this Account, we summarize the more common approaches adopted in the study of the organic components of paint materials. Our progress in developing GC/MS analytical procedures in the field of cultural heritage is presented, focusing on problems that arise from (i) the presence of mixtures of many chemically complex and degraded materials, (ii) the interference of inorganic species, (iii) the small size of the samples, and (iv) the risk of contamination. We outline some critical aspects of the analytical strategy, such as the need to optimize specific wet-chemical sample pretreatments in order to separate the various components, hydrolyze macromolecular analytes, clean-up inorganic ions, and derivatize polar molecules for subsequent GC/MS separation and identification. We also discuss how to interpret the chromatographic data so as to be able to identify the materials. This identification is based on the presence of specific biomarkers (chemotaxonomy), on the evaluation of the overall chromatographic profile, or on the quantitative analysis of significant compounds.

GC/MS-based analytical procedures have for 20 years provided important contributions to conservation science, but challenges and opportunities still coexist in the field of organic-based paint materials. We give selected examples and provide case studies showing how a better understanding of the chemical composition of organic paint materials and of their degradation pathways contribute to a better knowledge our cultural heritage, and to its preservation for future generations.

- New Frontiers in Materials Science for Art Conservation: Responsive Gels and Beyond
  Carretti, E.; Bonini, M.; Dei, L.; Berrie, B. H.; Angelova, L. V.; Baglioni, P.; Weiss, R. G. *Acc. Chem. Res.* **2010**, *43*, 751–760.
  Abstract:



The works of art and artifacts that constitute our cultural heritage are subject to deterioration, both from internal and from external factors. Surfaces that interact with the environment are the most prone to aging and decay; accordingly, soiling is a prime factor in the degradation of surfaces and the attendant disfigurement of a piece. Coatings that were originally intended to protect or contribute aesthetically to an artwork should be removed if they begin to have a destructive impact on its appearance or surface chemistry.

Since the mid-19th century, organic solvents have been the method of choice for cleaning painted surfaces and removing degraded coatings. Care must be taken to choose a solvent mixture that minimizes swelling of or leaching from the original paint films, which would damage and compromise the physical integrity of all the layers of paint. The use of gels and poultices, first advocated in the 1980s, helps by localizing the solvent and, in some cases, by reducing solvent permeation into underlying paint layers. Unfortunately, it is not always easy to remove gels and their residues from a paint surface.

In this Account, we address the removal problem by examining the properties of three classes of innovative gels for use on artwork−rheoreversible gels, magnetic gels, and “peelable” gels. Their rheological properties and efficacies for treating the surfaces of works have been studied, demonstrating uniquely useful characteristics in each class:

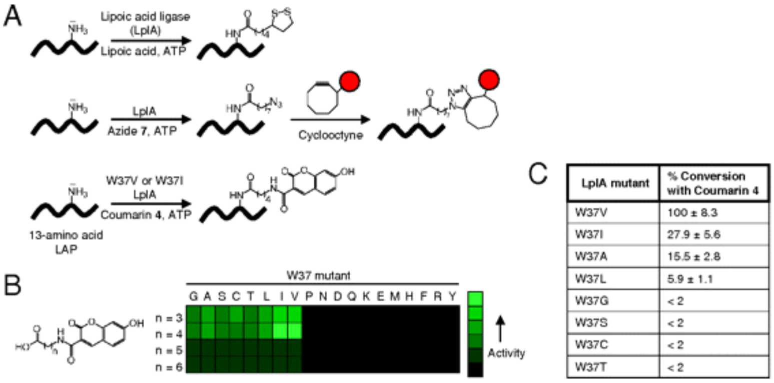
(1) Rheoreversible gels become free-flowing on application of a chemical or thermal “switch”. For art conservation, a chemical trigger is preferred. Stable gels formed by bubbling CO2 through solutions of polyallylamine or polyethylenimines (thereby producing ammonium carbamates, which act as chain cross-links) can be prepared with a wide range of solvent mixtures. After solubilization of varnish and dirt, addition of a weak acid (mineral or organic) displaces the CO2, and the resulting free-flowing liquid can be removed gently.

(2) Incorporation of magnetic, coated-ferrite nanoparticles into polyacrylamide gels adds functionality to a versatile system comprising oil-in-water microemulsions, aqueous micellar solutions, or xerogels that act as sponges. The ferrite particles allow the use of magnets both to place the gels precisely on a surface and to lift them from it after cleaning.

(3) Novel formulations of poly(vinyl alcohol)−borate gels, which accept a range of organic cosolvents, show promise for swelling and dissolving organic coatings. This family of gels can be quite stiff but can be spread. They are non-sticky and have sufficient strength to be removed by peeling or lifting them from a sensitive surface.

These three classes of gels are potentially very important soft materials to augment and improve the range of options available for conserving cultural heritage, and their interesting chemical–physical properties open a rich area for future scientific investigation.

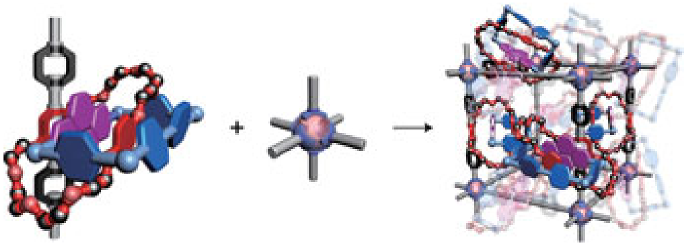
- A fluorophore ligase for site-specific protein labeling inside living cells
  Uttamapinant, C.; White, K. A.; Baruah, H.; Thompson, S.; Fernández-Suárez, M.; Puthenveetil, S.; Ting, A. Y. *Proc. Nat. Acad. Sci.* **2010**, *107*, 10914-10919.
  Abstract:



LplA mutant	% Conversion with Coumarin 4
W37V	100 ± 8.3
W37I	27.9 ± 5.6
W37A	15.5 ± 2.8
W37L	5.9 ± 1.1
W37G	< 2
W37S	< 2
W37C	< 2
W37T	< 2

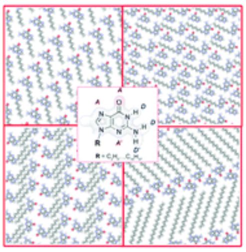
Biological microscopy would benefit from smaller alternatives to green fluorescent protein for imaging specific proteins in living cells. Here we introduce PRIME (PRobe Incorporation Mediated by Enzymes), a method for fluorescent labeling of peptide-fused recombinant proteins in living cells with high specificity. PRIME uses an engineered fluorophore ligase, which is derived from the natural *Escherichia coli* enzyme lipoic acid ligase (LplA). Through structure-guided mutagenesis, we created a mutant ligase capable of recognizing a 7-hydroxycoumarin substrate and catalyzing its covalent conjugation to a transposable 13-amino acid peptide called LAP (LplA Acceptor Peptide). We showed that this fluorophore ligation occurs in cells in 10 min and that it is highly specific for LAP fusion proteins over all endogenous mammalian proteins. By genetically targeting the PRIME ligase to specific subcellular compartments, we were able to selectively label spatially distinct subsets of proteins, such as the surface pool of neurexin and the nuclear pool of actin.

- Robust dynamics
  Deng, H.; Olson, M. A.; Stoddart, J. F.; Yaghi, O. M. *Nature Chemistry* **2010**, *2*, 439-443.
  Abstract:



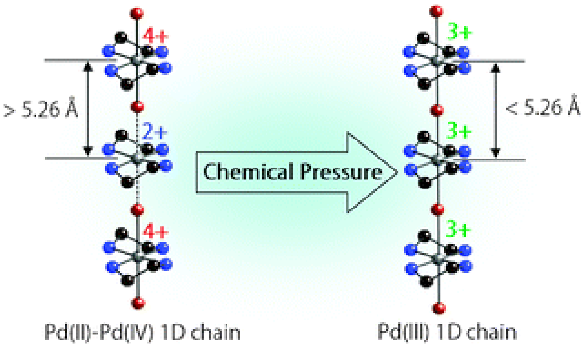
Although metal–organic frameworks are extensive in number and have found widespread applications, there remains a need to add complexity to their structures in a controlled manner. It is inevitable that frameworks capable of dynamics will be required. However, as in other extended structures, when they are flexible, they fail. We propose that mechanically interlocked molecules be inserted covalently into the rigid framework backbone such that they are mounted as integrated components, capable of dynamics, without compromising the fidelity of the entire system. We have coined the term 'robust dynamics' to describe constructs where the repeated dynamics of one entity does not affect the integrity of any others linked to it. The implication of this concept for dynamic molecules, whose performance has the disadvantages of random motion, is to bring them to a standstill in three-dimensional extended structures and thus significantly enhance their order, and ultimately their coherence and performance.

- Nanopatterning the surface with ordered supramolecular architectures of N^9-alkylated guanines: STM reveals.
  Ciesielski, A.; Perone, R.; Pieraccini, S.; Spada, G. P.; Samorì, P. *Chem. Commun*. **2010**, *46*, 4493 – 4495.
  Abstract :



STM study of the self-assembly at the solid–liquid interface of substituted guanines exposing in the N^9-position alkyl side chains with different lengths revealed the formation of distinct crystalline nanopatterns.

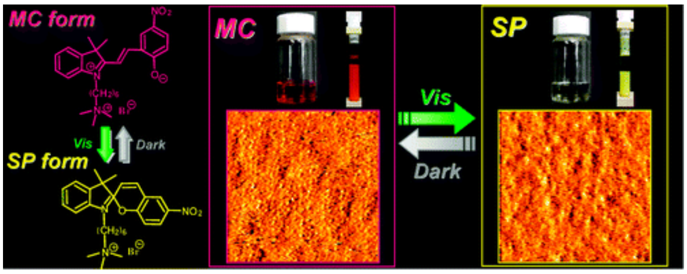
- Stabilization of Pd(III) states in nano-wire coordination complexes
  Yamashita, M.; Takaishi, S. *Chem. Commun.* **2010**, *46*, 4438 – 4448.
  Abstract:



In spite of a long history of quasi-one-dimensional halogen-bridged complexes (MX-chains), all Pt and Pd complexes form the charge-density wave (CDW) state (–$XM^{II}X–M^{IV}$–X), while all Ni complexes form Mott–Hubbard (MH) states (–X–Ni^{III}–X–Ni^{III}–X–), without exception. We have succeeded in stabilizing the Pd(III) MH state for the first time by utilizing the following two methods: partial substitution with Ni(III) ions, $[Ni_{1-}xPdx(chxn)_2Br]Br_2$, and chemical pressure via long alkyl chains introduced as counter-anions, $[Pd(en)_2Br](Cn–Y)_2 \cdot H_2O$. In both systems, it has been revealed that the electronic state of bromo-bridged Pd compounds are determined by the PdPd distances, in other words, CDW and MH states are stabilized when PdPd distances are longer and shorter than 5.26 Å, respectively.

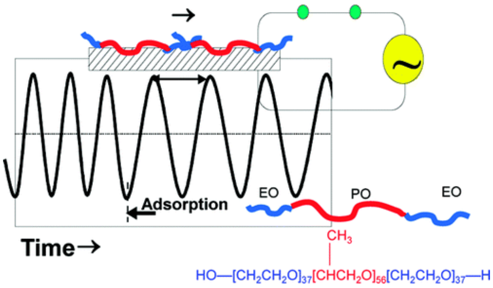
- Adsorption Characteristics of Spiropyran-Modified Cationic Surfactants at the Silica/Aqueous Solution Interface
  Sakai, K.; Imaizumi, Y.; Oguchi, T.; Sakai H.; Abe, M. *Langmuir* **2010**, *26,* 9283–9288.

Abstract:



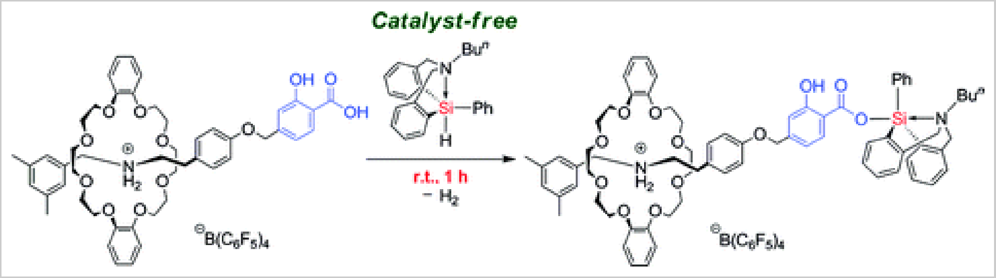
We have characterized the adsorption of a spiropyran-modified cationic surfactant at the silica/aqueous solution interface and the subsequent photoresponsive nature of the adsorbed molecular assemblies. The surfactant used in this study was 1′(6-trimethylammoniohexyl)-3′3′-dimethyl-6-nitrospiro-(2*H*-1-benzopyran-2,2′-indoline) bromide (SP-Me-6). Visible light incident to the aqueous solution of SP-Me-6 results in the isomerization from the merocyanine (MC) form to the spiro (SP) form, whereas the isomerized SP form reverts to the MC form when the surfactant solution is stored in the dark. The adsorption isotherms on colloidal silica particles reveal that the combination of electrostatic and intermolecular hydrophobic interactions drives the adsorption for both of the isomers, and the more hydrophobic SP form gives a greater adsorbed amount when compared with the zwitterionic MC form. In situ atomic force microscopy (AFM) has demonstrated that disklike or flattened spherical surface aggregates are formed in the adsorption plateau region on a flat silica plate, where the SP form gives larger surface aggregates as a result of its greater hydrophobic/associative character. Such a difference in the hydrophobic/associative nature between the two isomers induces reversible changes in the dispersion stability of silica suspensions as well as in the surface force, in response to the photoisomerization. By taking the in situ and ex situ color changes into consideration, it seems likely that the photoisomerization occurs reversibly even after surfactant adsorption on silica.

- Adsorption of a Nonionic Symmetric Triblock Copolymer on Surfaces with Different Hydrophobicity
  Liu, X.; Wu, D.; Turgman-Cohen, S.; Genzer, J.; Theyson, T. W.; Rojas, O. J. *Langmuir* **2010**, *26*, 9565-9574.
  Abstract:



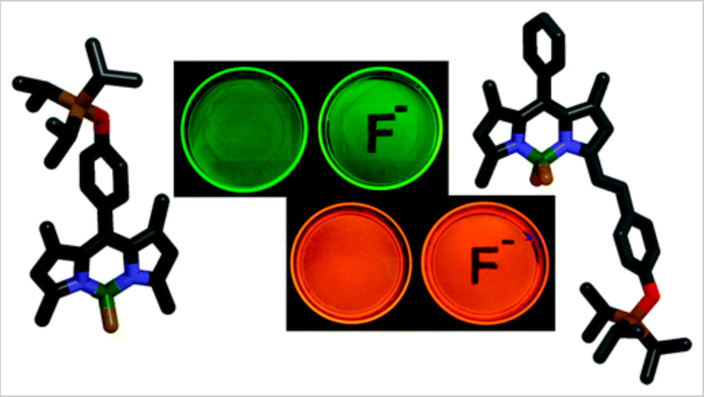
This study investigates the adsorption of a symmetric triblock nonionic polymer comprising ethylene oxide (EO) and propylene oxide (PO) blocks (Pluronic P-105, $EO_{37}PO_{56}EO_{37}$) on a range of substrates including hydrophobic, i.e., polypropylene (PP), poly(ethylene terephthalate) (PET), nylon, and graphite, and hydrophilic, i.e., cellulose and silica. The adsorption process and the structure of the hydrated adsorbed layers are followed by quartz crystal microgravimetry (QCM), surface plasmon resonance (SPR), and atomic force microscopy. The unhydrated surfaces are characterized by ellipsometry and contact angle techniques. The adsorption kinetics and the extent of adsorption are determined by monitoring the changes in resonance frequency and refractive index of sensors coated with ultrathin films of the various substrates. Langmuirian-type adsorption kinetics is observed in all cases studied. The amount of adsorbed Pluronic on hydrophobic polymer surfaces (PP, PET, and nylon) exceeds that on the hydrophilic cellulose. The hydrophobic (graphite) mineral surface adsorbs relatively low polymer mass, typical of a monolayer, while micellar structures are observed on the hydrophilic silica surface. The amount of water coupled to the adsorbed polymer layers is quantified by combining data from QCM, and SPR are found to increase with increasing polarity of the substrate. On the basis of contact angle data, the nonhydrated adsorbed structures produce modest increases in hydrophilicity of all the substrates investigated. Overall, insights are provided into the structure and stability of both hydrated and nonhydrated adsorbed triblock copolymer.

- Catalyst-Free Syntheses of [2]Rotaxanes Utilizing a Pentacoordinated Hydrosilane as an End-Capping Agent
  Domoto, Y.; Fukushima, A.; Kasuga, Y.; Sase, S.; Goto, K.; Kawashima, T. *Org. Lett.* **2010**, *12*, 2586–2589.
  <u>Abstract:</u>



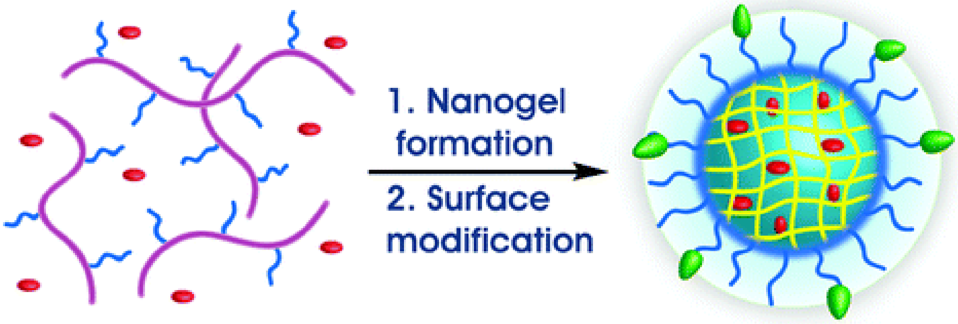
A pentacoordinated hydrosilane activated by an intramolecular nitrogen−silicon dative bond was utilized as an end-capping agent for catalyst-free syntheses of [2]rotaxanes. The end-capping reaction of a pseudo[2]rotaxane bearing a salicylic acid terminus with the pentacoordinated hydrosilane readily proceeded at room temperature to produce the corresponding silyl-capped [2]rotaxane
In summary, the efficient end-capping syntheses of [2]rotaxanes have been achieved by utilizing the high reactivity of a pentacoordinated hydrosilane toward oxygen nucleophiles such as phenol and salicylic acid. This end-capping procedure requires no catalyst and activating agent. Furthermore, the end-capping involving a salicylic acid functionality enabled a quick synthesis of a [2]rotaxane at room temperature. This procedure, which is performable under mild and additive-free conditions, is expected to serve as a promising tool for constructing a wide range of interlocked structures.

- Reaction-Based Sensing of Fluoride Ions Using Built-In Triggers for Intramolecular Charge Transfer and Photoinduced Electron Transfer
  Bozdemir, O. A.; Sozmen, F.; Buyukcakir, O.; Guliyev, R.; Cakmak, Y.; Akkaya, E. U. *Org. Lett.* 2010, *12*, 1400–1403.
  <u>Abstract:</u>



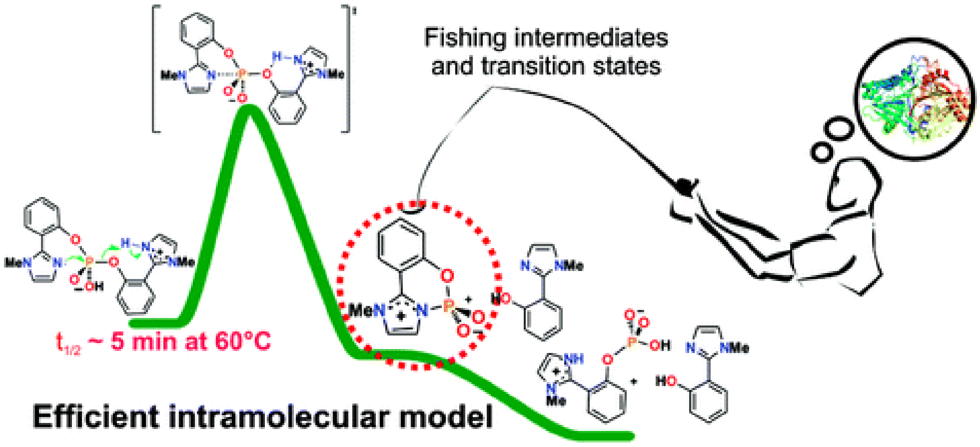
Two Bodipy derivatives with silyl-protected phenolic functionalities signal fluoride concentrations both in solution and in a poly(methyl methacrylate) matrix. The exact location of the "nascent" phenolate group is important. If it is at the *meso* position, photoinduced electron transfer is triggered; however, if it is in full conjugation *via* a styryl moiety to the Bodipy core, strong intramolecular charge transfer is triggered, resulting in a large red shift in the absorbance peak. In either case, a selective methodology for fluoride sensing is the invariable result.

- Surface-Functionalizable Polymer Nanogels with Facile Hydrophobic Guest Encapsulation Capabilities
  Ryu, J.; Jiwpanich, S.; Chacko, R.; Bickerton, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **2010**, *132*, 8246–8247.
  Abstract:



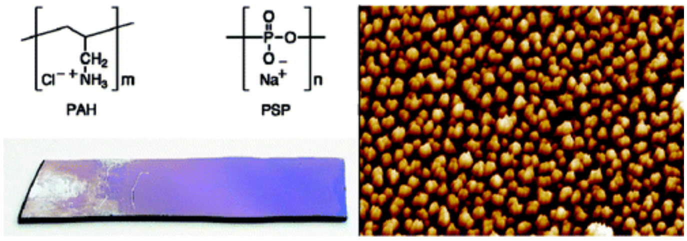
The stability of encapsulation in self-assembly systems is limited during blood circulation because of a requisite concentration for assembly formation. For deliberate molecular design for stable encapsulation, targeting, and triggered release, we have developed a facile synthetic method for highly stable, polymeric nanogels using a simple intra/interchain cross-linking reaction. We show a simple, emulsion-free method for the preparation of biocompatible nanogels that provides the ability to encapsulate hydrophobic guest molecules and surface functionalization which has potential for targeted delivery. We show that the noncovalently encapsulated guest molecules can be released in response to a biologically relevant stimulus.

- Intramolecular Catalysis of Phosphodiester Hydrolysis by Two Imidazoles
  Orth, E. S.; Brandao, T. A. S.; Souza, B. S.; Pliego, J. R.; Vaz, B. G.; Eberlin, M. N.; Kirby, A. J.; Nome, F. *J. Am. Chem. Soc.* **2010**, *132*, 8513–8523.
  Abstract:



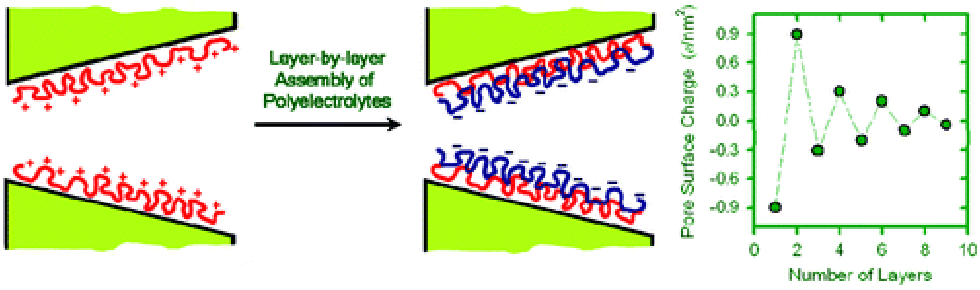
Two imidazole groups act together to catalyze the hydrolysis of the phosphodiester bis(2-(1-methyl-1H-imidazolyl)phenyl) phosphate (BMIPP). A full investigation involving searching computational and electrospray ionization (ESI-MS-/MS) and ultra mass spectrometry (LTQ-FT) experiments made possible a choice between two kinetically equivalent mechanisms. The preferred pathway, involving intramolecular nucleophilic catalysis by imidazole, assisted by intramolecular general acid catalysis by the imidazolium group, offers the first simple model for the mechanism used by the extensive phospholipase D superfamily.

- Step-by-Step Assembly of Self-Patterning Polyelectrolyte Films Violating (Almost) All Rules of Layer-by-Layer Deposition
  Cini, N.; Tulun, T.; Decher, G.; Ball, V. *J. Am. Chem. Soc.* **2010**, *132*, 8264–8265.
  Abstract:



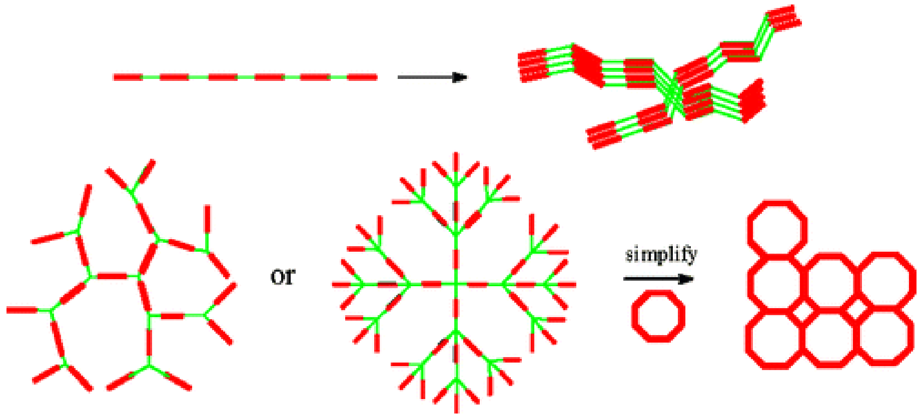
Because of its versatility, the layer-by-layer (LBL) assembly method has become a popular tool for preparing multimaterial films, yet astonishingly little is known about the fundamental rules governing their deposition. Here we show an unusual case of self-patterning LBL films made from poly(allylamine hydrochloride) and poly(sodium phosphate). In such films, both the film thickness and the film roughness increase linearly with the number of deposition steps up to a thickness of ~60 nm. Even more surprising is the fact that the adsorption of individual “layers” of polyanions and polycations proceeds without a regular inversion of the ζ potential and with the occurrence of a growth instability at ~75 layers. These findings underline the need to reconsider the fundamentals of polyelectrolyte multilayer film deposition.

- Layer-by-Layer Assembly of Polyelectrolytes into Ionic Current Rectifying Solid-State Nanopores: Insights from Theory and Experiment
  Ali, M.; Yameen, B.; Cervera, J.; Ramírez, P.; Neumann, R.; Ensinger, W.; Knoll, W.; Azzaroni, O. *J. Am. Chem. Soc.* **2010**, *132*, 8338–8348.
  Abstract:



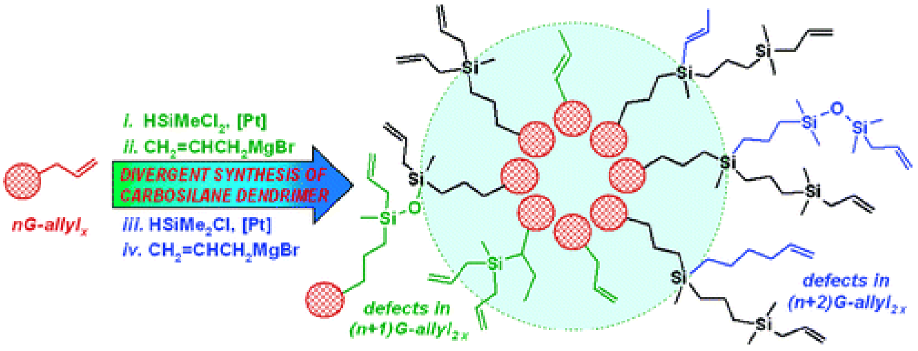
Molecular design of ionic current rectifiers created on the basis of single conical nanopores is receiving increasing attention by the scientific community. Part of the appeal of this topic relies on the interest in sensors and fluidic nanoactuators based on the transport of ions and molecules through nanopore architectures that can readily be integrated into functional systems. The chemical modification of the pore walls controls not only the diameter of these nanoarchitectures but also their selectivity and transport properties. In order to confer selectivity to solid-state nanopores, it is necessary to develop and explore new methods for functionalizing the pore walls. Hence, the creation of functional nanopores capable of acting as selective ion channels or smart nanofluidic sensors depends critically on our ability to assemble and build up molecular architectures in a predictable manner within confined geometries with dimensions comparable to the size of the building blocks themselves. In this context, layer-by-layer deposition of polyelectrolytes offers a straightforward process for creating nanoscopic supramolecular assemblies displaying a wide variety of functional features. In this work, we describe for the first time the integration of layer-by-layer polyelectrolyte assemblies into single conical nanopores in order to study and explore the functional features arising from the creation of charged supramolecular assemblies within the constrained geometry of the nanofluidic device. To address this challenging topic, we used a combined experimental and theoretical approach to elucidate and quantify the electrostatic changes taking place inside the nanopore during the supramolecular assembly process. The multilayered films were built up through consecutive layer-by-layer adsorption of poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) on the pore surface. Our results show that the charge transport properties of single conical nanopores functionalized with PAH/PSS assemblies are highly dependent on the number of layers assembled on the pore wall. In contrast to what happens with PAH/PSS films deposited on planar surfaces (quantitative charge reversal), the surface charge of the pore walls decreases dramatically with the number of PAH/PSS layers assembled into the nanopore. This behavior was attributed to the nanoconfinement-induced structural reorganization of the polyelectrolyte layers, leading to the efficient formation of ion pairs and promoting a marked decrease in the net fixed charges on the nanopore walls. We consider that these results are of paramount relevance for the modification of nanopores, nanopipets, and nanoelectrodes using charged supramolecular assemblies, as well as of importance in “soft nanotechnology” provided that structural complexity, induced by nanoconfinement, can define the functional properties of self-assembled polymeric nanostructures.

- Enhanced Electrical Conductivity by Macromolecular Architecture: Hyperbranched Electroactive and Degradable Block Copolymers Based on Poly(ε-caprolactone) and Aniline Pentamer
  Guo, B.; Finne-Wistrand, A.; Albertsson, A.-C. *Macromolecules* **2010**, *43*, 4472–4480.
  Abstract:



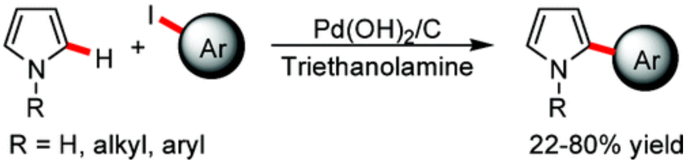
We present macromolecular architecture design as a useful tool to enhance the conductivity of degradable polymers. Linear and hyperbranched copolymers with electrical conductivity and biodegradability were synthesized by an “$A_2 + B_n$ ($n = 2, 3, 4$)” strategy using carboxyl-capped aniline pentamer (CCAP) and branched poly(ε-caprolactone)s (PCLs) by coupling reactions. A more hydrophilic surface and lower crystallinity of the doped emeraldine state of aniline pentamer (EMAP) copolymer was achieved compared with PCLs, and TGA results demonstrated that the CCAP contents in the copolymers were almost the same. The structure of the polymers was characterized by FT-IR, NMR, and SEC. Good electroactivity of the copolymers was confirmed by UV and cyclic voltammetry (CV), and CV showed three pairs of redox peaks. The hyperbranched copolymers had a higher conductivity than the linear ones. It is suggested that the higher conductivity of the hyperbranched copolymer is due to the ordered distribution of peripheral EMAP segments that more easily form a conductive network. Therefore, the conductivity of the polymers is improved and controlled by the macromolecular architecture.

- Structural Defects in Polyallylcarbosilane Dendrimers and Their Polyol Derivatives Characterized by NMR and MALDI-TOF Mass Spectrometry
  Krupkova, A.; Cermak, J. *Macromolecules* **2010**, *43*, 4511–4519.
  Abstract:



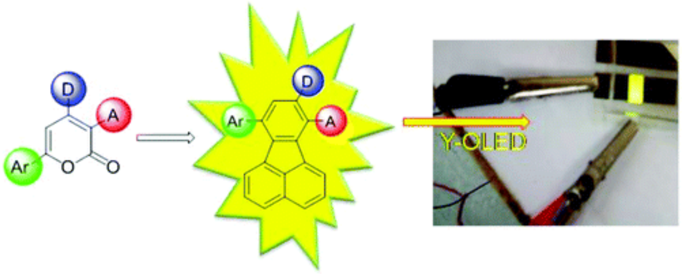
A series of polyallylcarbosilane dendrimers and carbosilane-based dendritic polyols up to third generation was analyzed by means of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and multinuclear NMR spectroscopy to determine the character, origin, and number of structural defects. Besides occasionally reported α-hydrosilylation, several side reactions accompanying hydrosilylation, such as isomerization of terminal double bonds, were detected during the synthesis of carbosilane skeleton. Despite increased steric hindrance, internal double bonds react in subsequent addition reactions. Depending on the synthetic sequence applied, the retained reactivity of the internal double bonds can lead either to suppression of the defect in the next generation or to creation of more significant defects such as dendrimer dimers. Hydroboration of allyl groups using dicyclohexylborane proceeded with near quantitative conversion; a small amount of hydrolysis accompanying the following oxidation step producing nonreactive alkyl groups at the periphery was detected.

- Triethanolamine-Mediated Palladium-Catalyzed Regioselective C-2 Direct Arylation of Free NH-Pyrroles
  Jafarpour, F.; Rahiminejadan, S.; Hazrati, H. *J. Org. Chem.* **2010**, *75*, 3109–3112.
  <u>Abstract:</u>



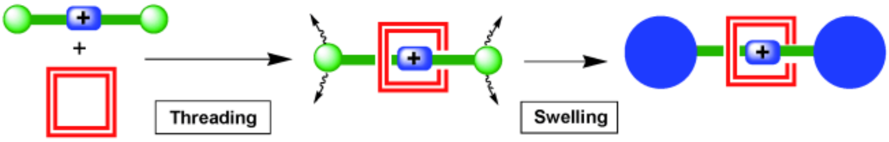
An atom-economical phosphane-free palladium-catalyzed direct C-2 arylation of unactivated free NH-pyrroles is devised. This method provides a straithforward route to a wide variety of substituted 2-aryl-1*H*-pyrroles from readily accessible starting materials. Iodoarenes bearing electron-withdrawing and electron-donating substituents are tolerated under the presented reaction conditions. The scope of the reaction is also expanded to *N*-aryl and -alkylpyrroles albeit in lower yields.

- Synthesis, Electrochemical and Optical Properties of Stable Yellow Fluorescent Fluoranthenes
  Goel, A.; Kumar, V.; Chaurasia, S.; Rawat, M.; Prasad, R.; Anand, R. S. *J. Org. Chem.* **2010**, *75*, 3656–3662.
  <u>Abstract:</u>



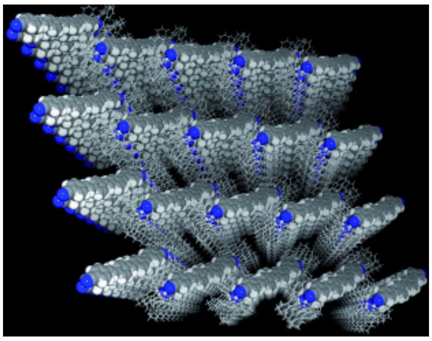
A novel series of thermally stable yellow light emitting fluoranthenes with an amine donor and a nitrile acceptor was prepared from a ketene-*S*,*S*-acetal under mild conditions without using an organometal catalyst. The organic light emitting device of yellow fluoranthene **10b** exhibited substantially low turn-on voltage (2.6 V) and maximum brightness of 470 Cd/m^2 with luminance efficiency of 2.0 Cd/A without using any dopant.

- Using a Threading-Followed-by-Swelling Approach to Synthesize [2]Rotaxanes
  Ko, J.-L.; Ueng, S.-H.; Chiu, C.-W.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Chem. Eur. J.* **2010**, *16*, 6950-6960.
  <u>Abstract:</u>



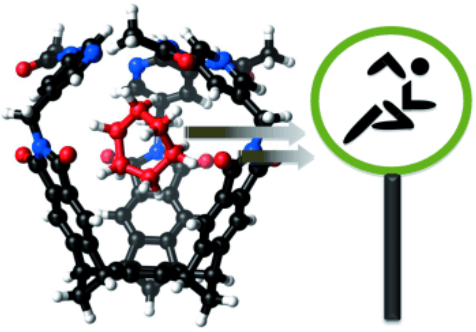
We have developed a "threading-followed-by-swelling" protocol to synthesize [2]rotaxanes efficiently and atom economically. Our protocol employs *cis*-1-[(*Z*)-alk-1´-enyl]-2-vinylcyclopropane units as the termini of the threadlike components; these end groups are converted into more-sizable cycloheptadiene motifs, which function as stopper units, through Cope rearrangements at elevated temperature. We used this approach to synthesize [2]rotaxanes in good yield from [2]pseudorotaxanes featuring either one or two swellable termini to interlock three different types of macrocycle. The chiral centers created by the swelling process were "erased" by hydrogenating the cycloheptadiene termini into the corresponding cycloheptane units, affording achiral molecular [2]rotaxanes as the only final products.

- Coordination-Driven Hierarchical Organization of π-Conjugated Systems: From Molecular to Supramolecular π-Stacked Assemblies
  Yao, Y.; Shen, W.; Nohra, B.; Lescop, C.; Réau, R. *Chem. Eur. J.* **2010**, *16*, 7143-7163.
  Abstract:



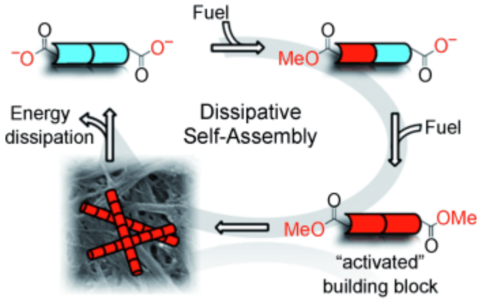
The reaction of U-shaped, bimetallic, Cu^{I} complexes, assembled from a heteroditopic pincer, with cyano-capped π-conjugated linkers gives a straightforward access to π-stacked metallocyclophanes in good yields. In these assemblies, the π-walls have an almost face-to-face arrangement. The versatility of this rational supramolecular synthesis is demonstrated with the use of linkers that have nanoscale lengths (up to 27.7 Å), different chemical compositions (oligo(*para*-phenylenevinylene)s OPVs, oligo(phenylene)s, oligo(phenylethynylene)s), and alternative geometries (linear, angular). Linkers that incorporate an internal pyridyne moiety can also be employed. X-ray diffraction studies revealed that the metallocyclophanes based on linear linkers self-organize into infinite π-stacked columns in the solid state with intermolecular distances of about 3.6 Å. This approach, based on coordination-driven self-assembly, provides a novel and rational strategy for the stacking of extended π-systems in the solid state.

- Molecular Recognition of a Transition State
  Bao, X.; Rieth, S.; Stojanovic, S.; Hadad, C. M.; Badjic, J. D. *Angew. Chem. Int. Ed.* **2010,** *49*, 4816 –4819.
  Abstract:



An inside job: The conformational interconversion of cyclohexane occurs at a higher rate in the interior of gated molecular baskets (see picture) than in bulk free solvent or a vacuum. The acceleration results from more favorable noncovalent bonding, and hence stabilization of the transition state, of the encapsulated compound.

- Dissipative Self-Assembly of a Molecular Gelator by Using a Chemical Fuel
  Boekhoven, J.; Brizard, A. M.; Kowlgi, K. N. K.; Koper, G. J. M.; Eelkema, R.; van Esch, J. H. *Angew. Chem. Int. Ed.* **2010,** *49*, 4825 –4828.
  Abstract:



Fueling the future: A fibrillar network (red fibers, see figure) is formed from an activated building block (red), which is obtained from a synthetic gelator (blue) in a dissipative self-assembly process that is fueled by an alkylating agent. When the available energy is depleted, the system reverts to its thermodynamic equilibrium, that is, an isotropic solution.