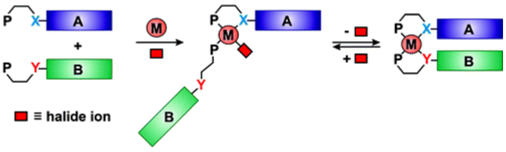
- Heteroligated Supramolecular Coordination Complexes Formed via the Halide-Induced Ligand Rearrangement Reaction
  Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618-1629.
  Abstract:

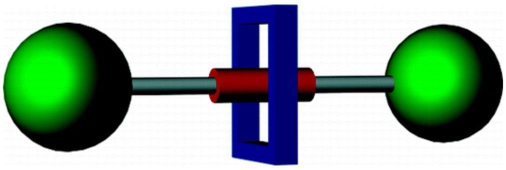


Supramolecular coordination chemistry allows researchers to synthesize higher-order structures that approach the nanoscale dimensions of small enzymes. Frequently, such structures have highly symmetric macrocyclic square or cage shapes. To build functional structures that mimic the complex recognition, catalytic, and allosteric properties of enzymes, researchers must do more than synthesize highly symmetric nanoscale structures. They must also simultaneously incorporate different functionalities into these structures and learn how to regulate their relative arrangement with respect to each other. Designing such *heteroligated* coordination complexes remains a significant challenge for supramolecular chemists.

This Account focuses on the discovery and development of a novel supramolecular reaction known as the halide-induced ligand rearrangement (HILR) reaction. Two hemilabile ligands with different binding strengths combine with d^8 transition metal precursors that contain halide ions. The reaction spontaneously results in heteroligated complexes and is highly modular and general. Indeed, it not only can be used to prepare tweezer complexes but also allows for the rapid and quantitative formation of heteroligated macrocyclic triple-decker/step and rectangular box complexes from a variety of different ligands and transition metal ions. The relative arrangement between functional groups A and B in these structures can be regulated *in situ* using small ancillary ligands such as halides, CO, and nitriles.

Based on this reaction, zinc- and magnesium-porphyrin moieties can be incorporated into heteroligated macrocyclic or tweezer scaffolds. These examples demonstrate the convergent and cofacial assembly of functional sites that are known to be involved in numerous processes in enzymes. They also show how the relative spatial and lateral distances of these sites can be varied, in many cases reversibly. Researchers can use such complexes to study a wide range of enzymatic processes, including catalysis, molecular recognition, electron transfer, and allosteric signal transfer.

- Kinetic and Thermodynamic Approaches for the Efficient Formation of Mechanical Bonds
  Dichtel, W. R.; Miljanić, O. S.; Zhang, W.; Spruell, J. M.; Patel, K.; Aprahamian, I.; Heath, J. R.; Stoddart, J. F. *Acc. Chem. Res.* **2008**, *41*, 1750-1761.
  Abstract:



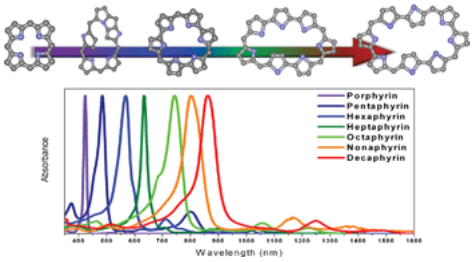
Among the growing collection of molecular systems under consideration for nanoscale device applications, mechanically interlocked compounds derived from electrochemically switchable bistable [2]rotaxanes and [2]catenanes show great promise. These systems demonstrate dynamic, relative movements between their components, such as shuttling and circumrotation, enabling them to serve as stimuli-responsive switches operated via reversible, electrochemical oxidation−reduction

rather than through the addition of chemical reagents. Investigations into these systems have been intense for a number of years, yet limitations associated with their synthesis have hindered incorporation of their mechanical bonds into more complex architectures and functional materials.

We have recently addressed this challenge by developing new template-directed synthetic protocols, operating under both kinetic and thermodynamic control, for the preparation of bistable rotaxanes and catenanes. These methodologies are compatible with the molecular recognition between the π-electron-accepting cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) host and complementary π-electron-donating guests. The procedures that operate under kinetic control rely on mild chemical transformations to attach bulky stoppering groups or perform macrocyclizations without disrupting the host–guest binding of the rotaxane or catenane precursors. Alternatively, the protocols that operate under thermodynamic control utilize a reversible ring-opening reaction of the $CBPQT^{4+}$ ring, providing a pathway for two cyclic starting materials to thread one another to form more thermodynamically stable catenaned products. These complementary pathways generate bistable rotaxanes and catenanes in high yields, simplify mechanical bond formation in these systems, and eliminate the requirement that the mechanical bonds be introduced into the molecular structure in the final step of the synthesis.

These new methods have already been put into practice to prepare previously unavailable rotaxane architectures and novel complex materials. Furthermore, the potential for utilizing mechanically interlocked architectures as device components capable of information storage, the delivery of therapeutic agents, or other desirable functions has increased significantly as a result of the development of these improved synthetic protocols.

- The photophysical properties of expanded porphyrins: relationships between aromaticity, molecular geometry and non-linear optical properties
  Lim, J. M.; Yoon, Z. S.; Shin, J.-Y.; Kim, K. S.; Yoon, M.-Y.; Kim, D. *Chem. Commun.* **2009**, 261 – 273.
  Abstract :

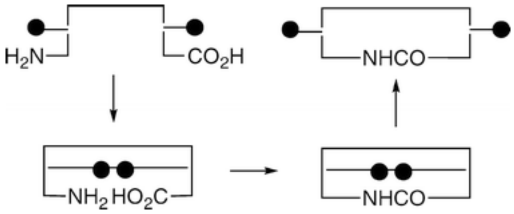


Porphyrins, which consist of four pyrrolic subunits, are a ubiquitous class of naturally occurring compound with versatile photophysical properties. As an extension of the basic structure of the porphyrin macrocycle, there have been a multitude of approaches to synthesize expanded porphyrins with more than four pyrrole rings, leading to the modification of the macrocyclic ring size, planarity, number of -electrons and aromaticity. However, the relationship between the photophysical properties and the structures of expanded porphyrins has not been systematically investigated. The main purpose of this article is to describe the structure–property relationships of a variety of expanded porphyrins based on experimental and theoretical results, which include steady-state and time-resolved spectroscopic characterizations, non-linear absorption ability and nucleus-independent chemical shift calculations.

- Metathesis assisted synthesis of cyclic peptides

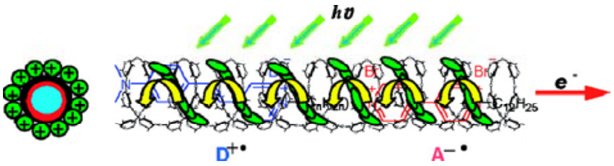
Illesinghe, J.; Guo, C. X.; Garland, R.; Ahmed, A.; Van Lierop, B.; Elaridi, J.; Jackson, W. R.; Robinson, A. J. *Chem. Commun.* **2009**, 295 – 297.

Abstract :



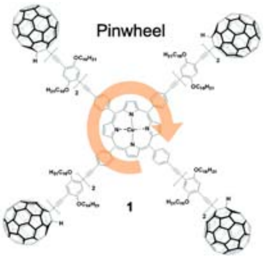
Installation of reversible, metathesis-active tethers into linear peptide sequences can be used to promote formation of cyclic peptide amides and esters.

- Supramolecular Device for Artificial Photosynthetic Mimics As Helix-Mediated Antenna/Reaction Center Ensemble
  Kim, O.-K.; Melinger, J.; Chung, S.-J.; Pepitone, M. *Org. Lett*. **2008**, *10*, 1625-1628.
  Abstract :



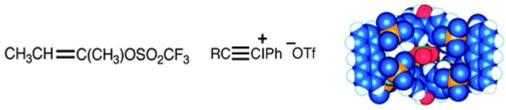
We have developed a novel integrated supramolecular device for a photosynthetic antenna/reaction center (RC) model based on a helical amylose, which plays an important role as the host for cyanine dye J-aggregation onto the helical surface and also for inclusion of a D-A chain chromophore inside the helical cavity, where the J-aggregates function as an array of photoreceptor antenna that funnel excitation across the helix to the chromophore.

- Synthesis of a Porphyrin-Fullerene Pinwheel
  Sasaki, T.; Osgood, A. J.; Kiappes, J. L.; Kelly, K. F.; Tour, J. M. *Org. Lett*. **2008**, *10*, 1377-1380.
  Abstract :



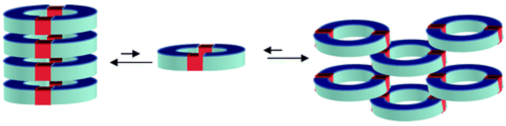
We disclose the synthesis of a porphyrin-fullerene pinwheel that was subsequently observed by scanning tunneling microscopy. The molecule was designed to further our understanding of fullerene-surface interactions, directional control, and surface-rolling versus pivoting capabilities of this class of nanomachines. The inner porphyrin provides the square planar configuration that might lead to realization of the pinwheel spiraling motion on surfaces.

- From Solvolysis to Self-Assembly.
  Stang, P. *J. Org. Chem.* **2009**, *74*, 2–20.
  Abstract:



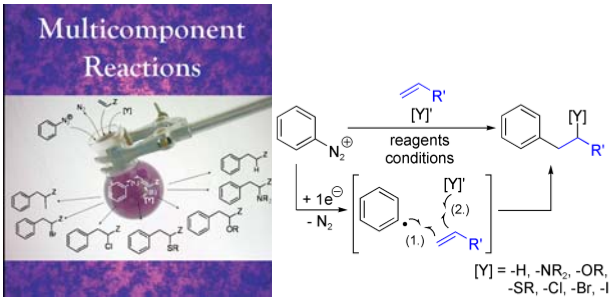
My sojourn from classical physical-organic chemistry and solvolysis to self-assembly and supramolecular chemistry, over the last forty years, is described. My contributions to unsaturated reactive intermediates, namely vinyl cations and unsaturated carbenes, along with my decade-long involvement with polyvalent iodine chemistry, especially alkynyliodonium salts, as well as my more recent research with metal−ligand, coordination driven, and directed self-assembly of finite supramolecular ensembles are discussed.

- Examination of the Structural Features That Favor the Columnar Self-Assembly of Bis-urea Macrocycles.
  Yang, J.; Dewal, M. B.; Sobransingh, D.; Smith, M. D.; Xu, Y.; Shimizu**,** L. S. *J. Org. Chem.* **2009**, *74*, 102–110.
  <u>Abstract:</u>



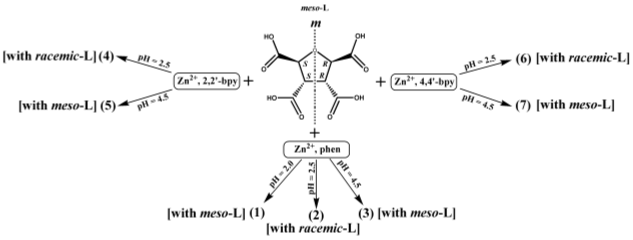
Second-generation self-assembling bis-urea macrocycles were designed that form columnar structures in the solid state. The new macrocycles were constructed from more flexible building blocks yielding greater solubility and a more efficient synthesis. In addition, heteroatoms in the form of ether oxygens were incorporated in the walls of the macrocycles to provide additional recognition sites for guest encapsulation. We observed reduced fidelity of the stacking motif and in some cases the intermolecular urea−urea hydrogen bonds were disrupted by the formation of intramolecular hydrogen bonds. We also observed new offset assembly motifs that maintained the urea−urea interaction. These results suggest that the stacking of the arene units in the rigid first-generation systems was an important factor in guiding the formation of the columnar stacks.

- Intermolecular Olefin Functionalisation Involving Aryl Radicals Generated from Arenediazonium Salts
  Heinrich, M. R. *Chem. Eur. J.* **2009**, *15*, 820 – 833.
  <u>Abstract:</u>



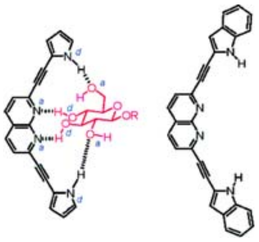
This minireview is aimed at giving an overview of recent advances in olefin functionalisation reactions involving aryl radicals generated from arenediazonium salts. Based on the well-known Meerwein arylation, in which an aryl and a halogen substituent are coupled to an olefinic substrate, new reaction types have been developed that allow the introduction of a broad spectrum of other atoms and functional groups at the place of the original halogen atom and that are applicable to an extended range of olefinic substrates.

- Breaking the Mirror: pH-Controlled Chirality Generation from a *meso* Ligand to a Racemic Ligand
  Zhang, L.; Zhang, J.; Li, Z.-J.; Qin, Y.-Y.; Lin, Q.-P.; Yao, Y.-G. *Chem. Eur. J.* **2009**, *15*, 989-1000.
  Abstract:



To study the conversion from a *meso* form to a racemic form of tetrahydrofurantetracarboxylic acid (H$_4$L), seven novel coordination polymers were synthesized by the hydrothermal reaction of Zn(NO$_3$)$_2$ ·6 H$_2$O with (2*S*,3*S*,4*R*,5*R*)-H$_4$L in the presence of 1,10-phenanthroline (phen), 2,2′-bipyridine (2,2′-bpy), or 4,4′-bipyridine (4,4′-bpy): [Zn$_2${(2*S*,3*S*,4*R*,5*R*)-L}(phen)$_2$(H$_2$O)]·2 H$_2$O (**1**), [Zn$_4${(2*S*,3*R*,4*R*,5*R*)-L}{(2*S*,3*S*,4*S*,5*R*)-L}(phen)$_2$(H$_2$O)$_2$] (**2**), [Zn$_2${(2*S*,3*S*,4*R*,5*R*)-L}(H$_2$O)$_2$]·H$_2$O (**3**), [Zn$_4${(2*S*,3*R*,4*R*,5*R*)-L}{(2*S*,3*S*,4*S*,5*R*)-L} (2,2′-bpy)$_2$(H$_2$O)$_2$]·2 H$_2$O (**4**), [Zn$_2$ {(2*S*,3*S*,4*R*,5*R*)-L}(2,2′-bpy)(H$_2$O)] (**5**), [Zn$_4${(2*S*,3*R*,4*R*,5*R*)-L}{(2*S*,3*S*,4*S*,5*R*)-L} (4,4′-bpy)$_2$(H$_2$O)$_2$] (**6**), and [Zn$_2$ {(2*S*,3*S*,4*R*,5*R*)-L}(4,4′-bpy)(H$_2$O)]· 2 H$_2$O (**7**). These complexes were obtained by control of the pH values of reaction mixtures, with an initial of pH 2.0 for **1**, 2.5 for **2**, **4**, and **6**, and 4.5 for **3**, **5**, and **7**, respectively. The expected configuration conversion has been successfully realized during the formation of **2**, **4**, and **6**, and the enantiomers of L, (2*S*,3*R*,4*R*,5*R*)-L and (2*S*,3*S*,4*S*,5*R*)-L, are trapped in them, whereas L ligands in the other four complexes retain the original *meso* form, which indicates that such a conversion is possibly pH controlled. Acid-catalyzed enol-keto tautomerism has been introduced to explain the mechanism of this conversion. Complex **1** features a simple 1D metal-L chain that is extended into a 3D supramolecular structure by π-π packing interactions between phen ligands and hydrogen bonds. Complex **2** has 2D racemic layers that consist of centrosymmetric bimetallic units, and a final 3D supramolecular framework is formed by the interlinking of these layers through π-π packing interactions of phen. Complex **3** is a 3D metal-organic framework (MOF) involving *meso*-L ligands, which can be regarded as (4,6)-connected nets with vertex symbol (4^5.6)(4^7.6^8). Complexes **4** and **5** contain 2D racemic layers and (6,3)-honeycomb layers, respectively, both of which are combined into 3D supramolecular structures through π-π packing interactions of 2,2′-bpy. The structure of complex **6** is a 2D network formed by 4,4′-bpy bridging 1D tubes, which consist of metal atoms and enantiomers of L. These layers are connected through hydrogen bonds to give the final 3D porous supramolecular framework of **6**. Complex **7** is a 3D MOF with novel (3,4,5)-connected (6^3)(4^2.6^4)(4^2.6^6.8^2) topology. The thermal stability of these compounds was also investigated.

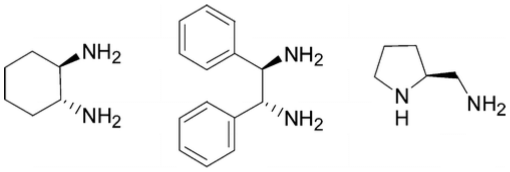
- Chirality-Sensing Supramolecular Systems
  Hembury, G. A.; Borovkov, V. V.; Inoue, Y. *Chem. Rev.* **2008**, *108*, 1-73.
  Abstract:



Chirality that is induced, monitored, controlled, or applied via the principles of a supramolecular approach is a modern interdisciplinary field of research that deals with asymmetry information transfer within multimolecular systems via noncovalent interactions. Since a chiral supramolecular sensing event may profoundly affect the nature of one part, or several parts, or even the whole of a multicomponent assembly, its implications are enormous for a broad range of molecular sciences. This intriguing phenomenon is widely seen in many natural (such as the DNA double helix and the secondary α-helix structure of proteins) and various artificial and biomimetic systems, making it of prime importance not only for fundamental science but also for a number of practical applications in such areas as catalysis, nonlinear optics, polymer and materials science, molecular and chiral recognition, molecular devices, and absolute configuration assignment.

Thus, in this review, we intended to present an overview of key areas and representative examples considered for successfully understanding and applying supramolecular systems for chirality-sensing purposes. First, we provide an introduction to the different manifestations of (supra)molecular chirality, in conjunction with commonly used analytical methods for observing and understanding these systems, along with consideration of associated theories with which data should be considered. Second, an overview of recent works that deal with the most widely considered areas of chiral supramolecular science, particularly asymmetry induction and control in various host−guest assemblies, followed by consideration of the phenomena of enantiodiscrimination in host−guest systems, will be presented. Third, an overview of work that considers how the various external (temperature, phase transition, solvent polarity, pH, viscosity, light, etc.) and internal (bonding strength, steric and electronic effects, stoichiometry, etc.) modulating stimuli can be appreciated and understood in a chirality context will be shown. Fourth, a consideration of recent work in different branches of chirogenesis such as chiral memory, surfaces, polymers, and nanostructures that well-illustrate the rational design of sophisticated supramolecular systems with potential for functional application will be done. Finally, a perspective of current limitations and possible approaches to overcoming these problems will be described, along with future opportunities for the wider advancement of supramolecular chirality.

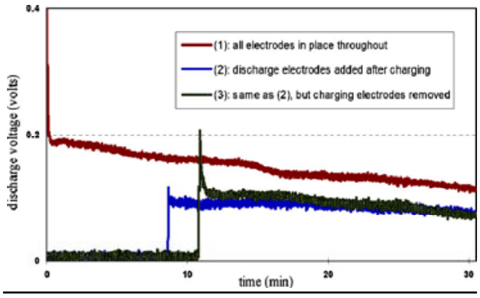
- Chiral Tertiary Diamines in Asymmetric Synthesis
  Kizirian, J.-C. *Chem. Rev.* **2008**, *108*, 140-205.
  Abstract:



In the development of new systems for asymmetric synthesis it has always been a big challenge to obtain optically active compounds with good yields and selectivities. For this purpose, diamines have shown, since their first use, much success in many important and useful transformations. They have become widely studied by many groups as chiral auxiliaries, chiral reagents, or chiral external ligands.

Some aspects of the use of these compounds have already been discussed. This review will focus more specifically on the use of bis-tertiary diamines (this term refers to the diamines for which both nitrogen atoms are tertiary) as chiral external ligands. As bis-secondary diamines and secondary-tertiary diamines are often used in the same reactions, they will be both mentioned and compared to tertiary diamines when necessary. We will consider any structures containing two tertiary nitrogen atoms regardless of the structure of the spacer. Diamines containing nitrogen atoms substituted with heteroatoms such as phosphorus and boron (etc.) as well as the corresponding ammonium salt of bis-tertiary diamines will not be covered. In the diamines we are discussing the element of chirality can be located in three places: between the nitrogen atoms (internal chirality), on the nitrogen substituents (external chirality), or on the nitrogen atom itself. Thus, the element of chirality is located with regard to the diamino functionality. It is common practice to compare emerging diamine ligands with the established, efficacious (−)-sparteine ligand; whenever this is possible comparisons have been made. Nevertheless, (−)-sparteine is a ligand apart for which the use in asymmetric synthesis has already been covered in several reviews, and we will overlap with them as little as possible. On the contrary, the C2-symmetric diastereoisomers, α- and β-isosparteine, have not aroused much interest as they are usually less efficient. Recently, many efforts have been made to understand the real reason for the efficiency of (−)-sparteine, and few analogues possessing a simpler structure have been synthesized and tested in several transformations. Furthermore, one major drawback is that only one enantiomer of sparteine is available. Considering its efficiency and the synthetic difficulties to access (+)-sparteine, sparteine surrogates available in both enantiomerically pure forms have been developed.

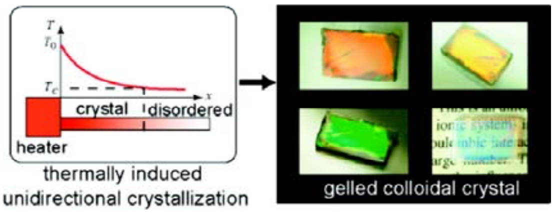
- Can Water Store Charge?
  Ovchinnikova, K.; Pollack, G. H. *Langmuir* **2009**, *25*, 542-547.
  Abstract:



Previous work from this and other laboratories has demonstrated large pH gradients in water. Established by passing current between immersed electrodes, pH gradients between electrodes were found to disappear slowly, persisting for tens of minutes after the current had been turned off. We find here that these pH gradients reflect a genuine separation of charge: at times well after disconnection of the power supply, current could be drawn through a resistor placed between the charging electrodes or between pairs of electrodes positioned on either side of the midline between original electrodes. In some experiments, it was possible to recover the majority of charge that had been imparted to the water. It appears, then, that water has the capacity to store and release substantial amounts of charge.

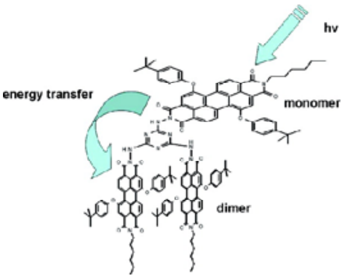
- Gel Immobilization of Centimeter-Sized and Uniform Colloidal Crystals Formed under Temperature Gradient

Toyotama, A.; Yamanaka, J.; Shinohara, M.; Onda, S.; Sawada, T.; Yonese, M.; Uchida, F. *Langmuir* **2009**, *25*, 589-593.
<u>Abstract</u>



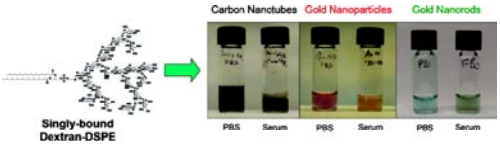
We report the fabrication of large and high-quality charged colloidal crystals that are incorporated in a polymer hydrogel matrix. The colloidal crystals are prepared by the thermally induced unidirectional crystallization of colloidal silica in coexistence with pyridine, whose dissociation degree increases with temperature. Their crystal structures are immobilized in the polymer hydrogel matrix by photoinduced polymerizations. The crystals are large sized (maximum dimensions: 1 × 10¡Á~30 mm), and their lattice planes are well oriented and parallel to the gel surface. Furthermore, they have excellent spatial uniformity in the Bragg wavelengths (<0.7% in standard deviation). The present gelled colloidal crystals, which are unique in that they have large sizes as well as good optical uniformity, will be useful as photonic materials.

- Fluorescence Quenching in a Perylenetetracarboxylic Diimide Trimer
  Wang, Y.; Chen, H.; Wu, H.; Li, X.; Weng, Y. *J. Am. Chem. Soc.* **2009**, *131*, 30–31.
  <u>Abstract:</u>



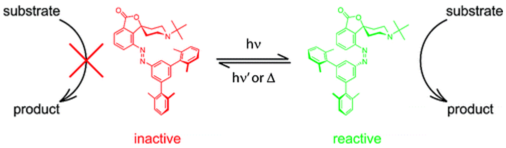
A perylenetetracarboxylic diimide (PDI) trimer (3) linked by a triazine ring has been prepared. The UV−vis absorption spectra together with the 1H NMR spectra revealed that two of the three PDI subunits in the trimer presents a face-to-face stacked configuration while the third one appended acts as a monomer. There is no strong interaction between the dimer and monomer at ground state. However, the fluorescence of the monomer was quenched efficiently by the dimer. The transient absorption and excitation spectra of this compound suggest that the energy transfer from the excited states of monomer to an excimer like state of dimer is responsible for this quick and efficient fluorescence quenching. The rate of the energy transfer is comparable to that from B800 to B850 in LH2.

- Phospholipid-Dextran with a Single Coupling Point: A Useful Amphiphile for Functionalization of Nanomaterials
  Goodwin, A. P.; Tabakman, S. M.; Welsher, K.; Sherlock, S. P.; Prencipe, G.; Dai, H. *J. Am. Chem. Soc.* **2009**, *131*, 289–296.
  <u>Abstract:</u>



Nanomaterials hold much promise for biological applications, but they require appropriate functionalization to provide biocompatibility in biological environments. For noncovalent functionalization with biocompatible polymers, the polymer must also remain attached to the nanomaterial after removal of its excess to mimic the high-dilution conditions of administration in vivo. Reported here are the synthesis and utilization of singly substituted conjugates of dextran and a phospholipid (dextran-DSPE) as stable coatings for nanomaterials. Suspensions of single-walled carbon nanotubes were found not only to be stable to phosphate buffered saline (PBS), serum, and a variety of pH's after excess polymer removal, but also to provide brighter photoluminescence than carbon nanotubes suspended by poly(ethylene glycol)-DSPE. In addition, both gold nanoparticles (AuNPs) and gold nanorods (AuNRs) were found to maintain their dispersion and characteristic optical absorbance after transfer into dextran-DSPE and were obtained in much better yield than similar suspensions with PEG-phospholipid and commonly used thiol-PEG. These suspensions were also stable to PBS, serum, and a variety of pH's after removal of excess polymer. dextran-DSPE thus shows great promise as a general surfactant material for the functionalization of a variety of nanomaterials, which could facilitate future biological applications.

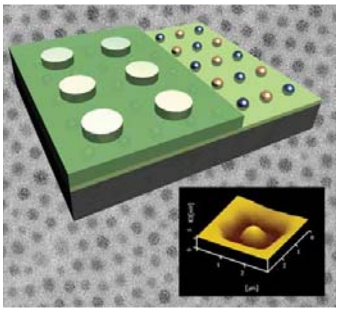
- Photoswitchable Catalysts: Correlating Structure and Conformational Dynamics with Reactivity by a Combined Experimental and Computational Approach
  Stoll, R. G.; Peters, M. V.; Kuhn, A.; Heiles, S.; Goddard, R.; Bühl, M.; Thiele, C. M.; Hecht, S. *J. Am. Chem. Soc.* **2009**, *131*, 357–367.
  Abstract:



Photocontrol of a piperidine's Brønsted basicity was achieved by incorporation of a bulky azobenzene group and could be translated into pronounced reactivity differences between ON- and OFF-states in general base catalysis. This enabled successful photomodulation of the catalyst's activity in the nitroaldol reaction (Henry reaction). A modular synthetic route to the photoswitchable catalysts was developed and allowed for preparation and characterization of three azobenzene-derived bases as well as one stilbene-derived base. Solid-state structures obtained by X-ray crystal structure analysis confirmed efficient blocking of the active site in the *E* isomer representing the OFF-states, whereas a freely accessible active site was revealed for a representative *Z* isomer in the crystal. To correlate structure with reactivity of the catalysts, conformational dynamics were thoroughly studied in solution by NMR spectroscopy, taking advantage of residual dipolar couplings (RDCs), in combination with comprehensive DFT computational investigations of conformations and proton affinities.

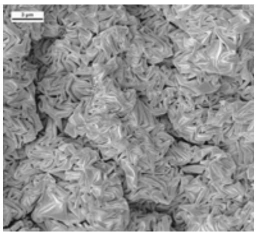
- Tunable Memory Characteristics of Nanostructured, Nonvolatile Charge Trap Memory Devices Based on a Binary Mixture of Metal Nanoparticles as a Charge Trapping Layer
  Lee, J.-S.; Kim, Y.-M.; Kwon, J.-H.; Shin, H.; Sohn, B.-H.; Jaegab, L. *Adv. Mater.* **2009**, *21*, 178-183.

<u>Abstract:</u>



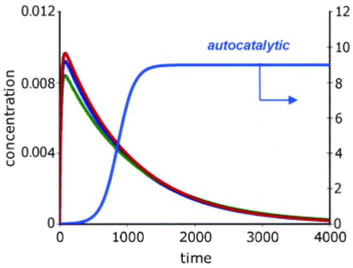
Tunable memory characteristics are investigated according to the metal-nanoparticle species being used in memory devices. The memory devices are fabricated using diblock copolymer micelles as templates to synthesize nanoparticles of cobalt, gold, and a binary mixture thereof. Programmable memory characteristics show different charging/discharging behaviors according to the storage element configurations as confirmed by nanoscale device.

- Characterization.Nanoporous Biodegradable Elastomers
  Hoshi, R. A.; Behl, S.; Ameer, G. A. *Adv. Mater*. **2009**, *21*, 188-192.
  <u>Abstract:</u>



A nanoporous biodegradable elastomer based on citric acid is described. Nanopores are used to control the mechanical and degradation properties of the elastomer. Furthermore, macromolecular drugs can be entrapped under mild conditions via pore collapse, which also delays the release of the drug. The nanoporous elastomer is biocompatible and a promising platform technology for engineering soft tissues.

- An Examination of the Role of Autocatalytic Cycles in the Chemistry of Proposed Primordial Reactions
  Blackmond, D. G. *Angew. Chem. Int. Ed.* **2009**, *48*, 386-390.
  <u>Abstract:</u>



Let's start at the very beginning: Reaction simulations were used to clarify differences between autoinductive and autocatalytic processes in the context of recent models pertaining to the chemical origin of life (see plot). The ability of a catalytic network to persist in the face of disruptive challenges is essential to its potential to play a role in prebiotic chemistry.