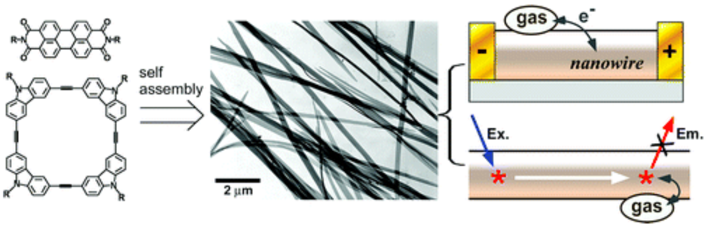
- One-Dimensional Self-Assembly of Planar π-Conjugated Molecules: Adaptable Building Blocks for Organic Nanodevices
  Zang, L.; Che, Y.; Moore, J. S. *Acc. Chem. Res.* **2008**, *41*, 1596–1608.
  <u>Abstract:</u>

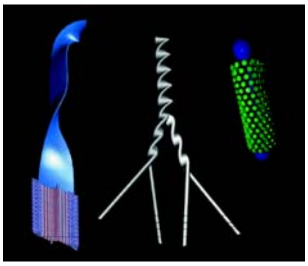


In general, fabrication of well-defined organic nanowires or nanobelts with controllable size and morphology is not as advanced as for their inorganic counterparts. Whereas inorganic nanowires are widely exploited in optoelectronic nanodevices, there remains considerable untapped potential in the one-dimensional (1D) organic materials. This Account describes our recent progress and discoveries in the field of 1D self-assembly of planar π-conjugated molecules and their application in various nanodevices including the optical and electrical sensors. The Account is aimed at providing new insights into how to combine elements of molecular design and engineering with materials fabrication to achieve properties and functions that are desirable for nanoscale optoelectronic applications. The goal of our research program is to advance the knowledge and develop a deeper understanding in the frontier area of 1D organic nanomaterials, for which several basic questions will be addressed: (1) How can one control and optimize the molecular arrangement by modifying the molecular structure? (2) What processing factors affect self-assembly and the final morphology of the fabricated nanomaterials; how can these factors be controlled to achieve the desired 1D nanomaterials, for example, nanowires or nanobelts? (3) How do the optoelectronic properties (e.g., emission, exciton migration, and charge transport) of the assembled materials depend on the molecular arrangement and the intermolecular interactions? (4) How can the inherent optoelectronic properties of the nanomaterials be correlated with applications in sensing, switching, and other types of optoelectronic devices?

The results presented demonstrate the feasibility of controlling the morphology and molecular organization of 1D organic nanomaterials. Two types of molecules have been employed to explore the 1D self-assembly and the application in optoelectronic sensing: one is perylene tetracarboxylic diimide (PTCDI, n-type) and the other is arylene ethynylene macrocycle (AEM, p-type). The materials described in this project are uniquely multifunctional, combining the properties of nanoporosity, efficient exciton migration and charge transport, and strong interfacial interaction with the guest (target) molecules. We see this combination as enabling a range of important technological applications that demand tightly coupled interaction between matter, photons, and charge. Such applications may include optical sensing, electrical sensing, and polarized emission. Particularly, the well-defined nanowires fabricated in this study represent unique systems for investigating the dimensional confinement of the optoelectronic properties of organic semiconductors, such as linearly polarized emission, dimensionally confined exciton migration, and optimal π-electronic coupling (favorable for charge transport). Combination of these properties will make the 1D self-assembly ideal for many orientation-sensitive applications, such as polarized light-emitting diodes and flat panel displays.

- Molecular Self-Assembly into One-Dimensional Nanostructures

Palmer, L. C.; Stupp, S. I. *Acc. Chem. Res.* **2008**, *41*, 1674–1684.
Abstract:



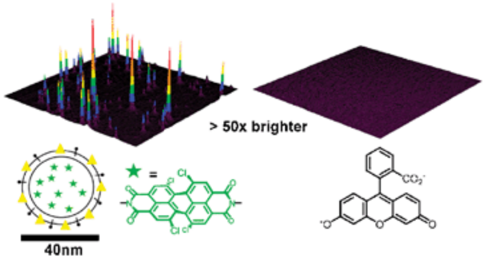
Self-assembly of small molecules into one-dimensional nanostructures offers many potential applications in electronically and biologically active materials. The recent advances discussed in this Account demonstrate how researchers can use the fundamental principles of supramolecular chemistry to craft the size, shape, and internal structure of nanoscale objects. In each system described here, we used atomic force microscopy (AFM) and transmission electron microscopy (TEM) to study the assembly morphology. Circular dichroism, nuclear magnetic resonance, infrared, and optical spectroscopy provided additional information about the self-assembly behavior in solution at the molecular level.

Dendron rod-coil molecules self-assemble into flat or helical ribbons. They can incorporate electronically conductive groups and can be mineralized with inorganic semiconductors.To understand the relative importance of each segment in forming the supramolecular structure, we synthetically modified the dendron, rod, and coil portions. The self-assembly depended on the generation number of the dendron, the number of hydrogen-bonding functions, and the length of the rod and coil segments. We formed chiral helices using a dendron-rod-coil molecule prepared from an enantiomerically enriched coil.

Because helical nanostructures are important targets for use in biomaterials, nonlinear optics, and stereoselective catalysis, researchers would like to precisely control their shape and size. Tripeptide-containing peptide lipid molecules assemble into straight or twisted nanofibers in organic solvents. As seen by AFM, the sterics of bulky end groups can tune the helical pitch of these peptide lipid nanofibers in organic solvents. Furthermore, we demonstrated the potential for pitch control using trans-to-cis photoisomerization of a terminal azobenzene group. Other molecules called peptide amphiphiles (PAs) are known to assemble in water into cylindrical nanostructures that appear as nanofiber bundles. Surprisingly, TEM of a PA substituted by a nitrobenzyl group revealed assembly into quadruple helical fibers with a braided morphology. Upon photocleavage of this the nitrobenzyl group, the helices transform into single cylindrical nanofibers.

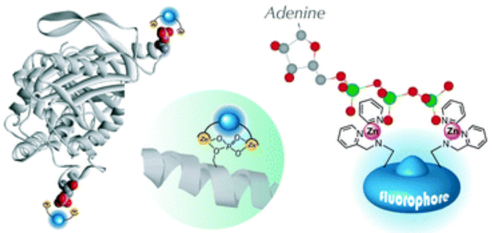
Finally, inspired by the tobacco mosaic virus, we used a dumbbell-shaped, oligo(phenylene ethynylene) template to control the length of a PA nanofiber self-assembly (<10 nm). AFM showed complete disappearance of long nanofibers in the presence of this rigid-rod template. Results from quick-freeze/deep-etch TEM and dynamic light scattering demonstrated the templating behavior in aqueous solution. This strategy could provide a general method to control size the length of nonspherical supramolecular nanostructures.

- Twisted perylene dyes enable highly fluorescent and photostable nanoparticles.
  Tian, Z.; Shaller, A. D.; Li, A. D. Q. *Chem. Commun.* **2009**, 180 – 182.
  Abstract :



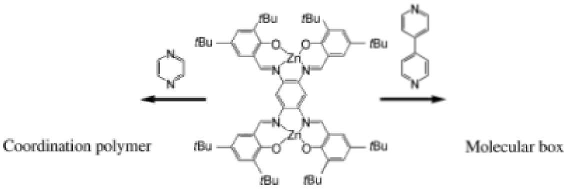
Polymeric fluorescent nanoparticles with covalently embedded perylene fluorophores were developed by facile synthesis strategy and their advanced features of extremely high fluorescence intensity, non-photoblinking and excellent photostability were experimentally confirmed at the single nanoparticle level.

- Molecular recognition, fluorescence sensing, and biological assay of phosphate anion derivatives using artificial Zn(II)–Dpa complexes.
  Sakamoto, T.; Ojida, A.; Hamachi, I. *Chem. Commun.* **2009**, 141 – 152.
  Abstract:



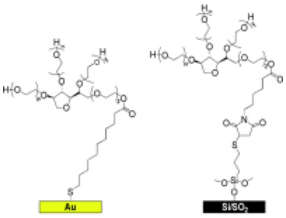
In this Feature Article, we focus on recent advances in our research on molecular recognition and fluorescence sensing of phosphate anion derivatives of biological importance. Because of their significant roles in biological systems, considerable efforts have been devoted to developing detection or determination systems. However, the recognition and sensing of these anion species under aqueous biological conditions using small-molecular chemosensors still remain as a challenging research topic. We have been developing a variety of artificial receptors and fluorescent chemosensors for phosphoproteins and nucleoside polyphosphates in recent years. They consist of a binuclear Zn(II)–dipicolylamine (Dpa) complex as a common binding motif for phosphate anion derivatives. Taking advantage of their strong binding affinities or high sensing abilities, a variety of biological assay systems have also been successfully developed, which includes the enzyme assays such as the kinase, phosphatase and glycosyltransferase reaction, as well as an inhibitor assay for the phosphoprotein–protein surface interaction.

- The Assembly of Supramolecular Boxes and Coordination Polymers Based on Bis-Zinc-Salphen Building Blocks
  Kuil, M.; Puijk, I.; Kleij, A.; Tooke, D.; Spek, A.; Reek, J. *Chem. Asian J.* **2009**, 4, 50 – 57.
  Abstract :



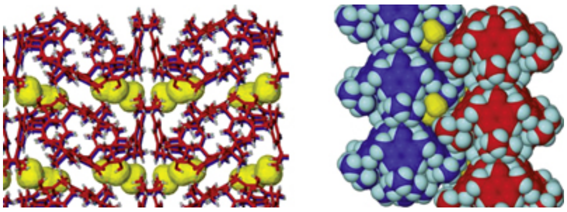
We report the assembly of supramolecular boxes and coordination polymers based on a rigid bis-zinc(II)-salphen complex and various ditopic nitrogen ligands. The use of the bis-zinc(II)-salphen building block in combination with small ditopic nitrogen ligands gave organic coordination polymers both in solution as well as in the solid state. Molecular modeling shows that supramolecular boxes with small internal cavities can be formed. However, the inability to accommodate solvent molecules (such as toluene) in these cavities explains why coordination polymers are prevailing over well-defined boxes, as it would lead to an energetically unfavorable vacuum. In contrast, for relatively longer ditopic nitrogen ligands, we observed the selective formation of supramolecular box assemblies in all cases studied. The approach can be easily extended to chiral analogues by using chiral ditopic nitrogen ligands.

- Asymmetrically Functionalized, Four-Armed, Poly(ethylene glycol) Compounds for Construction of Chemically Functionalizable Non-Biofouling Surfaces
  Chi,Y.; Lee, B.; Kil, M.; Jung, H.; Oh, E.; Choi, I. *Chem. Asian J.* **2009**, 4, 135 – 142.
  Abstract :



Asymmetrically functionalized, four-armed, Tween 20 derivatives that formed stable monomolecular films on solid substrates were designed and synthesized. Thiol-modified Tween 20 was used for forming self-assembled monolayers (SAMs) on gold, and maleimide-modified Tween 20 was introduced onto SiO_2 surfaces with SAMs of (3-mercaptopropyl)trimethoxysilane through Michael addition. These structurally modified Tween 20 compounds gave the original characteristics of Tween 20, non-biofouling (from ethylene glycol groups) and functionalizable (from OH groups) properties, to each substrate. The non-biofouling properties of the Tween 20-coated gold and SiO_2 surfaces were investigated by surface plasmon resonance spectroscopy and ellipsometry, and these surfaces showed strong resistance against nonspecific adsorption of proteins. In addition, the biospecific binding of streptavidin was achieved after coupling of (+)-biotinyl-3,6,9-trioxaundecanediamine onto the non-biofouling surfaces through amide-bond formation.

- Gas-induced transformation and expansion of a non-porous organic solid
  Thallapally, P. K.; McGrail, B. P.; Dalgarno, S. J.; Schaef, H. T.; Tian, J.; Atwood, J. L. *Nature Materials* **2008**, *7*, 146-150.
  Abstract:

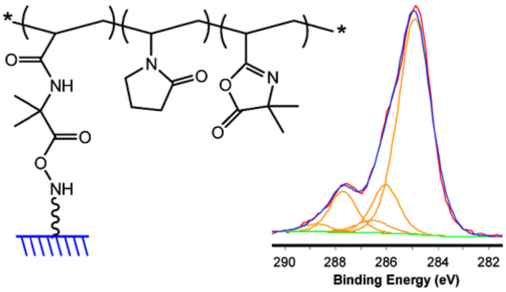


Organic solids composed by weak van der Waals forces are attracting considerable attention owing to their potential applications in gas storage, separation and sensor applications. Herein we report a gas-induced transformation that remarkably converts the high-density guest-free form of a well-known organic host (*p-tert*-butylcalix[4]arene) to a low-density form and vice versa, a process that would be expected to involve surmounting a considerable energy barrier. This transformation occurs despite the fact that the high-density form is devoid of channels or pores. Gas molecules seem to diffuse through the non-porous solid into small lattice voids, and initiate the transition to the low-density kinetic form with ~10% expansion of the crystalline organic lattice, which corresponds to absorption of CO_2 and N_2O. This suggests the possibility of a more general phenomenon that can be exploited to find more porous materials from non-porous organic and metal–organic frameworks that possess void space large enough to accommodate the gas molecules.

- Silver-nanoparticle-embedded antimicrobial paints based on vegetable oil
  Kumar, A.; Vemula, P. K.; Ajayan, P. M.; John, G. *Nature Materials* **2008**, *7*, 236-241.
  Abstract:

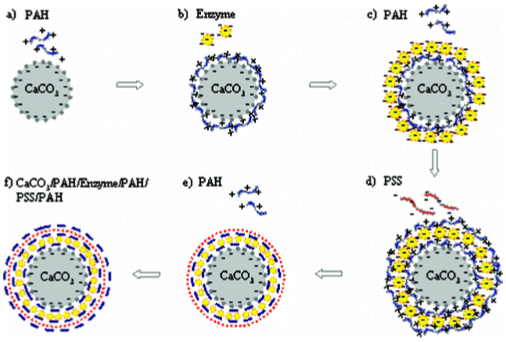
Developing bactericidal coatings using simple green chemical methods could be a promising route to potential environmentally friendly applications. Here, we describe an environmentally friendly chemistry approach to synthesize metal-nanoparticle (MNP)-embedded paint, in a single step, from common household paint. The naturally occurring oxidative drying process in oils, involving free-radical exchange, was used as the fundamental mechanism for reducing metal salts and dispersing MNPs in the oil media, without the use of any external reducing or stabilizing agents. These well-dispersed MNP-in-oil dispersions can be used directly, akin to commercially available paints, on nearly all kinds of surface such as wood, glass, steel and different polymers. The surfaces coated with silver-nanoparticle paint showed excellent antimicrobial properties by killing both Gram-positive human pathogens (*Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*). The process we have developed here is quite general and can be applied in the synthesis of a variety of MNP-in-oil systems.

- Immobilization of Biomolecules on Poly(vinyldimethylazlactone)-Containing Surface Scaffolds
  Barringer, J. E.; Messman, J. M.; Banaszek, A. L.; Meyer, H. M.; Kilbey, S. M. *Langmuir* **2009,** *25,* 262-268.
  Abstract:



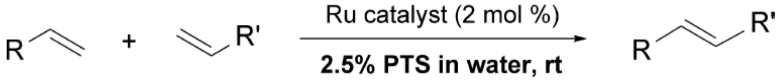
We describe the successful development of a procedure for the step-by-step formation of a reactive, multilayer polymer scaffold incorporating polymers based on 2-vinyl-4,4-dimethylazlactone (VDMA) on a silicon wafer and the characterization of these materials. Also discussed is the development of a procedure for the nonsite specific attachment of a biomolecule to a modified silicon wafer, including scaffolds modified via drop-on-demand (DOD) inkjet printing. VDMA-based polymers were used because of their hydrolytic stability and ability of the pendant azlactone rings to form stable covalent bonds with primary amines without byproducts via nucleophilic addition. This reaction proceeds without a catalyst and at room temperature, yielding a stable amide linkage, which adds to the ease of construction expected when using VDMA-based polymers. DOD inkjet printing was explored as an interesting method for creating surfaces with one or more patterns of biomolecules because of the flexibility and ease of pattern design.

- Encapsulation of Synthetically Valuable Biocatalysts into Polyelectrolyte Multilayer Systems
  Wiemann, L. O.; Buthe, A.; Klein, M.; van den Wittenboer, A.; Dähne, L.; Ansorge-Schumacher, M. B. *Langmuir* **2009,** *25,* 618-623.
  Abstract:



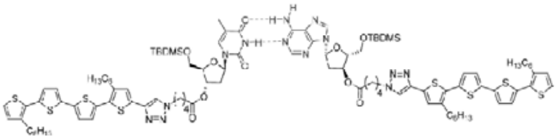
Layer-by-Layer (LbL) technology recently turned out to be a versatile tool for the encapsulation of bioactive entities. In this study, the factual potential of this technology to encapsulate synthetically valuable biocatalysts, that is enzymes and whole cells expressing a specific catalytic activity, was investigated. The biocatalysts were embedded into a polyelectrolyte multilayer system involving poly(allylamine) hydrochloride (PAH) and poly(styrene sulfonate) sodium salt (PSS). The enzymes were adsorbed to CaCO3 or DEAE-cellulose previous to encapsulation. A slight increase (32%) of the catalytic performance was observed for lipaseBfrom *Candida antarctica* when four layers of polyelectrolytes were applied. On the whole, however, the residual activity of the investigated enzymes after encapsulation was rather low. Similar results were obtained with whole-cell biocatalysts. It was found that the activity decrease can be attributed to mass transfer restrictions as well as direct interactions between polyelectrolytes and catalytically active molecules.Both effects need to be understood in more detail before LbL technology can be advanced to technically efficient biocatalysis.

- Olefin Cross-Metathesis Reactions at Room Temperature Using the Nonionic Amphiphile "PTS": Just Add Water
  Lipshutz B.H.; Aguinaldo G. T.; Ghorai S.; Voigtritter K. *Org. Lett*. **2008**, *10*, 1325-1328.
  Abstract :



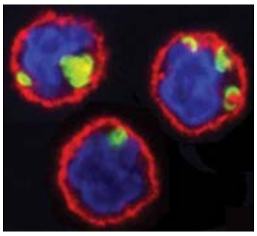
The first examples of unsymmetrical olefin cross-metathesis reactions in water, involving water-insoluble substrates, at room temperature and using commercially available catalysts are reported. The key to success is to include small percentages of the nonionic, vitamin E-based amphiphile "PTS". The nanometer micelles formed accommodate water-insoluble substrates, along with a readily available Ru-based metathesis catalyst. Reactions proceed at ambient temperatures with high efficiency and very high E-selectivity, and products are easily isolated.

- Self-Organizing Oligothiophene-Nucleoside Conjugates: Versatile Synthesis via "Click"-Chemistry
  Jatsch A.; Kopyshev A.; Mena-Osteritz E.; Bäuerle P. *Org. Lett.*, **2008**, *10*, 961-964.
  Abstract :



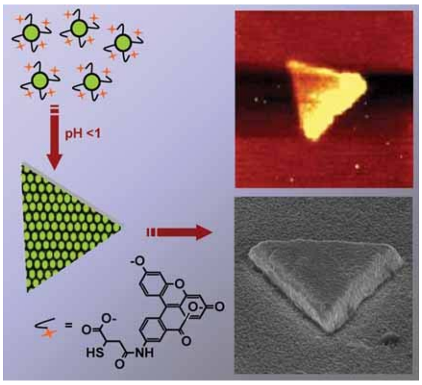
A versatile synthesis of novel oligothiophene-nucleoside conjugates based on Cu(I)-catalyzed alkyne-azide cycloaddition ("click-reaction") has been developed. Complementary thymidine- and adenosine-functionalized quaterthiophenes form recognition-driven superstructures via hydrogen bonding and other competing intermolecular forces. Self-aggregated fibers up to 30 μm in length were characterized with atomic force microscopy.

- Binding, Internalization, and Antigen Presentation of Vaccine-Loaded Nanoengineered Capsules in Blood
  De Rose, R.; Zelikin, A. N.; Johnston, A. P. R.; Sexton, A.; Chong, S.-F.; Cortez, C.; Mulholland, W.; Caruso, F.; Kent, S. F. *Adv. Mater*. **2008**, 20, 4698-4703
  Abstract :



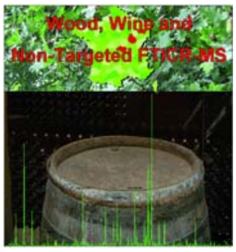
Nanoengineered microcapsules (shown in green) can be used to encapsulate vaccine antigens conferring protection of the cargo until the capsules are taken up by specialized antigen presenting cells in human blood such as dendritic cells (cell membrane in red, nucleus in blue). This technique offers potential applications for in vivo vaccine delivery.

- Fluorescent Gold Nanoparticle Superlattices
  Nishida, N.; Shibu, E. S.; Yao, H.; Oonishi, T.; Kimura, K.; Pradeep, T. *Adv. Mater*. **2008**, 20, 4719-4723.
  Abstract :



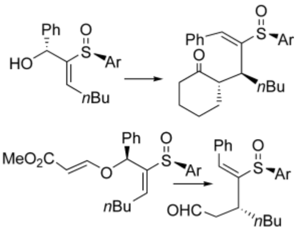
3D superlattices of fluorescent gold nanoparticles are prepared at an air/water interface. The hexagonal assembly extends over several micrometers, and crystals of triangular morphology are imaged using the fluorescence emission of the monolayers protecting the nanoparticles (see figure). Surprisingly, the superlattices are fluorescent even though the fluorescein derivative is close to the metallic core and strong quenching is expected.

- Expressing Forest Origins in the Chemical Composition of Cooperage Oak Woods and Corresponding Wines by Using FTICR-MS
  Gougeon, R. D.; Lucio, M.; De Boel, A.; Frommberger, M.; Hertkorn, N.; Peyron, D.; Chassagne, D.; Feuillat, F.; Cayot, P.; Voilley, A.; Gebefügi, I.; Schmitt-Kopplin, P. *Chem. Eur.J.* **2009**,*15*, 600-611.
  Abstract:



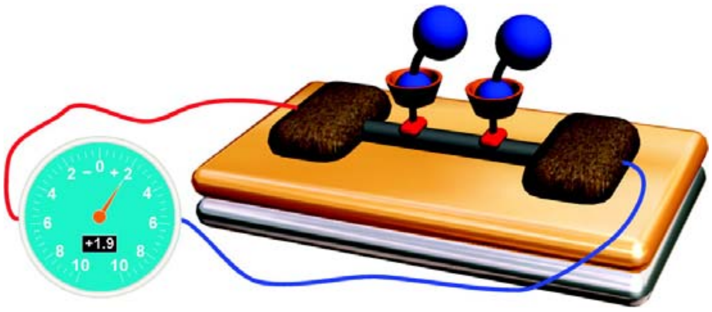
A non-targeted, ultra-high-resolution mass spectrometric, direct analysis of oak-wood extracts from two species (*Quercus robur* L. and *Quercus petraea* Liebl.) from three French forests, and of a wine aged in barrels derived therefrom has been performed to identify families of metabolites that could discriminate both the species and the geographical origin of woods. From 12 T ultra-high-resolution Fourier transform ion cyclotron resonance mass spectra of wood extracts, hundreds of mass signals were identified as possible significant biomarkers of the two species, with phenolic and carbohydrate moieties leading the differentiation between *Q. robur* and *Q. petraea*, respectively, as corroborated by both FTMS and NMR data. For the first time, it is shown that oak woods can also be discriminated on the basis of hundreds of forest-related compounds, and particular emphasis is put on sessile oaks from the Tronçais forest, for which sugars are significantly discriminant. Despite the higher complexity and diversity of wine metabolites, forest-related compounds can also be detected in wines aged in related barrels. It is only by using these non-targeted analyses that such innovative results, which reveal specific chemodiversities of natural materials, can be obtained.

- Asymmetric Claisen Rearrangements on Chiral Vinyl Sulfoxides
  Fernández de la Pradilla, R.; Montero, C.; Tortosa, M.; Viso, A. *Chem. Eur.J.* **2009**, *15*, 697-709.
  Abstract:



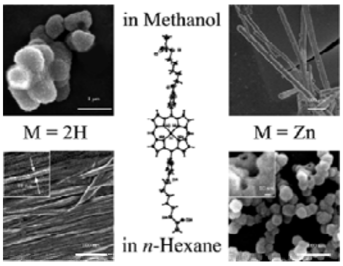
Highly diastereoselective Claisen rearrangements of acyclic allyl vinyl ethers bearing a chiral sulfoxide at C-5 provide γ-δ-unsaturated aldehydes or ketones with up to two consecutive asymmetric centers in the molecule whilst preserving a useful vinyl sulfoxide. The reactivity of related vinyl sulfides and sulfones has also been examined in this work.

- A Tunable Photosensor
  Zhao, Y.; Hu, L.; Grüner, G; Stoddart, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 16996–17003.
  Abstract:



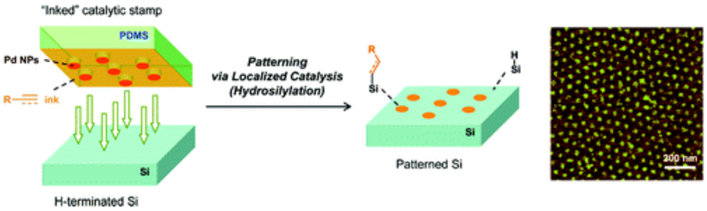
A pyrene-modified β-cyclodextrin (pyrenecyclodextrin)-decorated single-walled carbon nanotube (SWNT) field-effect transistor (FET) device was fabricated, which can serve as a tunable photosensor to sense a fluorescent adamantyl-modified Ru complex (ADA−Ru). When the light is on (I = 40 W m−2 and λ = 280 nm), the transfer curve of the pyrenecyclodextrin-SWNT/FET device shifts toward a negative gate voltage by about 1.6 V and its sheet resistance increases quickly, indicating a charge-transfer process from the pyrenecyclodextrins to the SWNTs. In contrast, the transfer curve of the pyrenecyclodextrin-SWNT/FET device in the presence of the ADA−Ru complex shifts toward a positive gate voltage by about 1.9 V and its sheet resistance decreases slowly when the light is on (I = 40 W m−2 and λ = 490 nm), showing a charge-transfer process from the pyrenecyclodextrin-SWNT hybrids to the ADA−Ru complex. Because these photoresponse processes are recoverable following the removal of the light, the present photosensor exhibits a promising application in the area of tunable light detection.

- Morphology-Controlled Self-Assembled Nanostructures of 5,15-Di[4-(5-acetylsulfanylpentyloxy)phenyl]porphyrin Derivatives. Effect of Metal−Ligand Coordination Bonding on Tuning the Intermolecular Interaction
  Gao, Y.; Zhang, X.; Ma, C.; Li, X; Jiang, J. *J. Am. Chem. Soc.*, **2008**, *130*, 13872–13873.
  Abstract:



Novel metal-free 5,15-di[4-(5-acetylsulfanylpentyloxy)phenyl]porphyrin H2[DP(CH3COSC5H10O)2P] (1) and its zinc congener Zn[DP(CH3COSC5H10O)2P] (2) were designed and synthesized. Single-crystal X-ray diffraction (XRD) analysis confirmed the tetrapyrrole nature of these two compounds, revealing the existence of metal−ligand coordination bond between the carbonyl oxygen in the aryloxy side chain of meso-attached phenyl group in the porphyrin molecule with the zinc center of neighboring porphyrin molecule in the crystal structure of 2. This intermolecular Zn−O coordination bond induces the formation of a supramolecular chain structure in which the porphyrinato zinc moieties are arranged in a “head-to-tail” mode (J-aggregate), which is in contrast to a “face-to-face” stacking mode (H-aggregate) in the supramolecular structure formed depending on the C−H···π interaction in the crystal of 1. Their self-assembling properties in MeOH and n-hexane were comparatively investigated by scanning electronic microscopy and XRD technique. Intermolecular π−π interaction of metal-free porphyrin 1 leads to the formation of hollow nanospheres and nanoribbons in MeOH and n-hexane, respectively. In contrast, introduction of additional Zn−O coordination bond for porphyrinato zinc complex 2 induces competition with intermolecular π−π interaction, resulting in nanostructures with nanorod and hollow nanosphere morphology in MeOH and n-hexane. The IR and XRD results clearly reveal the presence and absence of such metal−ligand coordination bond in the nanostructures formed from porphyrinato zinc complex 2 and metal-free porphyrin 1, respectively, which is further unambiguously confirmed by the single-crystal XRD analysis result for both compounds. Electronic absorption spectroscopic data on the self-assembled nanostructures reveal the H-aggregate nature in the hollow nanospheres and nanoribbons formed from metal-free porphyrin 1 due to the π−π intermolecular interaction between porphyrin molecules and J-aggregate nature in the nanorods and hollow nanospheres of 2 depending on the dominant metal−ligand coordination bonding interaction among the porphyrinato zinc molecules. The present result appears to represent the first effort toward controlling and tuning the morphology of self-assembled nanostructures of porphyrin derivatives via molecular design and synthesis through introduction of metal−ligand coordination bonding interaction. Nevertheless, availability of single crystal and molecular structure revealed by XRD analysis for both porphyrin derivatives renders it possible to investigate the formation mechanism as well as the molecular packing conformation of self-assembled nanostructures of these typical organic building blocks with large conjugated system in a more confirmed manner.

- Catalytic Stamp Lithography for Sub-100 nm Patterning of Organic Monolayers
  Mizuno, H.; Buriak, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 17656–17657.
  Abstract:



A stamp-based nanoscale patterning technique of organic monolayers, termed catalytic stamp lithography, is described. The surface of poly(dimethylsiloxane) was patterned with catalytic Pd nanoparticles (NPs) via the use of self-assembled block copolymers. Using this catalytic stamp, catalytic hydrosilylations of terminal alkenes/alkynes were performed on H-terminated Si(111) or Si(100) surfaces to create nanoscale patterns of organic monolayers. Since the reaction takes place exclusively underneath the patterned Pd NPs (localized catalysis), the pattern formation is less susceptible to ink diffusion and stamp deformation, even at this sub-100 nm scale. A range of different molecular inks can be utilized to produce monolayer patterns of different chemical functionalities, and the stamps can be reused multiple times. The potential utility of this kind of chemically patterned surfaces as the basis for more complicated nanoarchitectures was demonstrated through gold nanoparticle capture, with a thiol-terminated nanopatterned silicon surface.