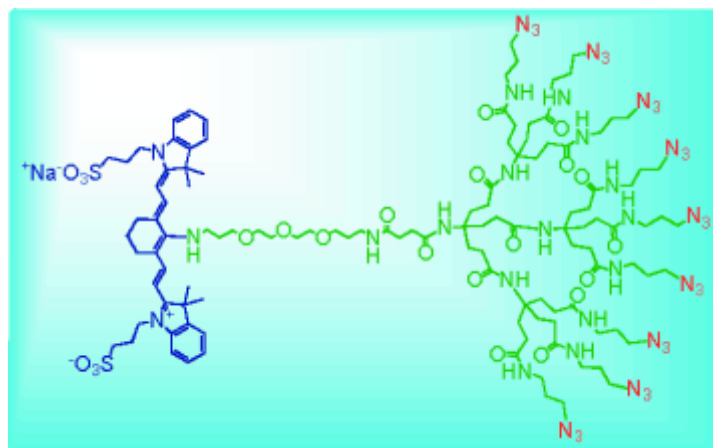


- Combining Aminocyanine Dyes with Polyamide Dendrons: A Promising Strategy for Imaging in the Near-Infrared Region

1

Ornelas, C.; Lodescar, R.; Durandin, A.; Canary, J. W.; Pennell, R.; Liebes, L. F.; Weck, M. *Chem.-Eur. J.* **2011**, *17*, 3619-3629.

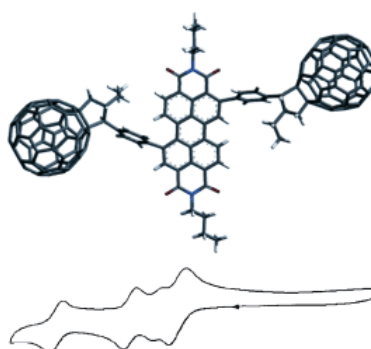
Abstract:



Cyanine dyes are known for their fluorescence in the near-IR (NIR) region, which is desirable for biological applications. We report the synthesis of a series of aminocyanine dyes containing terminal functional groups such as acid, azide, and cyclooctyne groups for further functionalization through, for example, click chemistry. These aminocyanine dyes can be attached to polyfunctional dendrons by copper-catalyzed azide alkyne cycloaddition (CuAAC), strain-promoted azide alkyne cycloaddition (SPAAC), peptide coupling, or direct  $S_{NR}1$  reactions. The resulting dendron–dye conjugates were obtained in high yields and displayed high chemical stability and photostability. The optical properties of the new compounds were studied by UV/Vis and fluorescence spectroscopy. All compounds show large Stokes shifts and strong fluorescence in the NIR region with high quantum yields, which are optimal properties for in vivo optical imaging.

- Multi-Electron-Acceptor Dyad and Triad Systems Based on Perylene Bisimides and Fullerenes Chamberlain, T. W.; Davies, E. S.; Khlobystov, A. N.; Champness, N. R. *Chem.-Eur. J.* **2011**, *17*, 3759-3767.

Abstract:

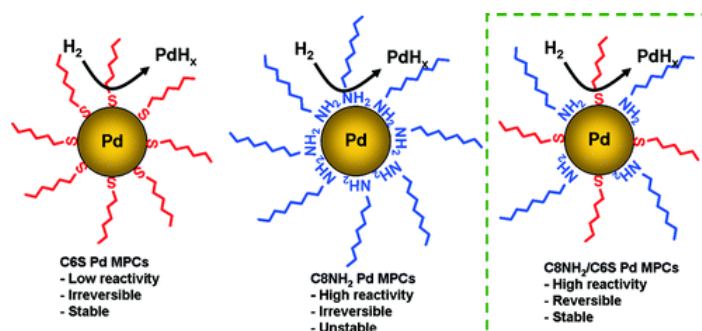


Fullerene ( $C_{60}$ ) and 3,4,9,10-perylene tetracarboxylic diimide (PTDCI) were used as building blocks for an electron acceptor dyad ( $C_{60}$ –PTDCI) and triad ( $C_{60}$ –PTDCI– $C_{60}$ ). As the first reduction potentials for  $C_{60}$  and PTDCI are very close, simultaneous introduction of two or three electrons is possible into the dyad and triad, respectively. Further stepwise electrochemical reduction leads to formation of a series of well-defined anionic species in which electrons associated with the fullerene or the PTDCI

components of the molecule can be clearly distinguished. In total, up to four electrons can be reversibly injected into the dyad C<sub>60</sub>-PTCDI and up to six into the triad C<sub>60</sub>-PTCDI-C<sub>60</sub> system. The optical absorption properties in the UV/Vis range are also crucially defined by the distribution of electrons between the acceptor parts, as the injection/removal of electrons causes drastic colour changes in the dyad and the triad systems.

- Hydrogen Reactivity of Palladium Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications  
Moreno, M.; Ibaez, F. J.; Jasinski, J. B.; Zamborini, F. P. *J. Am. Chem. Soc.* **2011**, *133*, 4389–4397.

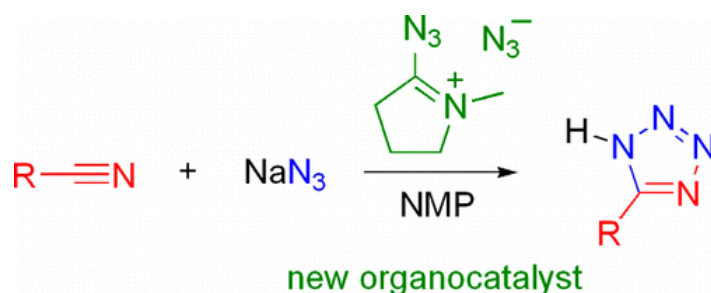
Abstract:



Palladium monolayer-protected clusters (MPCs) coated with octylamines (C<sub>8</sub>NH<sub>2</sub>), hexanethiolates (C<sub>6</sub>S), and mixed monolayers of C<sub>8</sub>NH<sub>2</sub> and C<sub>6</sub>S exhibit significantly different reactivities with hydrogen gas, depending on the relative amounts of the two ligands coating the Pd nanoparticle surface, as determined by UV–vis spectroscopy of Pd MPCs in solution and electronic measurements of films of Pd MPCs as a function of exposure time to hydrogen. The average estimated composition of the ~3.0 nm diameter Pd MPCs was Pd<sub>919</sub>(C<sub>6</sub>S)<sub>192</sub> or Pd<sub>919</sub>(C<sub>8</sub>NH<sub>2</sub>)<sub>177-x</sub>(C<sub>6</sub>S)<sub>x</sub>, where x was varied to be 0, 3, 10, 16, 32, or 81 by the synthesis of pure C<sub>8</sub>NH<sub>2</sub> Pd MPCs and subsequent liquid-phase place exchange with a varied amount of C<sub>6</sub>SH. When x = 0–10, the Pd MPCs react strongly with H<sub>2</sub>, leading to aggregated particles in solution and large irreversible changes in the morphology of films accompanied by an increase in film conductivity by 2–5 orders of magnitude. Pd<sub>919</sub>(C<sub>6</sub>S)<sub>192</sub> MPCs are stable against significant aggregation in solution and do not exhibit large film morphology changes, but they are also not highly reactive to H<sub>2</sub>, as determined by minimal changes in the optical properties of solutions and the small, irreversible changes in the conductivity of films in the presence of H<sub>2</sub>. Finally, when x is 32 and 81, the Pd MPCs are fairly stable, exhibit minimal aggregation or morphology changes, and readily react with H<sub>2</sub> based on the significant, reversible changes in film conductivity in the presence of H<sub>2</sub>. Pd MPCs with mixed monolayers have the benefit of high H<sub>2</sub> reactivity while maintaining the structural stability necessary for sensing and catalysis applications.

- Mechanistic Insights on Azide–Nitrile Cycloadditions: On the Dialkyltin Oxide–Trimethylsilyl Azide Route and a New Vilsmeier–Haack-Type Organocatalyst  
Cantillo, D.; Gutmann, B.; Kappe, C. O. *J. Am. Chem. Soc.* **2011**, *133*, 4465–4475.

Abstract:

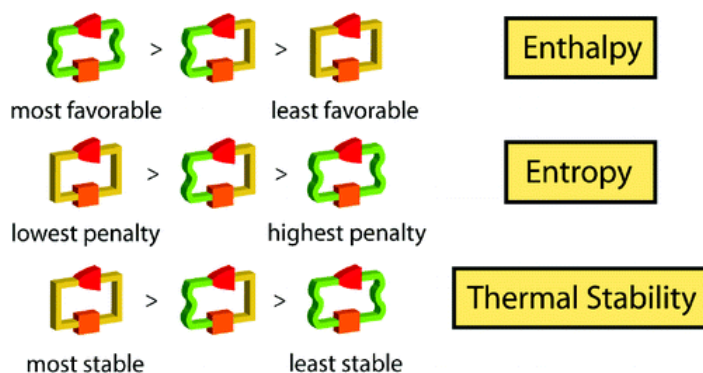


The mechanism of the azide–nitrile cycloaddition mediated by the known dialkyltin oxide–trimethylsilyl azide catalyst system has been addressed through DFT calculations. The catalytic cycle for this tin/silicon complex-based mechanism has been thoroughly examined, disclosing the most plausible intermediates and the energetics involved in the rate enhancement. In addition, a new catalyst, 5-azido-1-methyl-3,4-dihydro-2*H*-pyrrolium azide, is presented for the formation of tetrazoles by cycloaddition of sodium azide with organic nitriles under neutral conditions. The efficiency of this organocatalyst, generated in situ from *N*-methyl-2-pyrrolidone (NMP), sodium azide, and trimethylsilyl chloride under reaction conditions, has been examined by preparation of a series of 5-substituted-1*H*-tetrazoles. The desired target structures were obtained in high yields within 15–25 min employing controlled microwave heating. An in depth computational analysis of the proposed catalytic cycle has also been addressed to understand the nature of the rate acceleration. The computed energy barriers have been compared to the dialkyltin oxide–trimethylsilyl azide metal-based catalyst system. Both the tin/silicon species and the new organocatalyst accelerate the azide–nitrile coupling by activating the nitrile substrate. As compared to the dialkyltin oxide–trimethylsilyl azide method, the organocatalytic system presented herein has the advantage of higher reactivity, in situ generation from inexpensive materials, and low toxicity.

- DNA Nanostructures as Models for Evaluating the Role of Enthalpy and Entropy in Polyvalent Binding

Nangreave, J.; Yan, H.; Liu, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4490–4497.

Abstract:



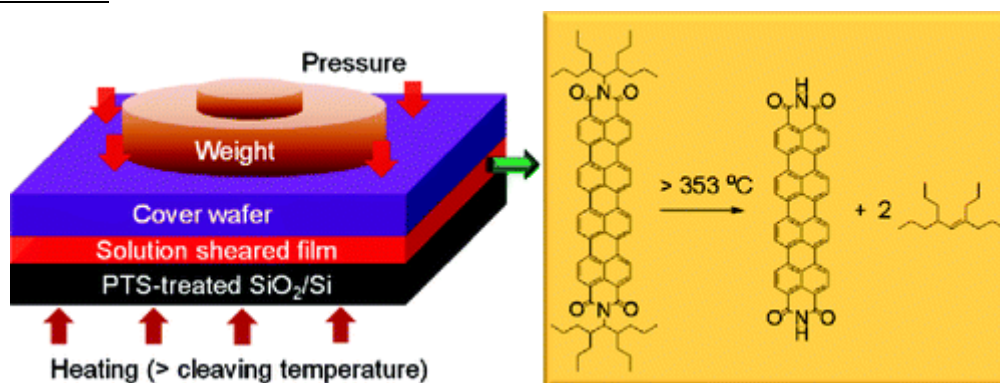
DNA nanotechnology allows the design and construction of nanoscale objects that have finely tuned dimensions, orientation, and structure with remarkable ease and convenience. Synthetic DNA nanostructures can be precisely engineered to model a variety of molecules and systems, providing the opportunity to probe very subtle biophysical phenomena. In this study, several such synthetic DNA nanostructures were designed to serve as models to study the binding behavior of polyvalent molecules and gain insight into how small changes to the ligand/receptor scaffolds, intended to vary their conformational flexibility, will affect their association equilibrium. This approach has yielded a

quantitative identification of the roles of enthalpy and entropy in the affinity of polyvalent DNA nanostructure interactions, which exhibit an intriguing compensating effect.

- Solution-Shear-Processed Quaterrylene Diimide Thin-Film Transistors Prepared by Pressure-Assisted Thermal Cleavage of Swallow Tails

Oh, J. H.; Lee, W. Y.; Noe, T.; Chen, W. C.; Kunemann, M.; Bao, Z. *J. Am. Chem. Soc.* **2011**, *133*, 4204–4207.

Abstract:

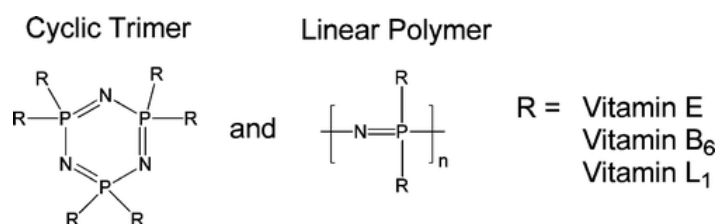


A scalable synthesis of swallow-tailed quaterrylene diimides (STQDIs) and a method for the solution processing of sparingly soluble quaterrylene diimide (QDI) thin films are described. The pressure-assisted thermal cleavage of swallow tails yields crystalline QDI layers with electron mobility up to  $0.088 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The developed method opens up a new route toward the solution processing of higher rylene diimides with poor solubility.

- Polyphosphazenes Containing Vitamin Substituents: Synthesis, Characterization, and Hydrolytic Sensitivity

Morozowich, N. L.; Weikel, A. L.; Nichol, J. L.; Chen, C.; Nair, L. S.; Laurencin, C. T.; Allcock, H. R. *Macromolecules*, **2011**, *44*, 1355–1364.

Abstract:

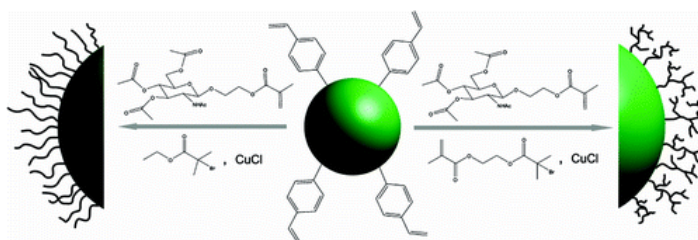


Novel polyphosphazenes containing various vitamin substituents were synthesized and characterized, and their sensitivity to hydrolysis and pH behavior was investigated. Vitamins  $L_1$ , E, and  $B_6$  were used because of their biocompatibility, their importance in a variety of biological functions, and their potential to increase the mechanical properties of the resulting polymers, thus making these materials promising candidates for hard tissue engineering scaffolds. Chlorine replacement reactions were carried out initially with the small molecule, hexachlorocyclotriphosphazene, as a model for high polymeric poly(dichlorophosphazene). Because of the steric hindrance generated by vitamin E as a substituent, co-substituted polymers were synthesized with either glycine ethyl ester or sodium ethoxide as the second substituent. Similarly, vitamin  $B_6$  was co-substituted with glycine ethyl ester or phenylalanine ethyl ester to favor biodegradability. To prevent cross-linking via multifunctional reagents, the hydroxyl groups in vitamin

B<sub>6</sub> were protected and subsequently deprotected under acidic conditions after side group linkage to the polymer backbone. The glass transition temperatures of the polymers ranged from -24.0 to 44.0 °C. Hydrolysis of the polymers in deionized water at 37 °C was used as an initial estimate of their hydrolytic sensitivity. Different solid polymers underwent 10–100% weight loss in 6 weeks with the generation of a broad pH range of  $\approx$ 2.5–9. The weight loss during preliminary hydrolysis experiments was attributed to cleavage of the polymer backbone and/or the polymers becoming soluble in the aqueous media during hydrolytic reactions.

- Hyperbranched Glycopolymer Grafted Microspheres  
Pfaff, A.; Müller, A. H. E. *Macromolecules* **2011**, *44*, 1266–1272.

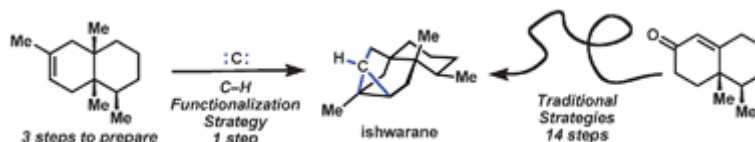
Abstract:



The synthesis and characterization of acetylglucosamine-displaying microspheres consisting of poly(divinylbenzene) (PDVB) cores onto which chains of linear and branched glycopolymer chains were grafted via atom transfer radical polymerization (ATRP) and self-condensing vinyl copolymerization (SCVCP), respectively, are reported. PDVB particles with a diameter of 1.5  $\mu$ m exhibit a layer of lightly cross-linked PDVB in the periphery of the particle and therefore enable a “grafting through” approach due to the residual vinyl groups on the surface. The incorporation of the hydrophobic initiator–monomer (inimer) 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM) led to compact and branched structures in the shell of the core–shell particles, whereas the ratio of BIEM to 1-methacryloyloxyethyl 2-acetamido-2-deoxy-3,4,6-triacetylglucopyranoside (tetAcGlc) affected the surface coverage. Lectin-binding experiments indicated a strong affinity of wheat germ agglutinin (WGA), a glucosamine-specific lectin, toward the hyperbranched glycopolymer covered spheres, increasing with the degree of branching.

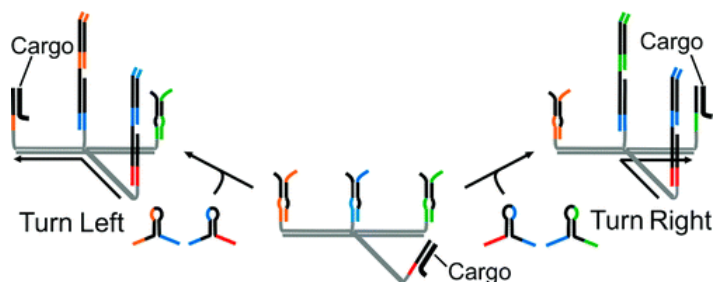
- C–H functionalization logic in total synthesis  
Gutekunst, W. R.; Baran, P. S. *Chem. Soc. Rev.* **2011**, *40*, 1976–1991.

Abstract:



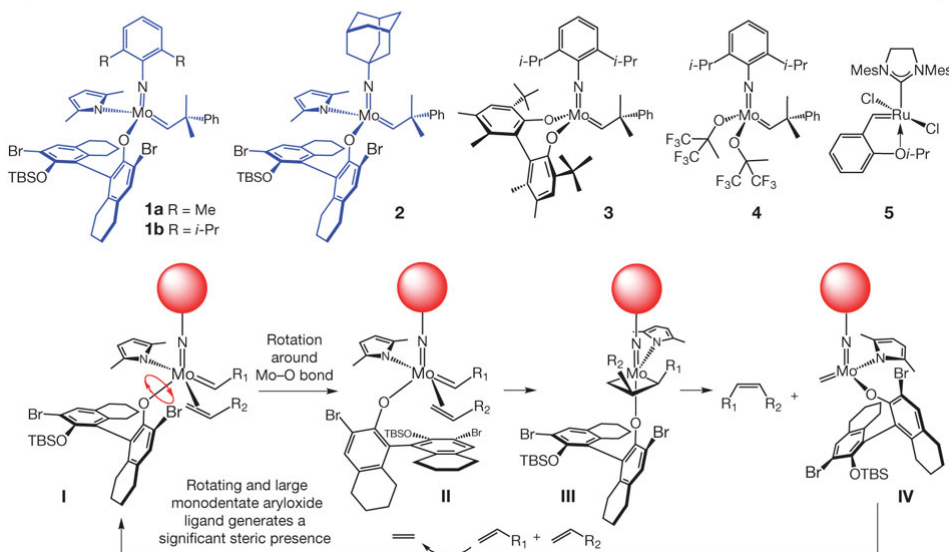
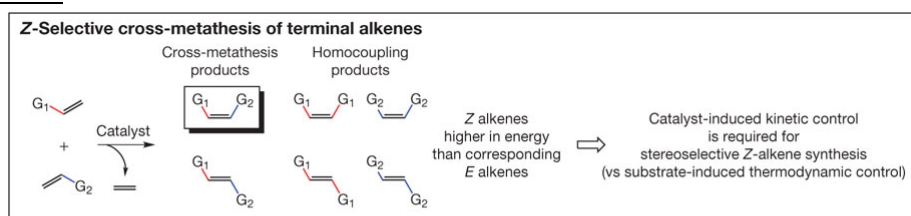
In this *critical review*, the strategic and economic benefits of C–H functionalization logic will be analyzed through the critical lens of total synthesis. In order to illustrate the dramatically simplifying effects this type of logic can potentially have on synthetic planning, we take the reader through a series of case studies in which it has already been successfully applied. In the first section, a chronological look at key historical syntheses will be examined, leading into modern day examples. In the second section, our own experience with applying and executing synthesis with a C–H functionalization “mindset” will be discussed (114 references).



Abstract:

We have developed a programmable and auton-omous molecular robot whose motion is fueled by DNA hybridization. Instructions determining the path to be followed are programmed into the fuel molecules, allowing precise control of cargo motion on a branched track.

- Catalytic Z-selective olefin cross-metathesis for natural product synthesis  
Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *471*, 461–466.

Abstract:

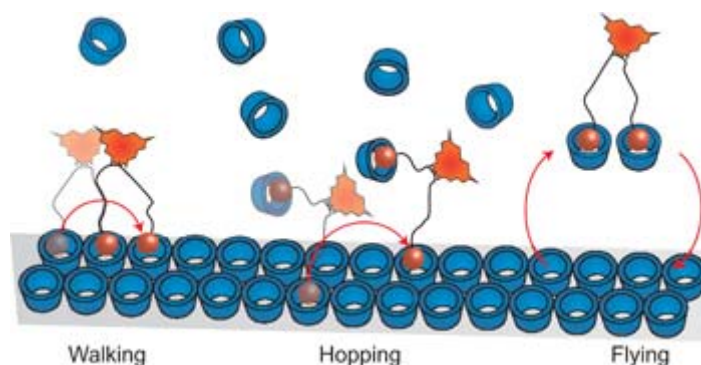
Alkenes are found in many biologically active molecules, and there are a large number of chemical transformations in which alkenes act as the reactants or products (or both) of the reaction. Many alkenes exist as either the *E* or the higher-energy *Z* stereoisomer. Catalytic procedures for the stereoselective formation of alkenes are valuable, yet methods enabling the synthesis of 1,2-disubstituted *Z* alkenes are scarce. Here we report catalytic *Z*-selective cross-metathesis reactions of terminal enol ethers, which have not been reported previously, and of allylic amides, used until now only in *E*-selective processes. The corresponding disubstituted alkenes are formed in up to >98% *Z* selectivity and 97% yield. These transformations, promoted by catalysts that contain the highly abundant and inexpensive metal molybdenum, are amenable to gram-scale operations. Use of reduced pressure is introduced as a simple and effective strategy for achieving high stereoselectivity.

The utility of this method is demonstrated by its use in syntheses of an anti-oxidant plasmalogen phospholipid, found in electrically active tissues and implicated in Alzheimer's disease, and the potent immunostimulant KRN7000.

- Gradient-driven motion of multivalent ligand molecules along a surface functionalized with multiple receptors

Perl, A.; Gomez-Casado, A.; Thompson, D.; Dam, H. H.; Jonkheijm, P.; Reinhoudt, D. N.; Huskens, J. *Nature Chemistry* **2011**, 3, 317–322.

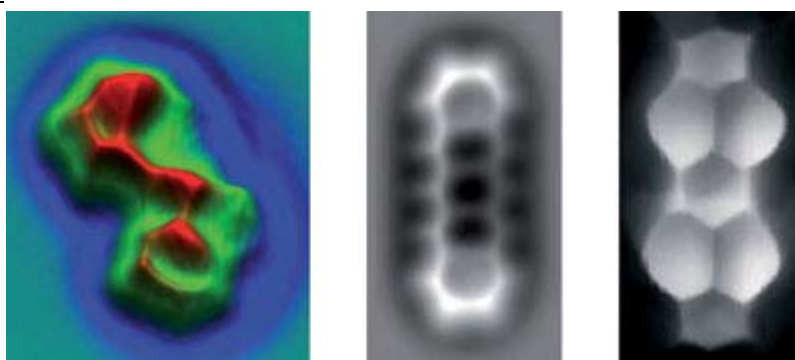
Abstract:



The kinetics of multivalent (multisite) interactions at interfaces is poorly understood, despite its fundamental importance for molecular or biomolecular motion and molecular recognition events at biological interfaces. Here, we use fluorescence microscopy to monitor the spreading of mono-, di- and trivalent ligand molecules on a receptor-functionalized surface, and perform multiscale computer simulations to understand the surface diffusion mechanisms. Analogous to chemotaxis, we found that the spreading is directional (along a developing gradient of vacant receptor sites) and is strongly dependent on ligand valency and concentration of a competing monovalent receptor in solution. We identify multiple surface diffusion mechanisms, which we call walking, hopping and flying. The study shows that the interfacial behaviour of multivalent systems is much more complex than that of monovalent ones.

- Recent advances in submolecular resolution with scanning probe microscopy  
Gross, L. *Nature Chemistry* **2011**, 3, 273 – 278.

Abstract:



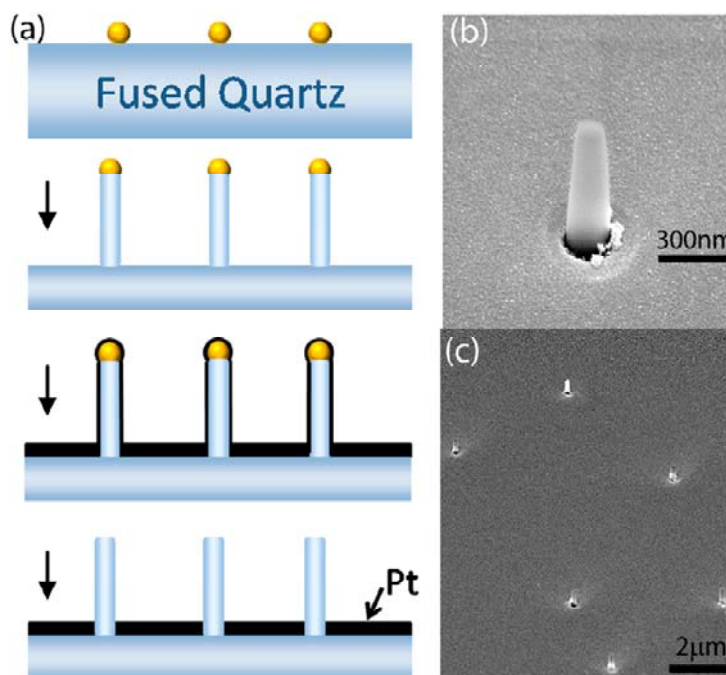
Recently scanning probe microscopy has made tremendous progress in imaging organic molecules with high lateral resolution. Atoms and bonds within individual molecules have been clearly resolved, indicating the exciting potential of this technique for studying molecular structures, bonding within and between molecules, molecular conformational changes and chemical reactions at the single-



molecule level. It turns out that the key step enabling such studies is an atomically controlled functionalization of the microscope tip. In this Perspective, the different techniques used for high-resolution molecular imaging, their implementations, advantages and limitations are described, and possible scientific areas of applications are discussed.

- Vertical nanopillars for highly localized fluorescence imaging  
Xie, C.; Hanson, L.; Cui, Y.; Cui, B. *Proc. Nat. Acad. Sci.* **2011**, *108*, 3894-3899.

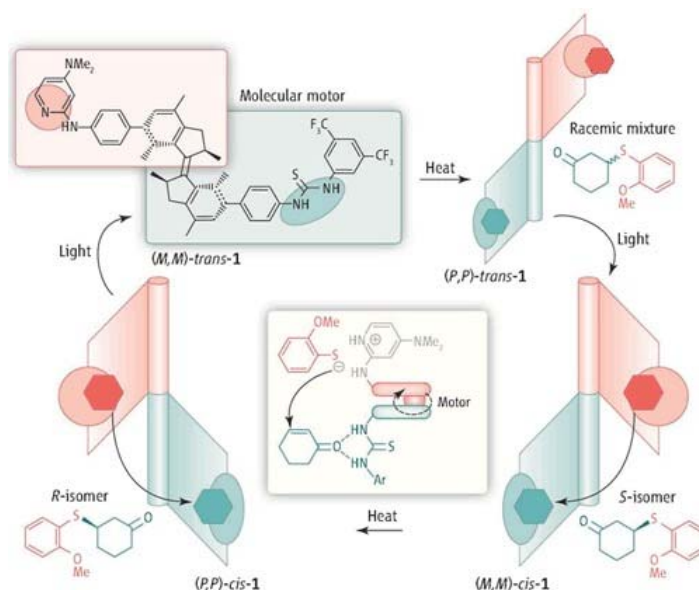
Abstract:



Observing individual molecules in a complex environment by fluorescence microscopy is becoming increasingly important in biological and medical research, for which critical reduction of observation volume is required. Here, we demonstrate the use of vertically aligned silicon dioxide nanopillars to achieve below-the-diffraction-limit observation volume in vitro and inside live cells. With a diameter much smaller than the wavelength of visible light, a transparent silicon dioxide nanopillar embedded in a nontransparent substrate restricts the propagation of light and affords evanescent wave excitation along its vertical surface. This effect creates highly confined illumination volume that selectively excites fluorescence molecules in the vicinity of the nanopillar. We show that this nanopillar illumination can be used for in vitro single-molecule detection at high fluorophore concentrations. In addition, we demonstrate that vertical nanopillars interface tightly with live cells and function as highly localized light sources inside the cell. Furthermore, specific chemical modification of the nanopillar surface makes it possible to locally recruit proteins of interest and simultaneously observe their behavior within the complex, crowded environment of the cell.

- Heat and Light Switch a Chiral Catalyst and Its Products  
Ooi, T. *Science* **2011**, *331*, 1395-1396.

Abstract:

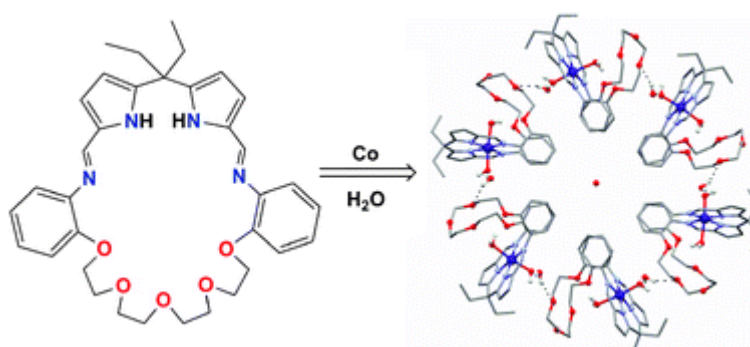


A right-handed glove won't fit a left hand because our hands are chiral. They are mirror images of each other, but despite this symmetry, their shapes cannot be superimposed one on the other. Molecules that are nonidentical mirror images are called enantiomers. Most biomolecules are found only as one of the two enantiomeric forms, and drug molecules that interact with biomolecular targets are usually more active in pure enantiomeric form. Chiral molecules can be prepared from the readily available, achiral starting materials, and many reactions that favor one chiral product (asymmetric reactions) do so by using a catalyst that itself is chiral. However, a versatile method must be able to make both left- and right-handed products, which usually requires having to make both enantiomers of the catalyst. On page 1429 of this issue, Wang and Feringa introduce a conceptually new approach in which the structure of a single catalyst can be manipulated by cycles of light and heat to pulses. These processes drive internal rotation around a carbon-carbon double bond and create two forms of the catalysts that give reaction products of opposite chirality.

- Hexagonal wheel formation through the hydrogen-bonded assembly of cobalt Pacman complexes

Leeland, J. W.; White, F. J.; Love, J. B. *Chem. Commun.* **2011**, 47, 4132-4134.

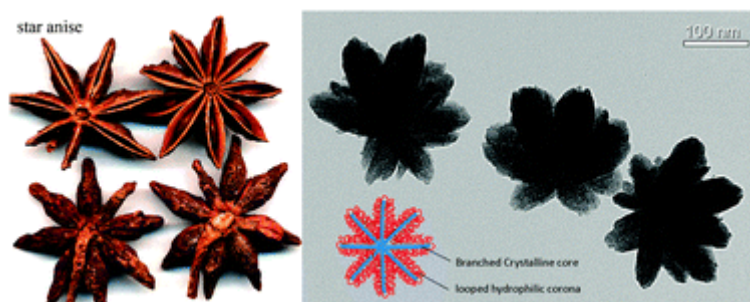
Abstract:



A cobalt aquo-hydroxo complex of a new ditopic Schiff-base pyrrole-crown ether macrocycle has been prepared and forms a rigid Pacman-clefted structure that assembles through hydrogen-bonding into a hexagonal wheel motif in the solid state.

- Novel “star anise”-like nano aggregate prepared by self-assembling of preformed microcrystals from branched crystalline-coil alternating multi-block copolymer  
Chen, S.-C.; Wu, G.; Shi, J.; Wang, Y.-Z. *Chem. Commun.* **2011**, 47, 4198-4200.

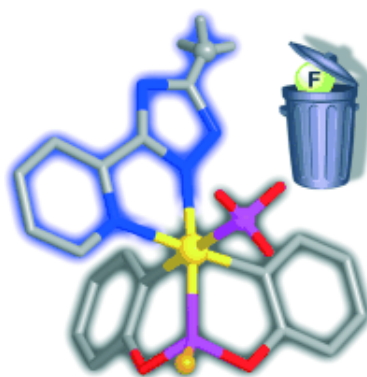
Abstract:



A novel anisotropic nano aggregate with “star anise”-like morphology was prepared by self assembling of preformed microcrystals from a crystalline-coil alternating multi-block copolymer with branched hydrophobic PPDO block.

- Iridium(III) Complexes of a Dicyclopentylated Phosphite Tripod Ligand: Strategy to Achieve Blue Phosphorescence Without Fluorine Substituents and Fabrication of OLEDs  
Lin, C. H.; Chang, Y. Y.; Hung, J. Y.; Lin, C. Y.; Chi, Y.; Chung, M. W.; Lin, C. L.; Chou, P. L.; Lee, G.; Chang, C. H.; Lin, W. C. *Angew. Chem. Int. Ed.* **2011**, 14, 3182-3186.

Abstract:



**Toss the F:** A new series of Ir<sup>III</sup> complexes functionalized with pyridyltriazolate chromophores and a tripodal dicyclopentylated phosphite achieved highly efficient blue phosphorescence without employing any fluorine substituents. OLEDs with dopant [Ir(P[C<sub>2</sub>](bptz)(PMe<sub>2</sub>Ph)] (see structure; bptz=3-*tert*-butyl-5-(2-pyridyl)-1,2,4-triazolate; P[C<sub>2</sub>=dicyclopentylated phosphite tripod) show outstanding performance.

- Leiodermatolide, a Potent Antimitotic Macrolide from the Marine Sponge *Leiodermatium* sp  
Paterson, I.; Dalby, S. M.; Roberts, J. C.; Naylor, G. J.; Guzmán, E. A.; Isbrucker, R.; Pitts, T. P.; Linley, P.; Divlianska, D.; Reed, J. K.; Wright, A. E. *Angew. Chem. Int. Ed.* **2011**, 50, 3219-3223.

Abstract:

