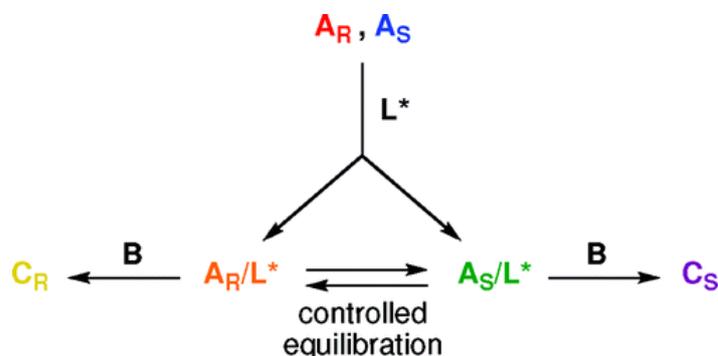


- Dynamic Thermodynamic Resolution: Advantage by Separation of Equilibration and Resolution

Lee, W. K.; Park, Y. S.; Beak, P. *Acc. Chem. Res.* **2009**, *42*, 224–234.

Abstract:



In the investigation of a chemical reaction, researchers typically survey variables such as time, temperature, and stoichiometry to optimize yields. This Account demonstrates how control of these variables, often in nontraditional ways, can provide significant improvements in enantiomeric ratios for asymmetric reactions. Dynamic thermodynamic resolution (DTR) offers a convenient method for the resolution of enantiomeric products in the course of a reaction. This process depends on an essential requirement: the equilibration of the penultimate diastereomers must be subject to external control. As a general case, the reaction of A_R , A_S with B under the influence of the chiral species, L^* , gives resolved products C_R and C_S .

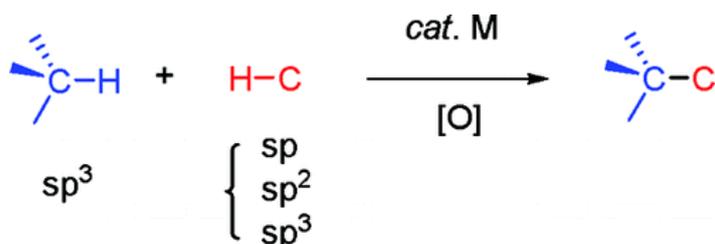
In the first step of dynamic resolution under thermodynamic control, the enantiomeric reactants A_R and A_S and L^* form the diastereomers A_R/L^* and A_S/L^* . The equilibrium between A_R and A_S can be rapid, slow, or not operative, and L^* can represent a ligand, an auxiliary, or a crystallization process that provides a chiral environment. Second, the populations of the diastereomers are controlled, usually by thermal equilibration. Finally, the reaction of the diastereomers with a reagent B provides the enantiomeric products C_R and C_S . The control of the diastereomeric equilibrium distinguishes DTR from other resolution techniques. By contrast, physical resolutions separate thermodynamically stable, nonequilibrating diastereomers, and dynamic kinetic resolutions utilize kinetic control for reactions of rapidly equilibrating diastereomers.

The dynamic thermodynamic resolutions discussed in this Account illustrate cases of significantly improved enantioselectivities using this technique. Although many of the well-recognized cases come from organolithium chemistry, the principles are general, and we also present cases facilitated by other chemistries. This approach has been used to control enantioselectivities in a number of different reactions, with improvements in enantiomeric ratios up to 99% from essentially racemic reactants.

- Cross-Dehydrogenative Coupling (CDC): Exploring C–C Bond Formations beyond Functional Group Transformations

Li, C.-J. *Acc. Chem. Res.* **2009**, *42*, 335–344.

Abstract:

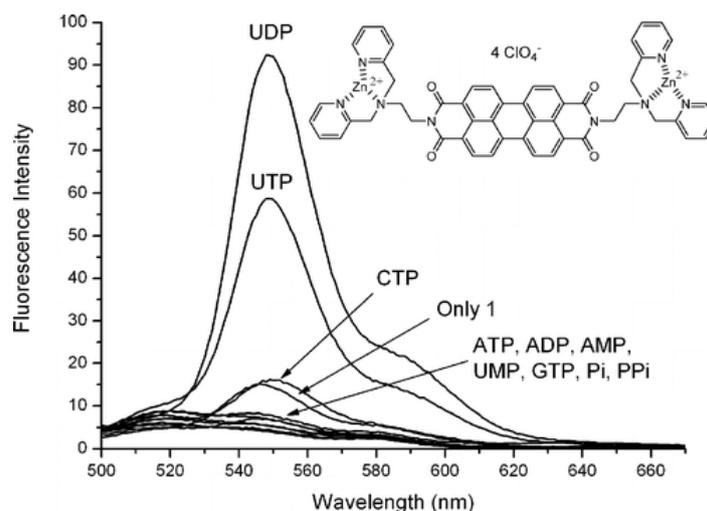


Synthetic chemists aspire both to develop novel chemical reactions and to improve reaction conditions to maximize resource efficiency, energy efficiency, product selectivity, operational simplicity, and environmental health and safety. Carbon-carbon bond formation is a central part of many chemical syntheses, and innovations in these types of reactions will profoundly improve overall synthetic efficiency.

This Account describes our work over the past several years to form carbon-carbon bonds directly from two different C-H bonds under oxidative conditions, cross-dehydrogenative coupling (CDC). We have focused most of our efforts on carbon-carbon bonds formed via the functionalization of sp^3 C-H bonds with other C-H bonds. In the presence of simple and cheap catalysts such as copper and iron salts and oxidants such as hydrogen peroxide, dioxygen, *tert*-butylhydroperoxide, and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), we can directly functionalize various sp^3 C-H bonds by other C-H bonds without requiring preactivation. We demonstrate (1) reaction of α -C-H bonds of nitrogen in amines, (2) reaction of α -C-H bonds of oxygen in ethers, (3) reaction of allylic and benzylic C-H bonds, and (4) reaction of alkane C-H bonds. These CDC reactions can tolerate a variety of functional groups, and some can occur under aqueous conditions. Depending on the specific transformation, we propose the in situ generation of different intermediates.

These methods provide an alternative to the separate steps of prefunctionalization and defunctionalization that have traditionally been part of synthetic design. As a result, these methods will increase synthetic efficiencies at the most fundamental level. On an intellectual level, the development of C-C bond formations based on the reaction of only C-H bonds (possibly in water) challenges us to rethink some of the most fundamental concepts and theories regarding chemical reactivities. A successful reaction requires the conventionally and theoretically less reactive C-H bonds to react selectively in the presence of a variety of functional groups. With further investigation, we expect that C-C bond formations based on cross-dehydrogenative coupling will have a positive economic and ecological impact on the next generation of chemical syntheses.

- An “Off-On” Type UTP/UDP Selective Fluorescent Probe and Its Application to Monitor Glycosylation Process
Chen, Y.; Jou, M. J.; Yoon, J. *Org. Lett.* **2009**, *11*, 2181-2184.
Abstract:

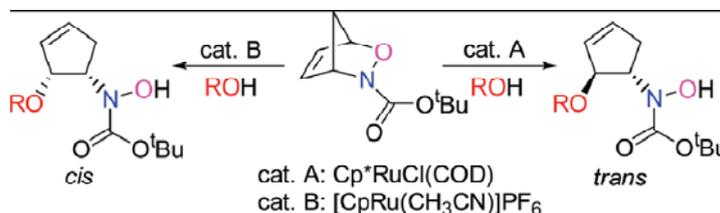


A New fluorescent sensor based on a perylene-dpa-Zn platform was synthesized. Selective “Off-On” type fluorescence changes were observed upon the addition of UTP and UDP, which was also applied to monitor glycosylation processes. A variety of anions, phosphates, pyrophosphates, and nucleotides are important species whose recognition and sensing can play a major role in understanding and evaluating key biological processes. Sensors of these anions, which are based on anion-induced changes in fluorescence intensities, are attractive in this regard owing to their potentially high levels of simplicity and sensitivities. Uridine triphosphate (UTP) and uridine diphosphate (UDP), key building blocks for the synthesis of RNA and in glycotransfer pathways, are widespread in living cells. As a result, they play pivotal roles in various biological events. Despite having many biological roles, to our knowledge, no fluorescent chemosensors that selectively respond to UTP/UDP in aqueous solution have been reported. Below, we describe the results of studies that have led to the development of a new fluorescent sensor **1** for this important target that is based on a perylene-dpa-Zn platform [dpa; bis(2-pyridylmethyl)amine]. This sensor operates under physiological conditions and exhibits high selectivity for UTP and UDP relative to other phosphate derivatives.

- Ruthenium-Catalyzed Nucleophilic Ring-Opening Reactions of a 3-Aza-2-oxabicyclo[2.2.1]hept-5-ene with Alcohols

Machin, B. P.; Howell, J.; Mandel, J.; Blanchard, N.; Tam, T. *Org. Lett.* **2009**, *11*, 2077-2080.

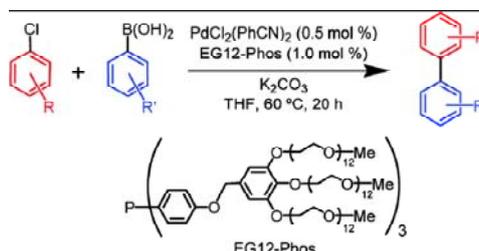
Abstract:



Ruthenium-catalyzed nucleophilic ring-opening reactions of a 3-aza-2-oxabicyclo[2.2.1]hept-5-ene with alcohols were investigated. When a neutral ruthenium(II) catalyst, Cp^{*}RuCl(COD), was used in MeOH, the *trans*-1,2-ring opened product was formed as the only regio- and stereoisomer. On the other hand, when a cationic ruthenium(II) catalyst, [CpRu(CH₃CN)]PF₆, was used in MeOH, the *cis*-1,2-ring opened product was formed exclusively. Moderate to excellent stereoselectivity (70:30 to 100:0) was observed with various alcohols.

- A Triarylphosphine Ligand Bearing Dodeca(ethyleneglycol) Chains: Enhanced Efficiency in the Palladium-Catalyzed Suzuki-Miyaura Coupling Reaction
Fujihara, T.; Yoshida, S.; Terao, J.; Tsuji, Y. *Org. Lett.* **2009**, *11*, 2121-2124.

Abstract:



A new phosphine bearing dodeca(ethylene glycol) chains has been synthesized and employed as a ligand in the palladium-catalyzed Suzuki-Miyaura coupling reaction. The system was found to be highly effective using unactivated aryl chlorides as the substrate.

- 2,7-Substituted Hexafluoroheterofluorenes as Potential Building Blocks for Electron Transporting Materials
Geramita, K.; McBee, J.; Tilley, T. D. *J. Org. Chem.* **2009**, *74*, 820–829.

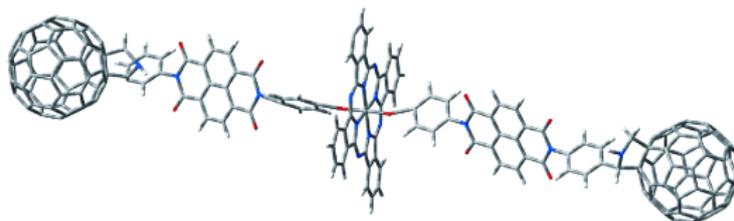
Abstract:



A series of 2,7-substituted hexafluoro-9-heterofluorenes was synthesized via nucleophilic aromatic substitution (S_NArF) reactions of phenyllithium, thienyllithium, and lithium phenylacetylide with various octafluoroheterofluorenes and 2,2'-dibromo-octafluorobiphenyl. These compounds are of interest as possible building blocks for materials with useful electron transport properties, since they possess relatively low LUMO energy levels. The HOMO–LUMO energy gaps, as determined by UV–vis spectroscopy, range between 3.0 and 3.9 eV, while photoluminescence emission spectra reveal λ_{em} values in the range of 365 to 420 nm (corresponding to ultraviolet to violet/blue emission). Dilute solution state quantum yields vary significantly with the nature of the heteroatom and the 2,7-substituents, and approach unity for a number of the di(phenylethynyl) derivatives. The experimentally determined LUMO energy levels (–2.7 to –3.3 eV as determined by differential pulse voltammetry) suggest that these compounds may be good candidates for electron transport applications. Single-crystal X-ray analyses of a number of compounds revealed cofacial packing in all cases, with intermolecular distances as short as 3.4 Å.

- Synthesis and Photoinduced Intramolecular Processes of Light-Harvesting Silicon Phthalocyanine-Naphthalenediimide-Fullerene Connected Systems
El-Khouly, M. E.; Kim, J. H.; Kay, K.-Y.; Choi, C. S.; Ito, O.; Fukuzumi, S. *Chem. Eur. J.* **2009**, *15*, 5301-5310.

Abstract:

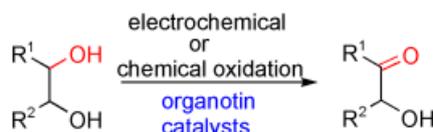


Fast moving: A new pentad (see figure) composed of silicon phthalocyanine (SiPc), as electron donor, that is connected with two units of naphthalenediimide (NDI) and fullerene C₆₀, as electron acceptors, undergoes fast and efficient charge-separation processes via the NDI and SiPc singlet excited states.

Photoinduced intramolecular processes of a newly synthesized pentad composed of silicon phthalocyanine (SiPc) that is connected with two units of naphthalenediimide (NDI) and fullerene C₆₀ to form SiPc-(NDI)₂-(C₆₀)₂ have been studied and the results are compared with the reference compounds, namely, the SiPc-(NDI)₂ triad and NDI-C₆₀ dyad. Upon photoexcitation, the main quenching pathway in polar solvents involved electron transfer via the singlet excited states of SiPc-(NDI)₂-(C₆₀)₂ and SiPc-(NDI)₂, but not NDI-C₆₀ for which the energy transfer is dominant. The occurrence of electron-transfer processes of SiPc-(NDI)₂-(C₆₀)₂ and SiPc-(NDI)₂ were studied by time-resolved emission and transient absorption techniques and confirmed by redox measurements and molecular orbital calculations with ab initio B3 LYP/3-21G(*) methods. Fast and efficient charge-separation processes via the singlet excited states of NDI and SiPc were monitored, followed by charge recombination to populate the C₆₀ and SiPc triplet states. The lifetimes of charge-separated states were estimated as 1000 and 250 ps for SiPc-(NDI)₂-(C₆₀)₂ and SiPc-(NDI)₂, respectively.

- Efficient Oxidation of 1,2-Diols into α -Hydroxyketones Catalyzed by Organotin Compounds
Maki, T.; Iikawa, S.; Mogami, G.; Harasawa, H.; Matsumura, Y.; Onomura, O. *Chem. Eur. J.* **2009**, *15*, 5364-5370.

Abstract:

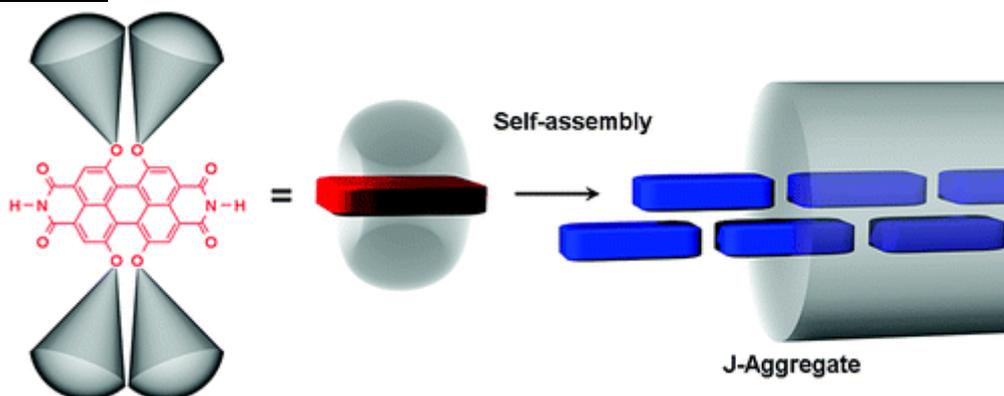


Get selective! A selective oxidation of 1,2-diols to α -hydroxyketones catalyzed by organotin compounds has been developed (see scheme). Invaluable chemo- and stereoselectivity were found in the reaction. The catalytic system has been achieved by electrochemical and chemical oxidation. Electrochemical oxidation of 1,2-diols with a catalytic amount of an organotin compound and a bromide ion as mediators has been developed. Various cyclic and acyclic 1,2-diols were oxidized into the corresponding α -hydroxyketones in good to excellent yields without C—C bond cleavage. Also, oxidation with the use of chemical oxidants was accomplished in the presence of a catalytic amount of an organotin compound. These reactions could discriminate 1,2-diols from isolated hydroxyl groups or 1,3-diols. In the case of a conformationally restricted cyclic 1,2-diol, the axial hydroxyl group was oxidized exclusively. Mono-, di-, and trialkylated tin compounds were examined as mediators and dialkylated tin compounds showed higher catalytic activity than mono- and trisubstituted ones. Me₂SnCl₂ was found to be the most suitable mediator for the selective oxidation.

- Fluorescent J-Aggregates of Core-Substituted Perylene Bisimides: Studies on Structure–Property Relationship, Nucleation–Elongation Mechanism, and Sergeants-and-Soldiers Principle

Kaiser, T. E.; Stepanenko, V.; Wurthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6719–6732.

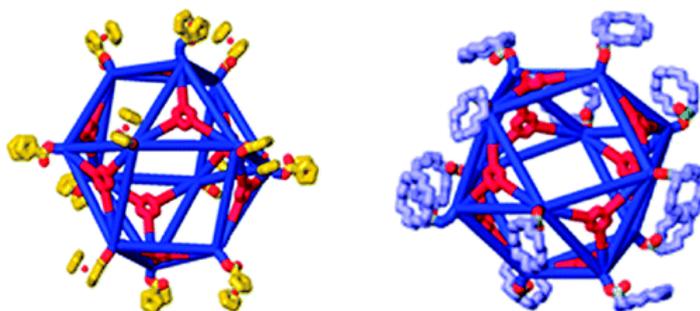
Abstract:



A series of highly soluble and fluorescent, at core tetraaryloxy-substituted and in imide positions hydrogen atom containing perylene bisimide (PBI) dyes 1a–e with varying peripheral side chains have been synthesized and thoroughly characterized. The self-assembly of these PBIs has been studied in detail by UV/vis, linear dichroism (LD) and circular dichroism (CD) spectroscopy, and scanning probe microscopy (AFM, STM). These studies revealed that the present PBIs self-assemble into extended double string cables, which consist of two hydrogen-bonded supramolecular polymeric chains of densely packed and strongly excitonically coupled PBI chromophores, providing highly fluorescent J-aggregates. The aggregation strength (“melting” temperature) and the fluorescence properties of these J-aggregates are dependent on the number and chain length of the peripheral alkoxy substituents, thus revealing a structure–property relationship. In contrast to previously reported assemblies of PBIs, for which the aggregation process is described by the isodesmic (or equal K) model, a cooperative nucleation–elongation mechanism applies for the aggregation of the present assemblies as revealed by concentration-dependent UV/vis absorption studies with the chiral PBI 1e, providing equilibrium constants for dimerization (= nucleation) of $K_2 = 13 \pm 11 \text{ L mol}^{-1}$ and for elongation of $K = 2.3 \pm 0.1 \times 10^6 \text{ L mol}^{-1}$ in methylcyclohexane (MCH). LD spectroscopic measurements have been performed to analyze the orientation of the monomers within the aggregates. The nonlinearity of chiral amplification in PBI aggregates directed by sergeants-and-soldiers principle has been elucidated by coaggregation experiments of different PBI dyes using CD spectroscopy. The dimensions as well as the molecular arrangement of the monomeric units in assemblies have been explored by atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

- Construction of Multifunctional Cuboctahedra via Coordination-Driven Self-Assembly
Ghosh, K.; Hu, J.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 6695–6697.

Abstract:

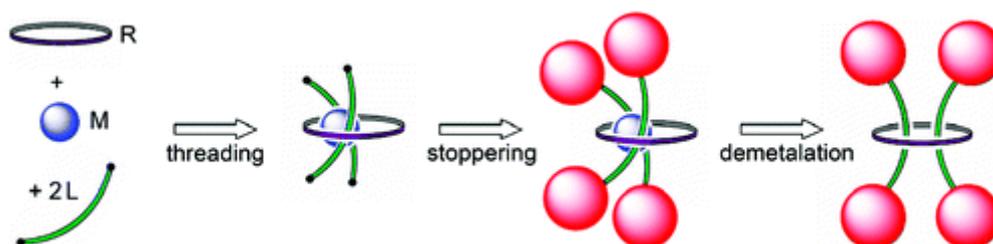


We present a general strategy for the synthesis of stable, multifunctional cuboctahedral complexes in which coordination-driven self-assembly allows for precise control over positioning of either ferrocene or crown ether functionalities. The appropriate stoichiometric combination of functionalized 120° diplatinum acceptor units with tritopic donor units afforded supramolecular cuboctahedra with covalently linked functional groups. The compounds are characterized by multinuclear NMR spectroscopy, electrospray ionization mass spectrometry, and electrochemistry.

- Passing Two Strings through the Same Ring Using an Octahedral Metal Center as Template: A New Synthesis of [3]Rotaxanes

Prikhod'ko, A. I.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2009**, *131*, 6794–6807.

Abstract:



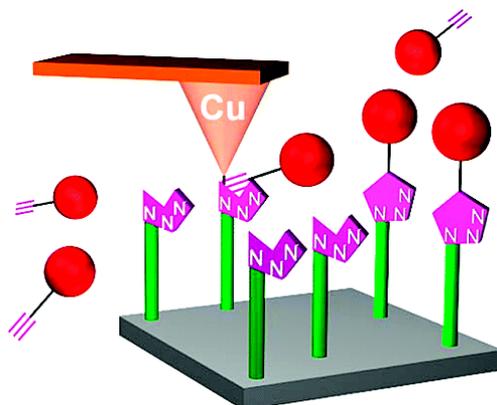
Octahedral transition metal centers such as Fe(II), Co(II), and Co(III) have been used as templates in the construction of [3]pseudorotaxanes and [3]rotaxanes from various acyclic and macrocyclic fragments. The species obtained consist of a ring threaded by two string-like compounds. Such systems are relatively uncommon in the [3]rotaxane family, the most usual form being made up of a single axis threaded through two rings. The key structural feature of the present systems is the coordinating unit incorporated in the various organic fragments and used in conjunction with the metal to gather and thread the two filaments through the ring. This bidentate chelate is derived from 8,8'-diphenyl-3,3'-bi-isoquinoline, a very rare example of an endotopic but nonsterically hindering ligand. The stoppered [3]rotaxanes were obtained by using an open-chain fragment bearing azide groups as end functions, followed by click chemistry using a propargyl ether attached to a very bulky group. A particularly attractive X-ray structure was obtained for a cobalt(III)-complexed [3]pseudorotaxane consisting of a 41-membered ring and two crescent-shaped threaded components. The Fe(II) and Co(III) complexes were characterized by ^1H NMR and ES-MS. By taking advantage of the markedly different kinetic properties of the two oxidation states, Co(II) and Co(III), it was possible to proceed to fast coordination or decoordination reactions (for the divalent state) or, when needed, to “freeze” the complexes due to the kinetic inertness of the trivalent state and to study them by ^1H NMR. Finally, demetalation of the two stoppered compounds prepared was performed. This demetalation reaction was fast for the Co(II)-complexed [3]rotaxane, whereas decomplexation of the Fe(II) equivalent required harsh conditions which were not compatible with the stability of the metal-free rotaxane. Interestingly, the thermal stability of the free [3]rotaxane

toward unthreading and formation of its constitutive elements was only limited. ^1H NMR measurements showed that the half-life of the rotaxane is about one week at room temperature in dichloromethane. A variable-temperature study revealed that the unthreading reaction leading to dissociation of the [3]rotaxane has a remarkably high entropy of activation, in agreement with the intuitive view that the unthreading process involves a highly ordered transition state.

- Heterogeneous Catalysis of a Copper-Coated Atomic Force Microscopy Tip for Direct-Write Click Chemistry

Paxton, W. F.; Spruell, J. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 6692–6694.

Abstract:

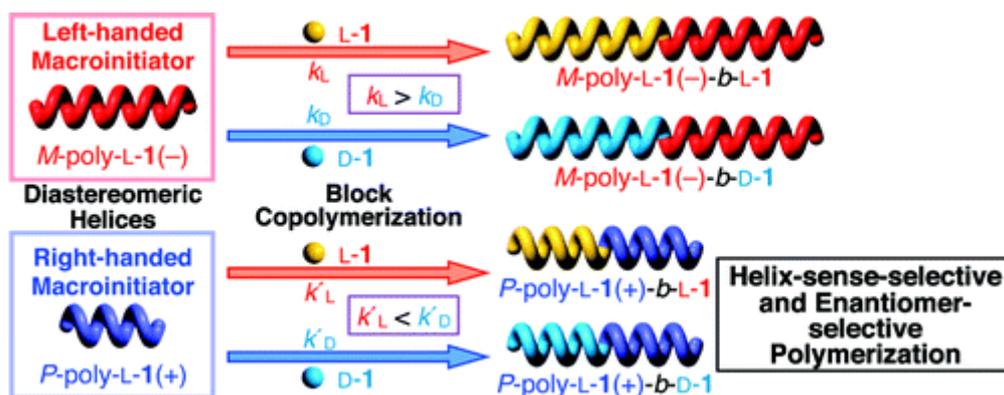


We report a constructive scanning probe lithography method that uses heterogeneous copper-coated atomic force microscopy tips to catalyze azide–alkyne cycloadditions (CuAAC) between solvated terminal alkyne molecules and azide-terminated self-assembled monolayers on silicon surfaces. Spatially controlled surface functionalization was carried out successfully with 50 mM ethanolic solutions of small molecules bearing terminal alkyne groups - propargylamine, 4-pentynoic acid, and an alkynyl-oligoethyleneoxide. We observed that reaction occurs only where the copper tip is in contact with an azide-terminated surface resulting in features with linewidths on the order of 50 nm. The extent of surface functionalization, as measured by changes in surface topography and lateral force microscopy, depends on the scanning force (31–350 nN) and scanning speed, with significant surface patterning observed even at speeds as high as 64 $\mu\text{m/s}$. In contrast with related SPL techniques, this approach affords a direct-write lithographic approach to constructively modifying and patterning surfaces at the nanoscale without the need for auxiliary reagents. All that is required is (1) an azide surface, (2) a solution of a terminal alkyne, and (3) a copper-coated AFM tip. These advantages allow the direct attachment of a potentially limitless library of molecules that bear terminal alkyne functionalities, including biomolecules, under relatively mild conditions, with sub-100 nm spatial resolution.

- Enantiomer-Selective and Helix-Sense-Selective Living Block Copolymerization of Isocyanide Enantiomers Initiated by Single-Handed Helical Poly(phenyl isocyanide)s

Wu, Z.-Q.; Nagai, K.; Banno, M.; Okoshi, K.; Onitsuka, K.; Yashima, E. *J. Am. Chem. Soc.* **2009**, *131*, 6708–6718.

Abstract:

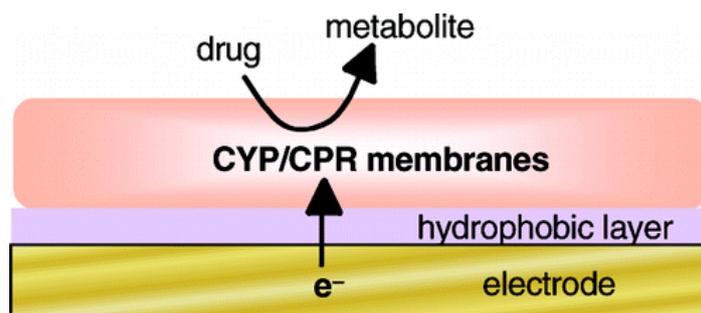


Rigid-rodlike right (*P*)- and left (*M*)-handed helical polyisocyanides (*P*-poly-I-1 and *M*-poly-I-1) prepared by the living polymerization of an enantiomerically pure phenyl isocyanide bearing an *l*-alanine pendant with a long *n*-decyl chain (I-1) with the μ -ethynediyl Pt-Pd catalyst were found to block copolymerize I-1 and d-1 in a highly enantiomer-selective manner while maintaining narrow molecular weight distributions. The *M*-poly-I-1 preferentially copolymerized I-1 over the antipode d-1 by a factor of 6.4–7.7, whereas the d-1 was preferentially copolymerized with *P*-poly-I-1 composed of the same I-1 units, but possessing the opposite helicity by a factor of 4.0. Circular dichroism and high-resolution atomic force microscopy revealed that the enantiomer-selective block copolymerizations proceed in an extremely high helix-sense-selective fashion, and the preformed helical handedness determines the overall helical sense of the polyisocyanides irrespective of the configuration of the monomer units of the initiators during the block copolymerizations. The block copolymers are rigid-rod helical polymers with a narrow molecular weight distribution and exhibit a lyotropic smectic liquid crystalline phase.

- Electrochemically Driven Drug Metabolism by Membranes Containing Human Cytochrome P450

Mie, Y.; Suzuki, M.; Komatsu, Y. *J. Am. Chem. Soc.* 2009, *131*, 6646–6647.

Abstract:

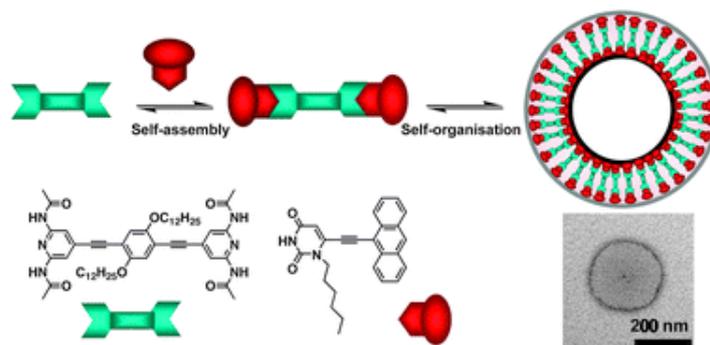


Rapid analyses of drug metabolism reactions by human cytochrome P450s (CYPs) that metabolize 95% of all current drugs are very important in drug development processes and effective therapies. Since CYPs need electrons to metabolize drugs, electrons supplied from electrodes to activate CYP molecules are expected to be very useful to develop rapid assay methods for CYP reactions. Although several studies on the direct electrochemistry of isolated and purified human CYPs have been reported, the use of microsomes (membranes) containing CYP is more suitable, because they are frequently used in drug research due to their easy preparation and low cost. Herein, we demonstrate electrons supplied from an electrode to microsomes containing CYP and CYP-reductase (CPR) on an electrode coated with hydrophobic thin films and observe electrochemically driven drug metabolisms by voltammetry for the first time. We tested the immobilization of microsomes on gold electrodes

coated with several thiolates and found that microsomes immobilized on thin hydrophobic surfaces of aromatic compounds showed well-defined redox peaks. Furthermore, electrochemically driven drug metabolism reactions of CYP3A4 were clearly observed by voltammetry, and these reactions were inhibited by a CYP3A4 inhibitor, ketoconazole. We also found that metabolism reactions were facilitated in the presence of CPR.

- Engineering spherical nanostructures through hydrogen bonds
Yoosaf, K.; Belbakra, A.; Armaroli, N.; Llanes-Pallas, A.; Bonifazi, D. *Chem. Commun.* **2009**, 2830 – 2832.

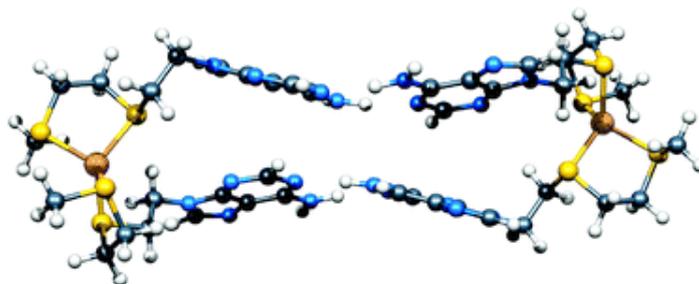
Abstract :



Chromophoric acetylenic scaffolds bearing complementary uracyl and 2,6-di(acetylamino)pyridyl moieties undergo supramolecular recognition and generate uniform nanoparticles, as observed by UV-Vis, AFM and TEM measurements.

- Self-assembly of a bis(adeninyl)–Cu(I) complex: a cationic nucleobase duplex mimic.
Galindo, M. A.; Amantia, D.; Clegg, W.; Harrington, R. W.; Eyre, R. J.; Goss, J. P.; Briddon, P. R.; McFarlane, W.; Houlton, A. *Chem. Commun.* **2009**, 2833 – 2835.

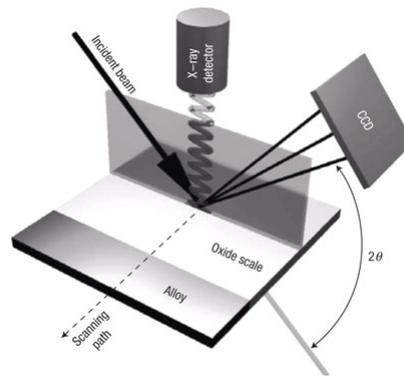
Abstract :



The tetrahedral bis(adeninyl)–Cu(I) complex, **1**, self-associates in polar solvent through complementary hydrogen-bonding interactions and appears to mimic the natural assembly of duplex DNA.

- The role of metal nanoparticles and nanonetworks in alloy degradation
Zeng, Z.; Natesan, K.; Cai, Z.; Darling, S. B. *Nature Materials* **2008**, 7, 641-646.

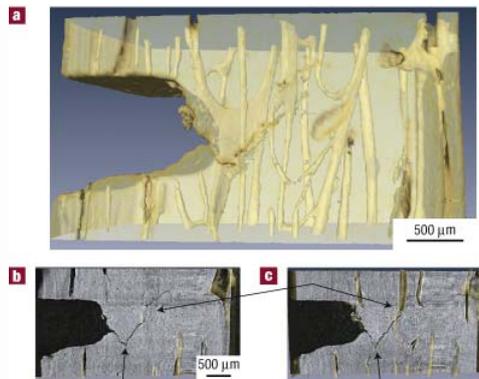
Abstract:



Oxide scale, which is essential to protect structural alloys from high-temperature degradation such as oxidation, carburization and metal dusting, is usually considered to consist simply of oxide phases. Here, we report on a nanobeam X-ray and magnetic force microscopy investigation that reveals that the oxide scale actually consists of a mixture of oxide materials and metal nanoparticles. The metal nanoparticles self-assemble into nanonetworks, forming continuous channels for carbon transport through the oxide scales. To avoid the formation of these metallic particles in the oxide scale, alloys must develop a scale without spinel phase. We have designed a novel alloy that has been tested in a high-carbon-activity environment. Our results show that the incubation time for carbon transport through the oxide scale of the new alloy is more than an order of magnitude longer compared with commercial alloys with similar chromium content.

- The true toughness of human cortical bone measured with realistically short cracks
Koester, K. J.; Ager III, J. W.; Ritchie, R. O. *Nature Materials* **2008**, 7, 672-677.

Abstract:

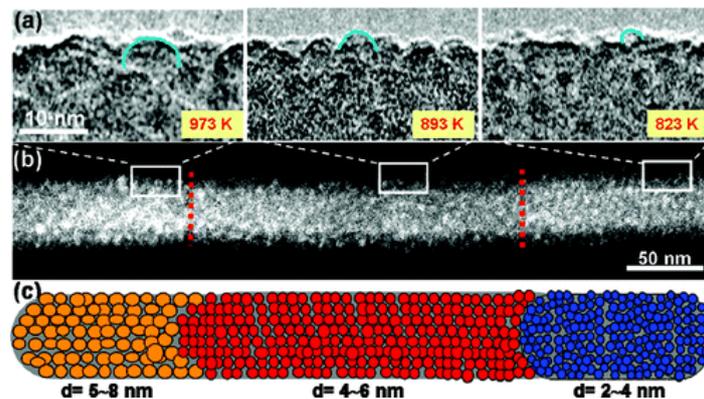


Bone is more difficult to break than to split. Although this is well known, and many studies exist on the behaviour of long cracks in bone, there is a need for data on the orientation-dependent crack-growth resistance behaviour of human cortical bone that accurately assesses its toughness at appropriate size scales. Here, we use in situ mechanical testing to examine how physiologically pertinent short (<600 μm) cracks propagate in both the transverse and longitudinal orientations in cortical bone, using both crack-deflection/twist mechanics and nonlinear-elastic fracture mechanics to determine crack-resistance curves. We find that after only 500 μm of cracking, the driving force for crack propagation was more than five times higher in the transverse (breaking) direction than in the longitudinal (splitting) direction owing to major crack deflections/twists, principally at cement sheaths. Indeed, our results show that the true transverse toughness of cortical bone is far higher than previously reported. However, the toughness in the longitudinal orientation, where cracks tend to follow the cement lines, is quite low at these small crack sizes; it is only when cracks become

several millimetres in length that bridging mechanisms can fully develop leading to the (larger-crack) toughnesses generally quoted for bone.

- A High-Density Array of Size-Controlled Silicon Nanodots in a Silicon Oxide Nanowire by Electron-Stimulated Oxygen Expulsion
Park, G.-S.; Lee, E. K.; Lee, J. H.; Park, H.; Kim, S. K.; Li, X. S.; Park, J. C.; Chung, J. G.; Jeon, W. S.; Heo, S.; Lee, J. H.; Choi, B. L.; Kim, B. L. *Nano Lett.* **2009**, *9*, 1780–1786.

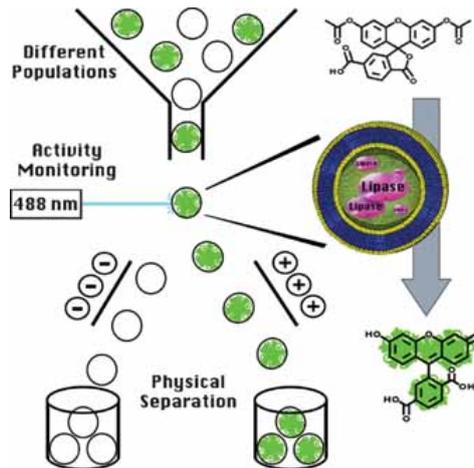
Abstract:



Methods of producing Si nanodots embedded in films of silicon oxide and silicon nitride abound, but fabrication of Si nanodots in a nanowire of these materials is very rare despite the fact that nanowire architecture enhances the charge collection and transport efficiencies for solar cells and field-effect transistors. We report a novel fabrication method for a high-density array of size-controlled silicon nanodots from a silicon oxide nanowire using electron-beam irradiation. Our results demonstrate that a highly dense phase of Si nanodots with a narrow size distribution can be made from a silicon oxide nanowire with a core-shell structure of crystalline silicon-rich oxide (c-SRO)/amorphous silicon oxide (a-SiO₂). This new nanomaterial shows the carrier transport characteristics of a semiconductor. The initially produced amorphous Si nanodots can be readily turned into crystalline Si (c-Si) nanodots by thermal annealing. Key characteristics of c-Si nanodots such as their size, number density, and rate of nucleation and growth are easily controlled by varying the electron radiation dose and annealing temperature. Nanodot formation is mechanistically initiated by electron trapping at the c-SRO core as well as at the core-shell interface, which leads to out-diffusion of the negatively charged oxygen through Coulomb repulsion, fostering the aggregation of Si atoms.

- Sorting Catalytically Active Polymersome Nanoreactors by Flow Cytometry
Nallani, M.; Woestenenk, R.; de Hoog, H. P. M.; van Dongen, S. F. M.; Boezeman, J.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; van Hest, J. C. M. *Small* **2009**, *5*, 1138 – 1143.

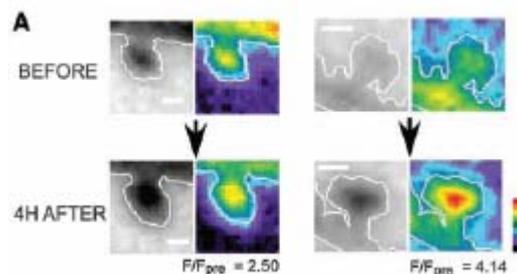
Abstract:



Enzyme-filled stable polymeric capsules (polymersomes) that are permeable to low-molecular-weight (pro-fluorescent) substrates can be sorted based on the activity of encapsulated enzymes using flow cytometry (see image). Enzymatic activity is screened by the build-up of fluorescent product that is prevented from leaking out by co-encapsulation of a trapping agent.

- Input-Specific Spine Entry of Soma-Derived Vesl-1S Protein Conforms to Synaptic Tagging
Okada, D.; Ozawa, F.; Inokuchi, K. *Science* **2009**, 324, 904-909.

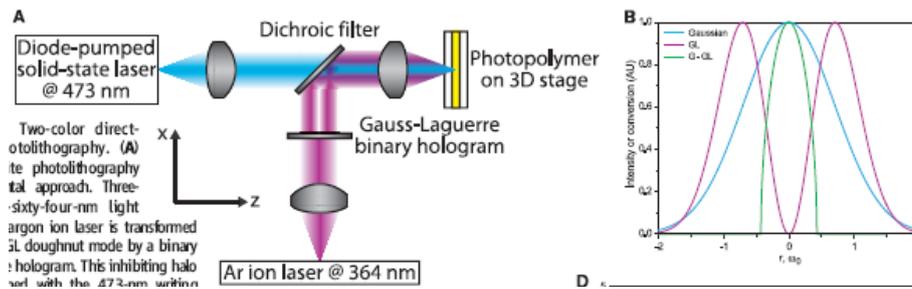
Abstract:



Late-phase synaptic plasticity depends on the synthesis of new proteins that must function only in the activated synapses. The synaptic tag hypothesis requires input-specific functioning of these proteins after undirected transport. Confirmation of this hypothesis requires specification of a biochemical tagging activity and an example protein that behaves as the hypothesis predicts. We found that in rat neurons, soma-derived Vesl-1S (Homer-1a) protein, a late-phase plasticity-related synaptic protein, prevailed in every dendrite and did not enter spines. N-methyl-D-aspartate receptor activation triggered input-specific spine entry of Vesl-1S proteins, which met many criteria for synaptic tagging. These results suggest that Vesl-1S supports the hypothesis and that the activity-dependent regulation of spine entry functions as a synaptic tag.

- Two-Color Single-Photon Photoinitiation and Photoinhibition for Subdiffraction Photolithography
Scott, T. F.; Kowalski, B. A.; Sullivan, A. C.; Bowman, C. N.; McLeod, R. R. *Science* **2009**, 324, 913-917.

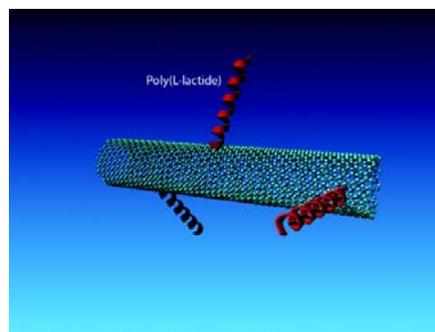
Abstract:



Controlling and reducing the developed region initiated by photoexposure is one of the fundamental goals of optical lithography. Here, we demonstrate a two-color irradiation scheme whereby initiating species are generated by single-photon absorption at one wavelength while inhibiting species are generated by single-photon absorption at a second, independent wavelength. Co-irradiation at the second wavelength thus reduces the polymerization rate, delaying gelation of the material and facilitating enhanced spatial control over the polymerization. Appropriate overlapping of the two beams produces structures with both feature sizes and monomer conversions otherwise unobtainable with use of single- or two-photon absorption photopolymerization. Additionally, the generated inhibiting species rapidly recombine when irradiation with the second wavelength ceases, allowing for fast sequential exposures not limited by memory effects in the material and thus enabling fabrication of complex two- or three-dimensional structures.

- Surface-Initiated Titanium-Mediated Coordination Polymerization from Catalyst-Functionalized Single and Multiwalled Carbon Nanotubes. Priftis, D.; Petzetakis, N.; Sakellariou, G.; Pitsikalis, M.; Baskaran, D.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **2009**, *42*, 3340-3346.

Abstract:

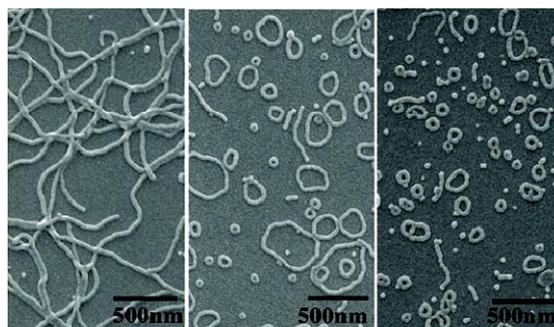


Single (SWNTs) and multiwalled (MWNTs) carbon nanotubes were functionalized with a titanium alkoxide catalyst through a Diels-Alder cycloaddition reaction. The catalyst-functionalized carbon nanotubes (CNTs) were used for the surface initiated titanium-mediated coordination polymerizations of L-lactide (L-LA), ϵ -caprolactone (ϵ -CL) and *n*-hexyl isocyanate (HIC) employing the “grafting from” technique. ¹H NMR, IR and Raman spectra showed that the precursor catalyst was successfully synthesized and covalently attached on the CNTs surface. Thermogravimetric analysis (TGA) revealed that the grafted poly(L-lactide) (PLLA) content could be controlled with time. The final polymer-grafted CNTs were readily dissolved in organic solvents as compared to the insoluble pristine and catalyst-functionalized CNTs. The presence of thick layers of polymers around the CNTs was observed through transmission electron microscopy (TEM). Differential scanning calorimetry (DSC) proved that the glass transition (*T_g*) and melting (*T_m*) temperatures of the PLLA are affected by the presence of the CNTs, while PLLA R-helix conformation remains intact, as revealed by the circular dichroism (CD) spectra.

- Effect of Shear Flow on the Formation of Ring-Shaped ABA Amphiphilic Triblock Copolymer Micelles.

Yu, H.; Jiang, W. *Macromolecules* **2009**, *42*, 3399-3404.

Abstract:



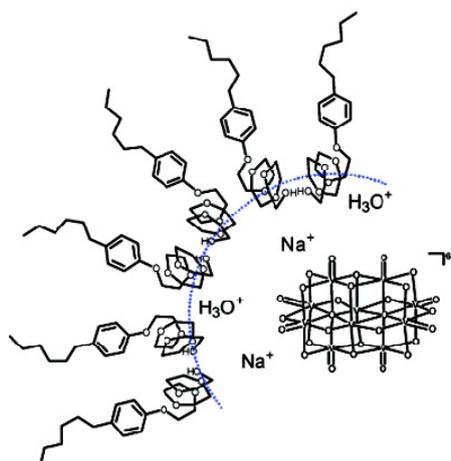
Increasing stirring rate

We have investigated the effect of shear flow on the formation of ring-shaped ABA triblock copolymer (P4VP43-*b*-PS260-*b*-P4VP43) micelles. The results reveal that shear flow plays an important role in the formation of the rings. Both ring size and its distribution are found to be dependent sensitively on the stirring rate. Sizable rings are more likely to be formed at moderate stirring rate. Interestingly, the ring formation mechanism is also dependent on the shear flow. Copolymers are likely to form rings via end-to-end cylinder connection at low stirring rates, whereas they tend to form rings via the pathway of the rod-sphere-vesicle-ring at high stirring rates.

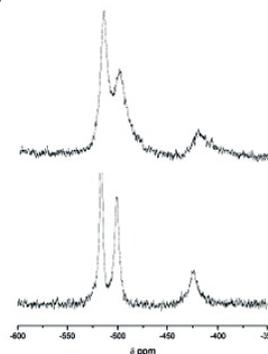
- What Is Inside a Nonionic Reverse Micelle? Probing the Interior of Igepal Reverse Micelles Using Decavanadate

Sedgwick, M. A.; Crans, D. C.; Levinger, N. E. *Langmuir* **2009**, *25*, 5496-5503.

Abstract:



**⁵¹V NMR
Spectrum of V₁₀**

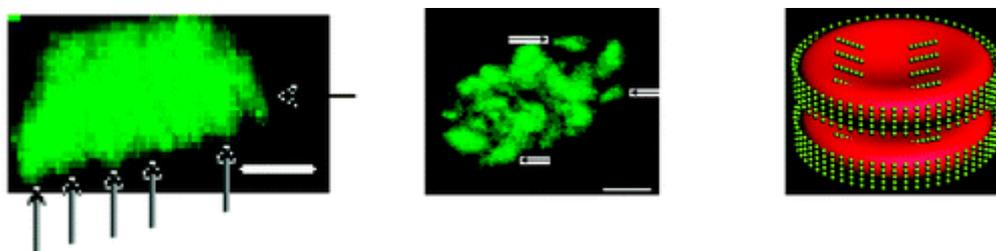


The interiors of reverse micelles formed using nonionic surfactants to sequester water droplets in a nonpolar environment have been investigated using the decavanadate molecule as a probe. Chemical shifts and line widths of the three characteristic signals in the ⁵¹V MR spectrum of decavanadate, corresponding to vanadium atoms in equatorial peripheral, equatorial interior, and axial locations, measure the local proton concentration and characteristics of the reverse micellar interior near the decavanadate probe. All samples investigated indicate deprotonation of the

vanadate probe in the reverse micelle environment. However, the relative mobility of the decavanadate molecule depends on the reverse micellar components. Specifically, the ^{51}V NMR signals of the decavanadate in reverse micelles formed using only the Igepal CO-520 surfactant display sharp signals indicating that the decavanadate molecule tumbles relatively freely while reverse micelles formed from a mixture of Igepal CO-610 and -430 present a more viscous environment for the decavanadate molecule; the nature of the interior of the nonionic reverse water pool varies significantly depending on the specific Igepal. The ^{51}V NMR spectra also indicate that the interior core water pool of the reverse micelles is less acidic than the bulk aqueous solution from which the samples were created. Together, these data provide a description that allows for a comparison of the water pools in these different nonionic reverse micelles.

- Self-Assembly of F_0F_1 -ATPase Motors and Ghost
Tao, N.; Cheng, J.; Wei, L.; Yue, J. *Langmuir* **2009**, *25*, 5747–5752.

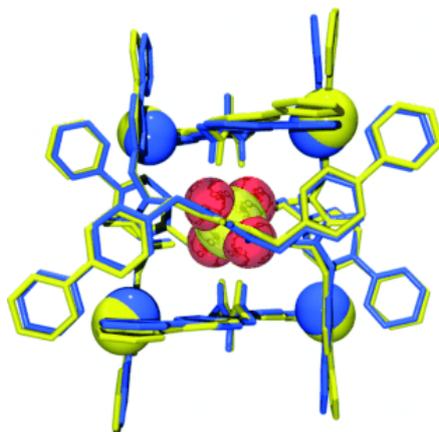
Abstract:



F_0F_1 -ATPase motors have unique mechanical properties, making them attractive building blocks in the field of nanotechnology. However, their organization into well-defined structures with practical functions remains a critical challenge. Here, we describe a self-assembling complex formed by F_0F_1 -ATPase and a ghost which is ordered. Formation of the complex includes two steps: the molecular motors first self-assemble into filaments and then attach to the ghost. The ghost and attached filaments then aggregate into large self-assembled complexes. On illumination, these complexes disassemble because of the rotation force of the molecular motors. The complexes are macroscopic, having a diameter greater than 1 mm. Such complexes of a flexible biomaterial (ghost) self-assembled with a dynamic biomaterial (F_0F_1 -ATPase molecular motor) have several advantages, including flexibility, stability, and ability to be controlled by light, and could be used as controllable rotational molecular machines.

- Computer-Aided Design of a Sulfate-Encapsulating Receptor
Custelcean, R.; Bosano, J.; Bonnesen, P. V.; Kertesz, V.; Hay, B. P. *Angew. Chem. Int. Ed.* **2009**, *48*, 4025–4029.

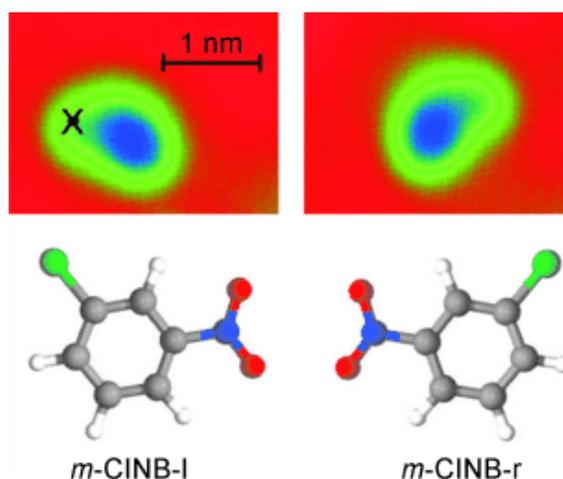
Abstract:



Custom built: A promising new approach towards more efficient self-assembled cage receptors through computer-aided design is demonstrated. The resulting M_4L_6 tetrahedral cage, internally functionalized with accurately positioned urea hydrogen-bonding groups (see structure; yellow: predicted, blue: experimental, space-filling: SO_4^{2-}), proved to be a remarkably strong sulfate receptor in water.

- Chirality Change of Chloronitrobenzene on Au(111) Induced by Inelastic Electron Tunneling
Simic-Milosevic, V.; Meyer, J.; Morgenstern, K. *Angew. Chem. Int. Ed.* **2009**, 48, 4061–4064.

Abstract:



Chirality chameleon: Inelastic electron tunneling manipulation can be used to change a single chloronitrobenzene (CINB) molecule, randomly adsorbed on Au(111), into its desired enantiomeric form (r or l, see STM images and ball-and-stick representation) and to vary its rotational orientation. The different threshold voltages for chirality change (260 mV) and rotation (380 mV) allow these processes to be induced separately.