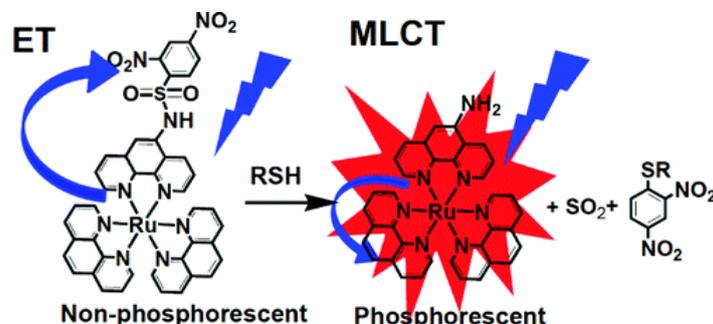


- A Highly Selective OFF-ON Red-Emitting Phosphorescent Thiol Probe with Large Stokes Shift and Long Luminescent Lifetime

Ji, S.; Guo, H.; Yuan, X.; Li, X.; Ding, H.; Gao, P.; Zhao, C.; Wu, W.; Wu, W.; Zhao, J. *Org. Lett.* **2010**, *12*, 2876-2879.

Abstract:

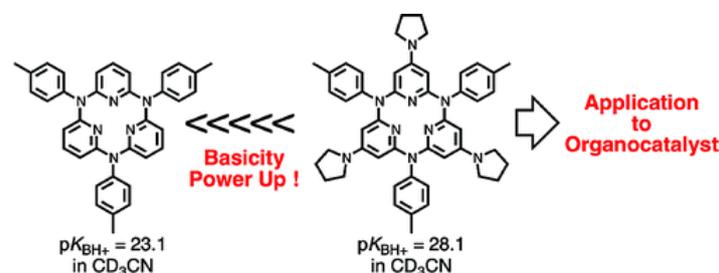


An OFF-ON red-emitting phosphorescent thiol probe is designed by using the 3MLCT photophysics of Ru(II) complexes, i.e., with Ru(II) as the electron donor. The probe is non-luminescent because the MLCT is corrupted by electron transfer from Ru(II) to an intramolecular electron sink (2,4-dinitrobenzenesulfonyl). Thiols cleave the electron sink, and the MLCT is re-established. Phosphorescence at 598 nm was enhanced by 90-fold, with a 143 nm (5256 cm^{-1}) Stokes shift and a $1.1\ \mu\text{s}$ luminescent lifetime.

- Synthesis, Characterization, and Catalytic Reactivity of a Highly Basic Macrotricyclic Aminopyridine

Uchida, N.; Taketoshi, A.; Kuwabara, J.; Yamamoto, T.; Inoue, Y.; Watanabe, Y.; Kanbara, T. *Org. Lett.* **2010**, *12*, 5242-5245.

Abstract:

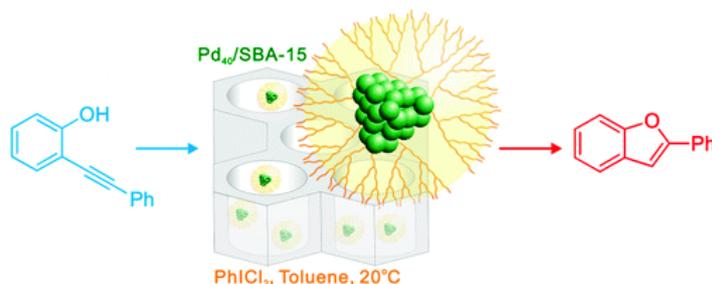


The synthesis methods, physicochemical and structural characteristics, and catalytic reactivity of new macrocyclic proton chelators, *N,N',N''*-tris(*p*-tolyl)azacalix[3](2,6)(4-pyrrolidinopyridine) and *N,N',N''*-tris(*p*-tolyl)azacalix[3](2,6)(4-piperidinopyridine), are studied. The introduction of pyrrolidino and piperidino groups into the pyridine unit enables the enhancement of the synergistic proton affinity of the cavity of the macrotricyclic giving a high basicity ($pK_{\text{BH}^+} = 28.1$ and 27.1 in CD_3CN), resulting in a catalytic activity for the Michael addition of nitromethane with α,β -unsaturated carbonyl compounds.

- Highly Active Heterogeneous Palladium Nanoparticle Catalysts for Homogeneous Electrophilic Reactions in Solution and the Utilization of a Continuous Flow Reactor

Huang, W.; Hung-Chang Liu, J.; Alayoglu, P.; Li, Y.; Witham, C. A.; Tsung, C. K.; Toste, D. F.; Somorjai, G. A. *J. Am. Chem. Soc.* **2010**, *132*, 16771-16773.

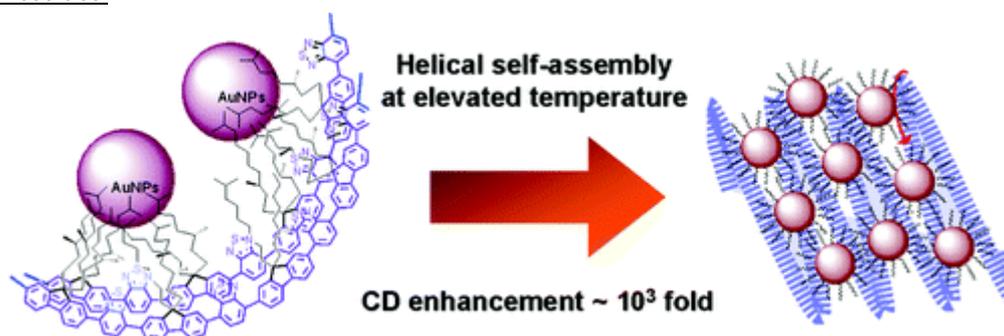
Abstract:



A highly active heterogeneous Pd-nanoparticle catalyst for the intramolecular addition of phenols to alkynes was developed and employed in a continuous flow reaction system. Running the reaction in flow mode revealed reaction kinetics, such as the activation energy and catalyst deactivation, and provides many potential practical advantages.

- Chiral Poly(fluorene-alt-benzothiadiazole) (PFBT) and Nanocomposites with Gold Nanoparticles: Plasmonically and Structurally Enhanced Chirality
Oh, H. S.; Liu, S.; Jee, H.; Baev, A.; Swihart, M. T.; Prasad, P. N. *J. Am. Chem. Soc.* **2010**, *132*, 17346–17348.

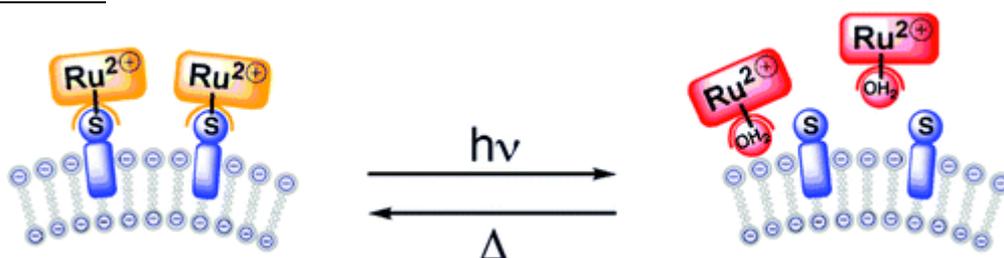
Abstract:



Materials with large chiral optical activity at visible wavelengths are of great interest in photonics, particularly as a route to chiral optical metamaterials. Here, we demonstrate the plasmonic enhancement of the chiral optical activity of chiral poly(fluorene-alt-benzothiadiazole) (PFBT) doped with gold nanoparticles. The supramolecular helical organization of polymeric chains with simultaneous dipole–dipole interaction of the helically ordered nanoparticles with the polymer and one another results in unprecedented values of chirality parameter ($\kappa \sim 0.02$) at visible wavelengths in thin films.

- Ruthenium-Decorated Lipid Vesicles: Light-Induced Release of $[\text{Ru}(\text{terpy})(\text{bpy})(\text{OH}_2)]^{2+}$ and Thermal Back Coordination
Bonnet, S.; Limburg, B.; Meeldijk, J. D.; Gebbink, R. J. M. K.; Killian, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 252–261.

Abstract:

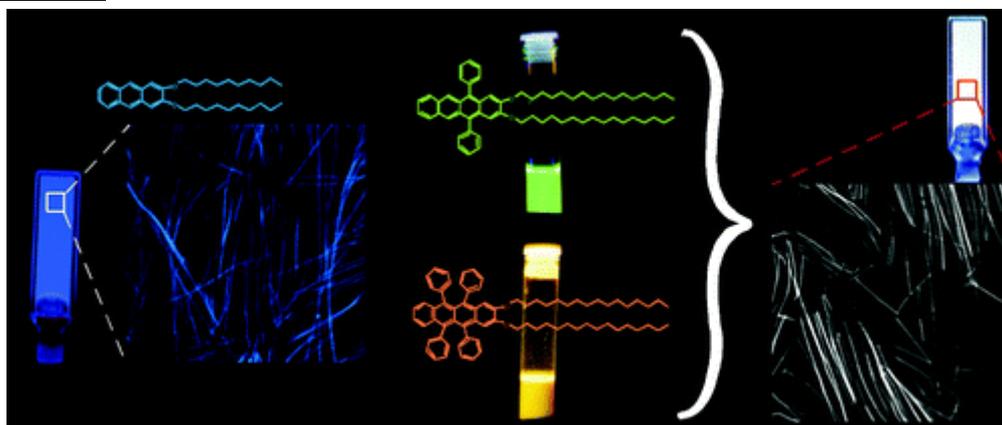


Electrostatic forces play an important role in the interaction between large transition metal complexes and lipid bilayers. In this work, a thioether-cholestanol hybrid ligand (4) was synthesized, which coordinates to ruthenium(II) via its sulfur atom and intercalates into lipid bilayers via its apolar tail. By mixing its ruthenium complex $[\text{Ru}(\text{terpy})(\text{bpy})(4)]^{2+}$ (terpy = 2,2',6',2''-terpyridine; bpy = 2,2'-bipyridine) with either the negatively charged lipid dimyristoylphosphatidylglycerol (DMPG) or with the zwitterionic lipid dimyristoylphosphatidylcholine (DMPC), large unilamellar vesicles decorated with ruthenium polypyridyl complexes are formed. Upon visible light irradiation the ruthenium-sulfur coordination bond is selectively broken, releasing the ruthenium fragment as the free aqua complex $[\text{Ru}(\text{terpy})(\text{bpy})(\text{OH}_2)]^{2+}$. The photochemical quantum yield under blue light irradiation (452 nm) is 0.0074(8) for DMPG vesicles and 0.0073(8) for DMPC vesicles (at 25 °C), which is not significantly different from similar homogeneous systems. Dynamic light scattering and cryo-TEM pictures show that the size and shape of the vesicles are not perturbed by light irradiation. Depending on the charge of the lipids, the cationic aqua complex either strongly interacts with the membrane (DMPG) or diffuses away from it (DMPC). Back coordination of $[\text{Ru}(\text{terpy})(\text{bpy})(\text{OH}_2)]^{2+}$ to the thioether-decorated vesicles takes place only at DMPG bilayers with high ligand concentrations (25 mol %) and elevated temperatures (70 °C). During this process, partial vesicle fusion was also observed. We discuss the potential of such ruthenium-decorated vesicles in the context of light-controlled molecular motion and light-triggered drug delivery.

- White-Light-Emitting Self-Assembled NanoFibers and Their Evidence by Microspectroscopy of Individual Objects

Giansante, C.; Raffy, G.; Schafer, C.; Rahma, H.; Kao, M. T.; Olive, A. G. L.; Guerso, A. D. *J. Am. Chem. Soc.* **2011**, *133*, 316–325.

Abstract:



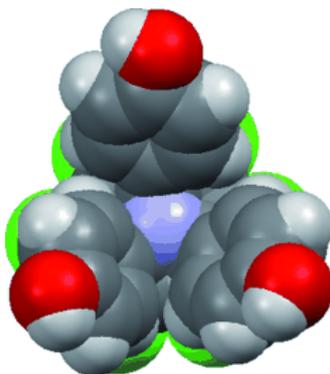
The self-assembly of a blue-emitting light-harvesting organogelator and specifically designed highly fluorescent tetracenes yields nanofibers with tunable emissive properties. In particular, under near-UV excitation, white light emission is achieved in organogels and dry films of nanofibers. Confocal fluorescence microspectroscopy demonstrates that each individual nanofiber emits white light. A kinetic study shows that an energy transfer (ET) occurs between the blue-emitting anthracene derivative and the green- and red-emitting tetracenes, while inter-tetracene ETs also take place. Moreover, microscopy unravels that the nanofibers emit polarized emission in the blue spectral region, while at wavelengths higher than 500 nm the emission is not significantly polarized.

- Azatriquinane as a Platform for Tripodal Metal Complexes and Calixiform Scaffolds
Jevric, M.; Zheng, T.; Meher, N. K.; Fettingner, J. C.; Mascal, M. *Angew. Chem. Int. Ed.* **2011**, *50*,

717-719.

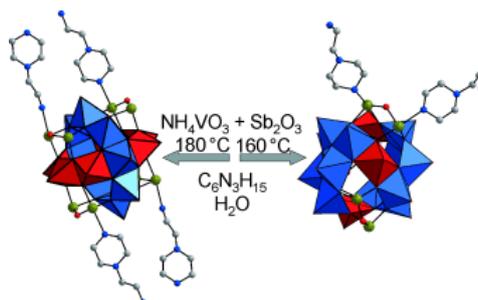
Abstract:

4



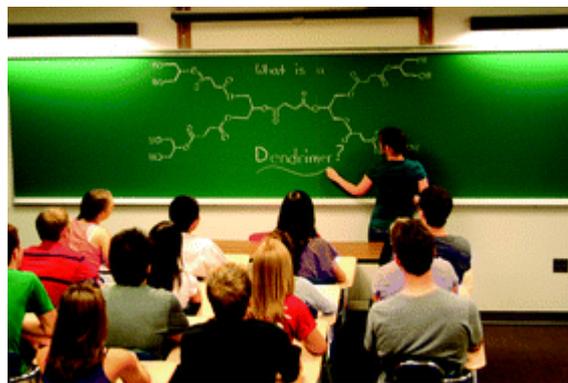
A puckered platform: Azatriquinanes and azatriquinacenes are convex, rigid molecular scaffolds for constructing tripodal ligands and calix-like structures with a basic nitrogen site at the bottom of the cavity (see space-filling structure; blue N, green Cl, red O, gray C, light gray H)

- Organic Functionalization of Polyoxovanadates: SbN Bonds and Charge Control
Antonova, E.; Näther, C.; Kögerler, P.; Bensch, W. *Angew. Chem. Int. Ed.* **2011**, *50*, 764-767.

Abstract:

New docking sites: SbN bonds formed under hydrothermal conditions enable the attachment of primary and secondary organic amines (see structures, Cgray, Nblue) to antimonato polyoxovanadate cluster anions (polyhedral representations; O red, Sb yellow), whose charge can be compensated by protonated amines.

- Biomedical applications of dendrimers: a tutorial
Mintzer, M. A.; Grinstaff, M. W. *Chem. Soc. Rev.* **2011**, *40*, 173-190.

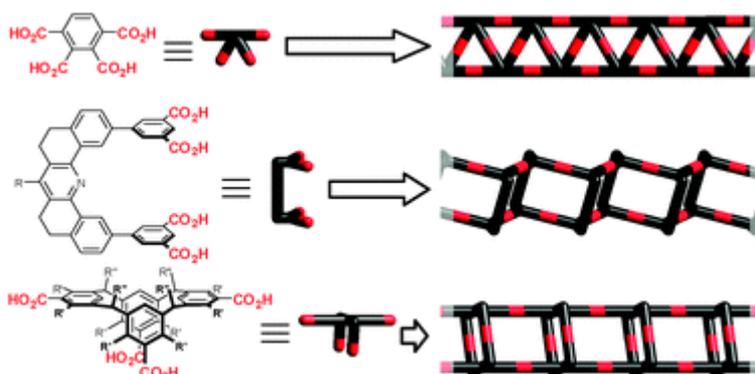
Abstract:

Since their development in the mid-80s, dendrimers have become prominent synthetic macromolecules in the field of biomedical science. This *tutorial review* begins by discussing pertinent background information about dendrimers, focusing on their behavior in solution, how they are synthesized and what advantages they have over linear polymers. Then the focus of the review shifts to the biomedical applications of dendrimers, including their use in drug delivery, tissue engineering, gene transfection, and contrast enhancement for magnetic resonance imaging. This *tutorial review* is written for first-year graduate students or senior undergraduates and “asks” and “answers” many of the questions that arise in our first discussions of dendrimers.

- Mastering fundamentals of supramolecular design with carboxylic acids. Common lessons from X-ray crystallography and scanning tunneling microscopy

Ivasenko, O.; Perepichka, D. F. *Chem. Soc. Rev.* **2011**, *40*, 191-206.

Abstract:

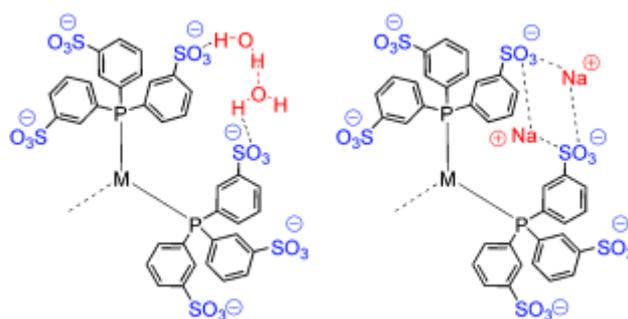


Hydrogen bonding is one of the most important non-covalent interactions in both biological (DNA, peptides, saccharides *etc.*) and artificial systems (various soft materials, host–guest architectures, molecular networks, *etc.*). Carboxylic acids are some of the most simple yet powerful hydrogen-bonding building blocks, that possess a particularly rich supramolecular chemistry. This *tutorial review* focuses on the structural diversity of supramolecular architectures accessible *via* hydrogen bonding of carboxylic acids, as observed both in single crystals using X-ray analysis and in monolayers on surfaces using scanning probe techniques. It provides a concise overview of the key concepts and principles of modern supramolecular design and is given in the form of case studies of finely selected literature examples, covering formation of macrocycles, chains, ladders, rotaxanes, catenanes, various 2D and 3D nets, host–guest systems and some applications thereof.

- Steric, Electronic, and Secondary Effects on the Coordination Chemistry of Ionic Phosphine Ligands and the Catalytic Behavior of Their Metal Complexes

Snelders, D. J. M.; van Koten, G.; Gebbink, R. J. M. K. *Chem.-Eur. J.* **2011**, *17*, 42-57.

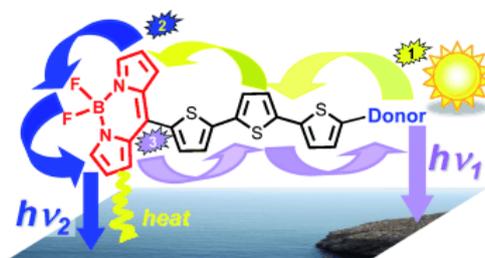
Abstract:



The effects of introducing ionic functionalities in phosphine ligands on the coordination chemistry of these ligands and the catalytic behavior of the corresponding metal complexes are reviewed. The steric and electronic consequences of such functionalizations are discussed. Apart from these steric and electronic effects, the presence of charged groups often leads to additional, supramolecular interactions that occur in the second coordination sphere of the metal complex, such as intramolecular, interligand hydrogen bonding and Coulombic repulsion. These interactions can significantly alter the behavior of the phosphine ligand in question. Such effects have been observed in phosphine–metal association/dissociation equilibria, ligand substitution reactions, and stereoisomerism in phosphine–metal complexes. By drawing general conclusions, this review offers an insight into the coordination and catalytic behavior of phosphine ligands containing ionic functionalities and their corresponding metal complexes.

- Enhanced Functionality for Donor–Acceptor Oligothiophenes by means of Inclusion of BODIPY: Synthesis, Electrochemistry, Photophysics, and Model Chemistry
Collado, D.; Casado, J.; Rodríguez-González, S.; López-Navarrete, J. T.; Suau, R.; Perez-Inestrosa, E.; Pappenfus, T. M.; Raposo, M. M. M. *Chem.-Eur. J.* **2011**, *17*, 498-507.

Abstract:

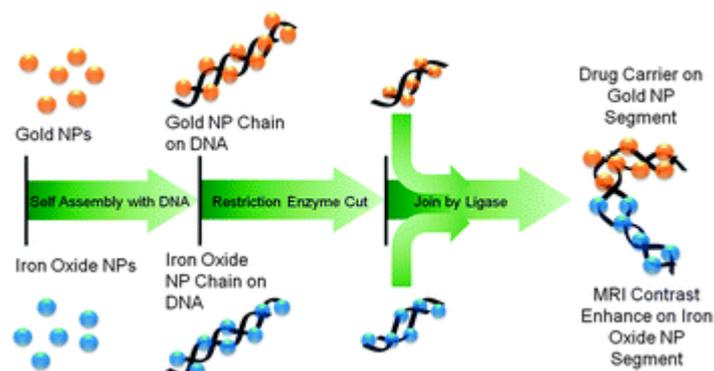


We have synthesized several new push–pull oligothiophenes based on the boron dipyrromethene (BODIPY) moiety as the electron acceptor and the more well-known oligothiophenes substituted with N,N-dialkylamino functions to enhance their electron-donor ability. A complete characterization of the electronic properties has been carried out; it consists of their photophysical, electrochemical, and vibrational properties. The compounds have been studied after chemical treatment with acids and after oxidation. In this regard, they can be termed as NIR dyes and amphoteric redox electroactive molecules. We have described the presence of dual fluorescence in these molecules and fluorescence quenching either by energy transfer or, in the push–pull molecules, by electron exchange. The combination of electrochemical and proton reversibility along with the interesting optical properties of the new species offer an interesting platform for sensor and material applications.

- Gold–iron oxide nanoparticle chains scaffolded on DNA as potential magnetic resonance imaging agents

Jaganathan, H.; Ivanisevic, A. *J. Mater. Chem.* **2011**, *21*, 939-943.

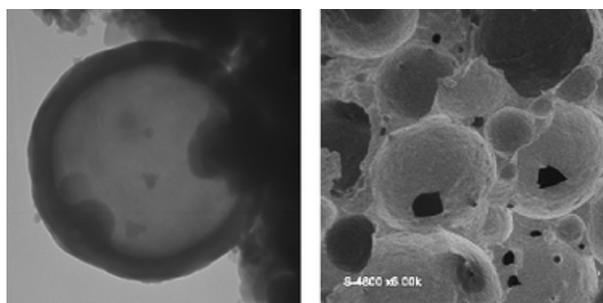
Abstract:



We present a unique nanostructure design using DNA that can serve as potential magnetic resonance imaging (MRI) agents. By attaching gold and iron oxide NPs on linear strands of DNA, NP chains are easily formed by self-assembly and through DNA-based enzymes. Furthermore, gold–iron oxide NP chains exhibit fast proton relaxation times that improve MRI signals and do not induce *in vitro* toxicity. This report highlights the use of DNA to create NP chains as a cost-effective, promising technology for the detection of diseases through MRI.

- Silica and hybrid silica hollow spheres from imidazolium-based templating agents
Trilla, M.; Cattoën, X.; Blanc, C.; Wong Chi Man, M.; Pleixats, R. *J. Mater. Chem.* **2011**, *21*, 1058-1063.

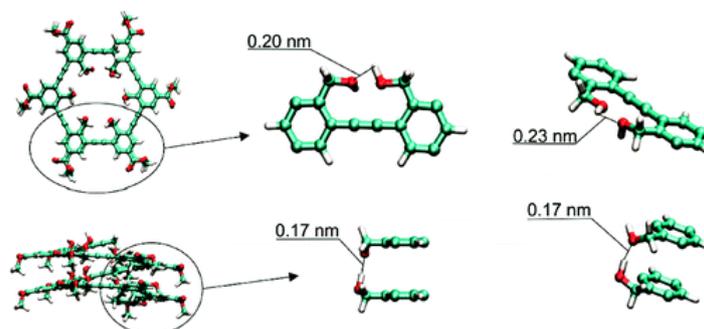
Abstract:



Hollow or dense silica spheres were synthesized by the hydrolysis-condensation of tetraethoxysilane templated by an ionic liquid crystal. A hydrolysable silylated analog of these ionic liquid crystals was also submitted to a sol–gel reaction in a binary toluene–water mixture, yielding hybrid vesicles. All the materials were fully characterized by solid state NMR, FTIR, electron microscopies, N_2 adsorption–desorption measurements, and their mechanism of formation was assessed thanks to *in situ* optical microscopy studies.

- Controlling the *m*-Poly(phenylene ethynylene) Helical Cavity Environment: Hydrogen Bond Stabilized Helical Structures
Nguyen, H. H.; McAliley, J. H.; Bruce, D. A. *Macromolecules*, **2011**, *44*, 60–67.

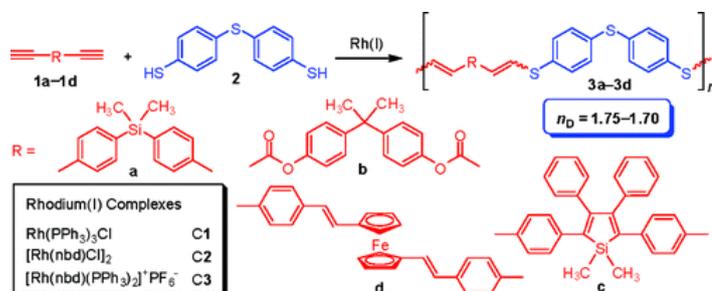
Abstract:



Replica exchange molecular dynamics (REMD) simulations using explicit solvents were used to study the folding behaviors of a group of *m*-poly(phenylene ethynylene)s (mPPEs), which are being actively investigated for a variety of biological and catalysis applications. The mPPEs considered in this study have different *endohelix* functional groups, which in the helical conformation of the polymer are localized within the helical cavity. The results showed that, for mPPEs with ester functional groups arranged on the exohelix of the helical polymer, altering the endohelix functional groups did not significantly affect folding behaviors in acetonitrile. This result is consistent with experimental data and indicates that the properties of the helical cavity may be tailored for certain applications without destabilizing the helix conformation, so long as the exohelix functional groups are esters. We also present simulation results for a set of mPPEs with endohelix functional groups that enhance the stability of the helical conformation via the formation of intra- and interturn hydrogen bonds (HBs). If mPPE folding is viewed as a nucleation/growth process, intraturn HB interactions facilitate both nucleation events and growth, while interturn HBs and π -stacking interactions affect only the growth process. These mPPEs, which lack exohelix functional groups, were shown to fold into stable helical secondary structures in acetonitrile, methanol, and even chloroform, although chlorinated solvents have previously been known to denature mPPE helical structures. Our results predict that this stabilization occurs to the extent that a variety of exohelix functional groups can be incorporated into mPPE backbones, while maintaining a stable helical secondary structure, including many functional groups that are known to destabilize the helix in non-hydrogen-bonded mPPEs.

- Thiol–Yne Click Polymerization: Regio- and Stereoselective Synthesis of Sulfur-Rich Acetylenic Polymers with Controllable Chain Conformations and Tunable Optical Properties
Liu, J.; Lam, J. W. Y.; Jim, C. K. W.; Ng, J. C. Y.; Shi, J.; Su, H.; Yeung, K. F.; Hong, Y.; Faisal, M.; Yu, Y.; Wong, K. S.; Tang, B. Z. *Macromolecules* **2011**, *44*, 68–79.

Abstract:



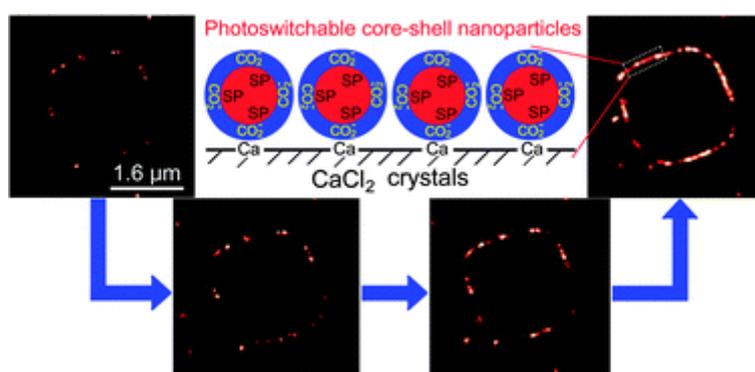
The atom-economical alkyne polyhydrothiolations of aromatic diynes (**1**) and dithiol (**2**) catalyzed by rhodium complexes proceed smoothly under mild conditions at room temperature in a regioselective manner, producing sole anti-Markovnikov products of poly(vinylene sulfide)s (**3**) with high molecular weights (M_w up to 31500) and stereoregularities (*E* content up to 100%) in high yields (up to 95.2%).

The stereostructures of the polymers are readily tuned by engineering control on the sequential addition of monomers during the polymerization process and postmanipulation by light irradiation. All the poly(vinylene sulfide)s are soluble in common organic solvents and exhibit good film-forming ability and high optical transparency. The functional pendants in **1** have endowed **3** with novel properties such as aggregation-enhanced emission characteristics, optical limiting to harsh laser pulses, and ceramization capability to semiconducting nanoparticles. The polymers are thermal and UV curable, enabling the fabrication of fluorescent photopatterns. Their thin films show high refractive indices ($n_D = 1.75\text{--}1.70$) and low optical dispersions (down to 0.006) at telecom important wavelengths. Their refractive indices vary with their stereostructures and can be modulated by UV irradiation.

- Super-resolution fluorescence nanoscopy applied to imaging core-shell photoswitching nanoparticles and their self-assemblies

Tian, Z.; Li, A. D. Q.; Hu, D. *Chem. Commun.* **2011**, *47*, 1258-1260.

Abstract:

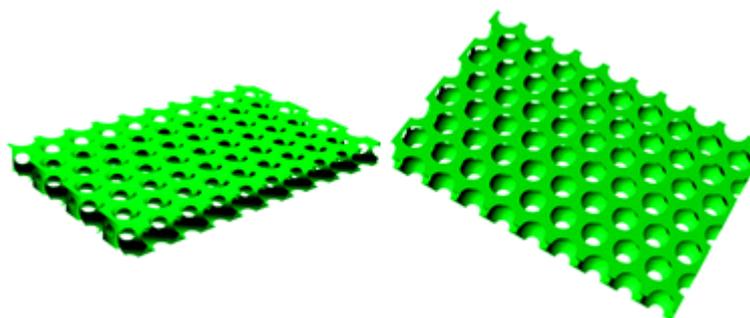


Using photo-actuated unimolecular logical switching attained reconstruction (PULSAR) nanoscopy, the structures of photoswitchable polymeric nanoparticles self-assembled on the surfaces of CaCl₂ crystals at the nanoscale were revealed; the photoswitching events and the locations of the photoswitchable fluorescent dyes inside the hydrophobic cores of the core-shell type polymeric nanoparticles were determined.

- Fabrication of freestanding honeycomb films with through-pore structures *via* air/water interfacial self-assembly

Ma, H.; Cui, J.; Song, A.; Hao, J. *Chem. Commun.* **2011**, *47*, 1154-1156.

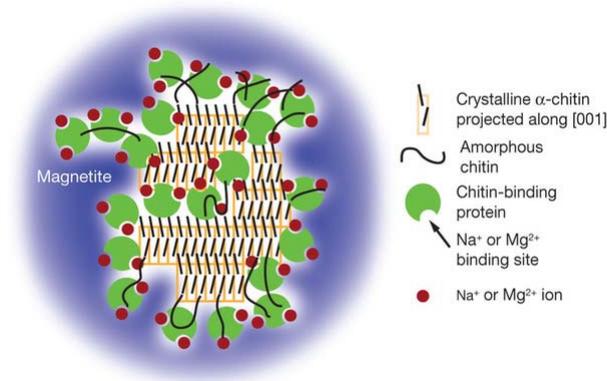
Abstract:



Highly ordered freestanding honeycomb films with asymmetric through-pore structures were prepared from polystyrene/gold-nanoparticles (PS/AuNPs) nanocomposite at an air/water interface using a one-step interfacial self-assembly method.

- Nanoscale chemical tomography of buried organic–inorganic interfaces in the chiton tooth
Gordon, L. M.; Joester, D. *Nature* **2011**, *469*, 194–197.

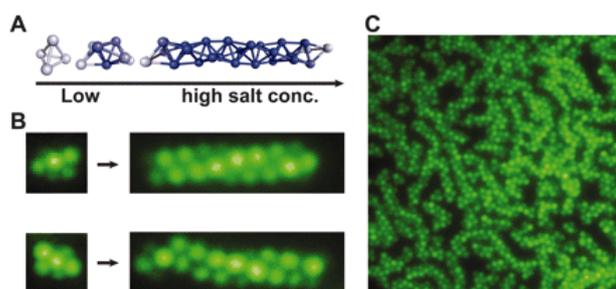
Abstract:



Biological organisms possess an unparalleled ability to control the structure and properties of mineralized tissues. They are able, for example, to guide the formation of smoothly curving single crystals or tough, lightweight, self-repairing skeletal elements. In many biominerals, an organic matrix interacts with the mineral as it forms, controls its morphology and polymorph, and is occluded during mineralization. The remarkable functional properties of the resulting composites—such as outstanding fracture toughness and wear resistance—can be attributed to buried organic–inorganic interfaces at multiple hierarchical levels. Analysing and controlling such interfaces at the nanometre length scale is critical also in emerging organic electronic and photovoltaic hybrid materials. However, elucidating the structural and chemical complexity of buried organic–inorganic interfaces presents a challenge to state-of-the-art imaging techniques. Here we show that pulsed-laser atom-probe tomography reveals three-dimensional chemical maps of organic fibres with a diameter of 5–10 nm in the surrounding nano-crystalline magnetite (Fe_3O_4) mineral in the tooth of a marine mollusc, the chiton *Chaetopleura apiculata*. Remarkably, most fibres co-localize with either sodium or magnesium. Furthermore, clustering of these cations in the fibre indicates a structural level of hierarchy previously undetected. Our results demonstrate that in the chiton tooth, individual organic fibres have different chemical compositions, and therefore probably different functional roles in controlling fibre formation and matrix–mineral interactions. Atom-probe tomography is able to detect this chemical/structural heterogeneity by virtue of its high three-dimensional spatial resolution and sensitivity across the periodic table. We anticipate that the quantitative analysis and visualization of nanometre-scale interfaces by laser-pulsed atom-probe tomography will contribute greatly to our understanding not only of biominerals (such as bone, dentine and enamel), but also of synthetic organic–inorganic composites.

- Supracolloidal Reaction Kinetics of Janus Spheres
Chen, Q.; Whitmer, J. K.; Jiang, S.; Bae, S. C.; Lijten, E.; Granick, S. *Science* **2011**, *331*, 199–202.

Abstract:

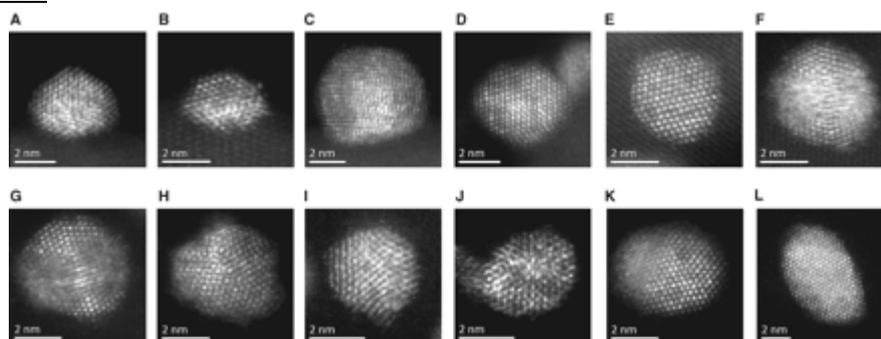


Clusters in the form of aggregates of a small number of elemental units display structural, thermodynamic, and dynamic properties different from those of bulk materials. We studied the kinetic pathways of self-assembly of “Janus spheres” with hemispherical hydrophobic attraction and found key differences from those characteristic of molecular amphiphiles. Experimental visualization combined with theory and molecular dynamics simulation shows that small, kinetically favored isomers fuse, before they equilibrate, into fibrillar triple helices with at most six nearest neighbors per particle. The time scales of colloidal rearrangement combined with the directional interactions resulting from Janus geometry make this a prototypical system to elucidate, on a mechanistic level and with single-particle kinetic resolution, how chemical anisotropy and reaction kinetics coordinate to generate highly ordered structures.

- Solvent-Free Oxidation of Primary Carbon-Hydrogen Bonds in Toluene Using Au-Pd Alloy Nanoparticles

Kesavan, L.; Tiruvalam, R.; Ab Rahim, M. H.; bin Saiman, M. I.; Enache, D. I.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Taylor, S. H.; Knight, D. W.; Kiely, C. J.; Hutchings, G. J. *Science* **2011**, *331*, 195-199.

Abstract:



Selective oxidation of primary carbon-hydrogen bonds with oxygen is of crucial importance for the sustainable exploitation of available feedstocks. To date, heterogeneous catalysts have either shown low activity and/or selectivity or have required activated oxygen donors. We report here that supported gold-palladium (Au-Pd) nanoparticles on carbon or TiO₂ are active for the oxidation of the primary carbon-hydrogen bonds in toluene and related molecules, giving high selectivities to benzyl benzoate under mild solvent-free conditions. Differences between the catalytic activity of the Au-Pd nanoparticles on carbon and TiO₂ supports are rationalized in terms of the particle/support wetting behavior and the availability of exposed corner/edge sites.