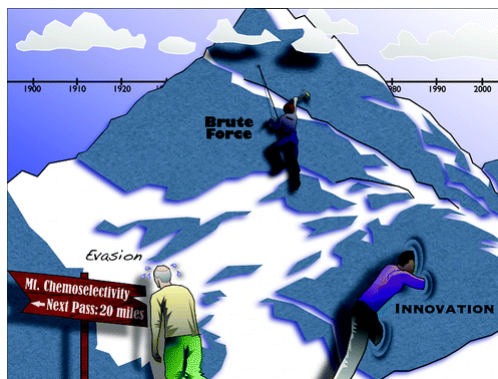


- Chemoselectivity: The Mother of Invention in Total Synthesis
Shenvi, R. A.; O'Malley, D. P.; Baran, P. S. *Acc. Chem. Res.* **2009**, 42, 530–541.

Abstract:



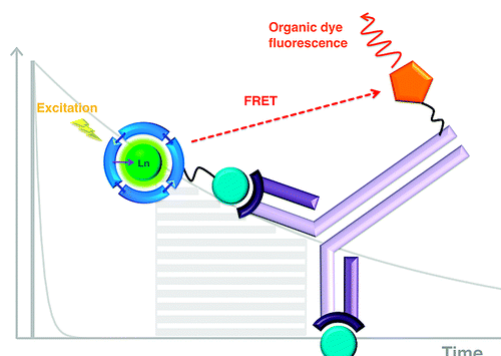
The true creator is necessity, who is the mother of our invention. – Plato

IUPAC defines chemoselectivity as “the preferential reaction of a chemical reagent with one of two or more different functional groups”, a definition that describes in rather understated terms the single greatest obstacle to complex molecule synthesis. Indeed, efforts to synthesize natural products often become case studies in the art and science of chemoselective control, a skill that nature has practiced deftly for billions of years but man has yet to master. Confrontation of one or perhaps a collection of functional groups that are either promiscuously reactive or stubbornly inert has the potential to unravel an entire strategic design. One could argue that the degree to which chemists can control chemoselectivity pales in comparison to the state of the art in stereocontrol. In this Account, we hope to illustrate how the combination of necessity and tenacity leads to the invention of chemoselective chemistry for the construction of complex molecules.

In our laboratory, a premium is placed upon selecting targets that would be difficult or impossible to synthesize using traditional techniques. The successful total synthesis of such molecules demands a high degree of innovation, which in turn enables the discovery of new reactivity and principles for controlling chemoselectivity. In devising an approach to a difficult target, we choose bond disconnections that primarily maximize skeletal simplification, especially when the proposed chemistry is poorly preceded or completely unknown. By choosing such a strategy—rather than adapting an approach to fit known reactions—innovation and invention become the primary goal of the total synthesis. Delivery of the target molecule in a concise and convergent manner is the natural consequence of such endeavors, and invention becomes a prerequisite for success.

- From Antenna to Assay: Lessons Learned in Lanthanide Luminescence
Moore, E. G.; Samuel, A. P. S.; Raymond, K. N. *Acc. Chem. Res.* **2009**, 42, 542–552.

Abstract:



Ligand-sensitized, luminescent lanthanide(III) complexes are of considerable importance because their unique photophysical properties (microsecond to millisecond lifetimes, characteristic and narrow emission bands, and large Stokes shifts) make them well suited as labels in fluorescence-based bioassays. The long-lived emission of lanthanide(III) cations can be temporally resolved from scattered light and background fluorescence to vastly enhance measurement sensitivity. One challenge in this field is the design of sensitizing ligands that provide highly emissive complexes with sufficient stability and aqueous solubility for practical applications.

In this Account, we give an overview of some of the general properties of the trivalent lanthanides and follow with a summary of advances made in our laboratory in the development of highly luminescent Tb(III) and Eu(III) complexes for applications in biotechnology. A focus of our research has been the optimization of these compounds as potential commercial agents for use in homogeneous time-resolved fluorescence (HTRF) technology. Our approach involves developing high-stability octadentate Tb(III) and Eu(III) complexes that rely on all-oxygen donor atoms and using multichromophore chelates to increase molar absorptivity; earlier examples utilized a single pendant chromophore (that is, a single “antenna”).

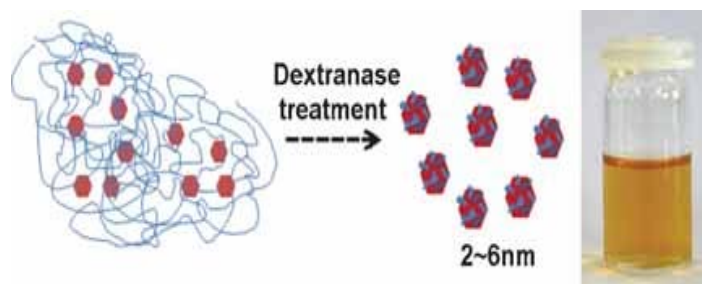
Ligands based on 2-hydroxyisophthalamide (IAM) provide exceptionally emissive Tb(III) complexes with quantum yield values up to ~60% that are stable at the nanomolar concentrations required for commercial assays. Through synthetic modification of the IAM chromophore and time-dependent density functional theory (TD-DFT) calculations, we have developed a method to predict absorption and emission properties of these chromophores as a tool to guide ligand design. Additionally, we have investigated chiral IAM ligands that yield Tb(III) complexes possessing both high quantum yield values and strong circularly polarized luminescence (CPL) activity.

To efficiently sensitize Eu(III) emission, we have used the 1-hydroxypyridin-2-one (1,2-HOPO) chelate to create remarkable ligands that combine excellent photophysical properties and exceptional aqueous stabilities. A more complete understanding of this chromophore has been achieved by combining low-temperature phosphorescence measurements with the same TD-DFT approach used with the IAM system. Eu(III) complexes with strong CPL activity have also been obtained with chiral 1,2-HOPO ligands. We have also undertaken kinetic analysis of radiative and nonradiative decay pathways for a series of Eu(III) complexes; the importance of the metal ion symmetry on the ensuing photophysical properties is clear. Lastly, we describe a Tb(III)-IAM compound—now carried through to commercial availability—that offers improved performance in the common HTRF platform and has the potential to vastly improve sensitivity.

- Controlled Nanoparticle Formation by Enzymatic Deshelling of Biopolymer-Stabilized Nanosuspensions

Kim, Y.-Y.; Hore, K.; Hall, S. R.; Walsh, D. *Small* **2009**, 5, 913 – 918.

Abstract:

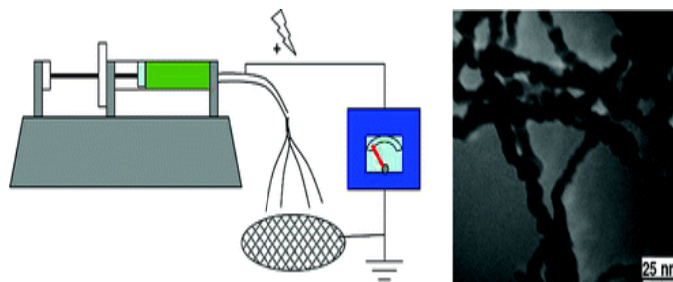


Formation of biopolymer-stabilized nanosuspensions followed by dextranase enzyme treatment is demonstrated for the liberation of monodisperse particles of controllable size up to 6 nm (see image). A range of metal oxide nanoparticles stabilized by remnant oligomer at ≈ 3 wt% are reliably prepared for applications that include catalysis and nanoparticle-based biosensors

3

- Platinum Nanowires Produced by Electrospinning
Shui, J.; Li, J. C. M. *Nano Lett.* **2009**, *9*, 1307–1314.

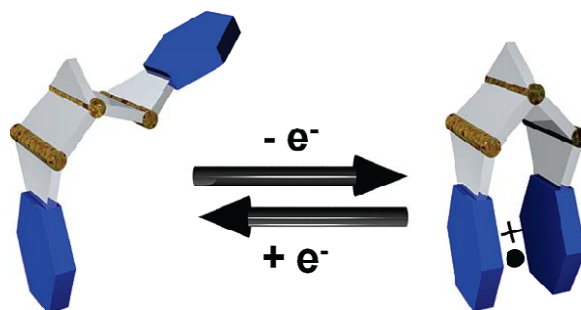
Abstract :



A method of making long (cm) Pt nanowires of a few nanometers diameter from electrospinning is described. A major problem of avoiding bead formation along the nanofibers is analyzed, and the conditions under which the bead formation is minimized are investigated. Our ultimate purpose is to make free-standing fuel cell electrodes from these nanowires.

- Molecular Actuator: Redox-Controlled Clam-Like Motion in a Bichromophoric Electron Donor
Chebny V. J.; Shukla R.; Lindeman S. V.; Rathore R. *Org. Lett.* **2009**, *11*, 1939-1942.

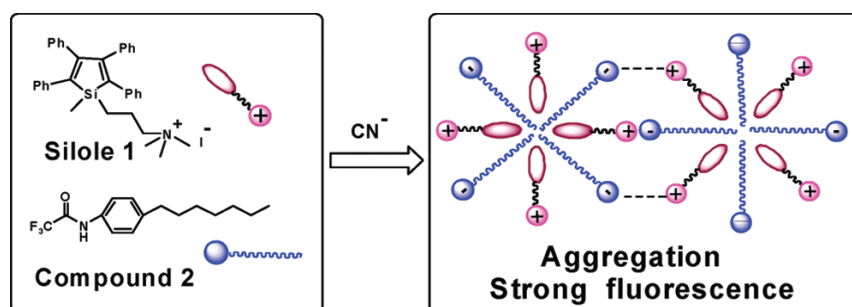
Abstract :



The one-electron oxidation of tetramethoxydibenzobicyclo[4.4.1]undecane (4) prompts it to undergo a clam-like electromechanical actuation into a cofacially π -stacked conformer as established by (i) electrochemical analysis, (ii) by the observation of the intense charge-resonance transition in the near IR region in its cation radical spectrum, and (iii) by X-ray crystallographic characterization of the isolated cation radical salt ($4^{+\bullet}$ SbCl₆⁻).

- A Fluorescence Turn-on Detection of Cyanide in Aqueous Solution Based on the Aggregation-Induced Emission
Peng L.; Wang M.; Zhang G.; Zhang D.; Zhu D. *Org. Lett.* **2009**, *11*, 1943-1946.

Abstract :

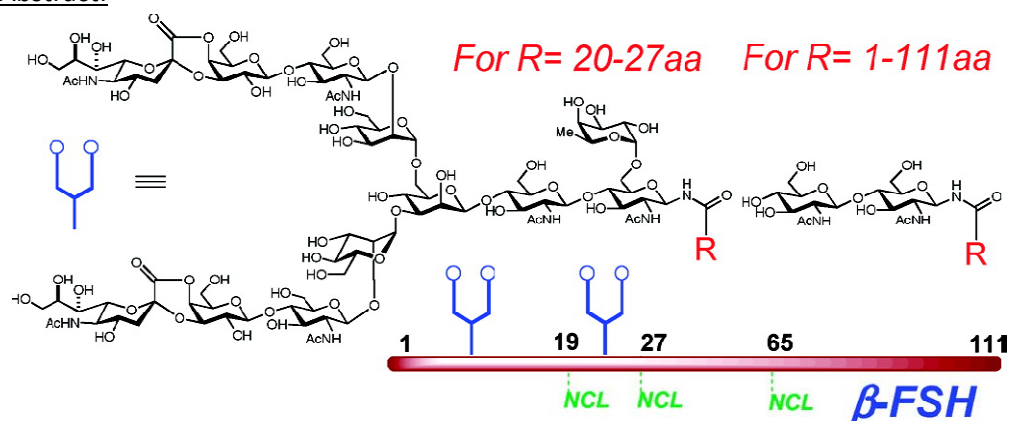


The nucleophilic addition of cyanide to the trifluoroacetylamino group in 2 yields an amphiphilic species which would induce the aggregation of silole 1, and as a result, the fluorescence of the ensemble increases largely. Accordingly, a fluorescence turn-on detection of cyanide in aqueous solution can be established with the ensemble of silole 1 and compound 2. Also, this ensemble displays good selectivity toward cyanide over other common inorganic anions.

- Toward Fully Synthetic Homogeneous β -Human Follicle-Stimulating Hormone (β -hFSH) with a Biantennary N-Linked Dodecasaccharide. Synthesis of β -hFSH with Chitobiose Units at the Natural Linkage Sites

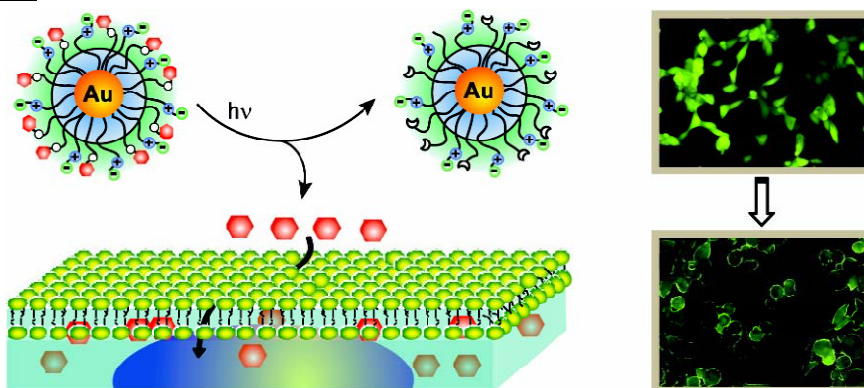
Nagorny, P.; Fasching, B.; Li, X.; Chen, G.; Aussedat, B.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2009**, *131*, 5792–5799.

Abstract:



A highly convergent synthesis of the sialic acid-rich biantennary N-linked glycan found in human glycoprotein hormones and its use in the synthesis of a fragment derived from the β -domain of human Follicle-Stimulating Hormone (hFSH) are described. The synthesis highlights the use of the Sinaÿ radical glycosidation protocol for the simultaneous installation of both biantennary side-chains of the dodecasaccharide as well as the use of glycal chemistry to construct the tetrasaccharide core in an efficient manner. The synthetic glycan was used to prepare the glycosylated 20-27aa domain of the β -subunit of hFSH under a Lansbury aspartylation protocol. The proposed strategy for incorporating the prepared N-linked dodecasaccharide-containing 20-27aa domain into β -hFSH subunit was validated in the context of a model system, providing protected β -hFSH subunit functionalized with chitobiose at positions 7 and 24.

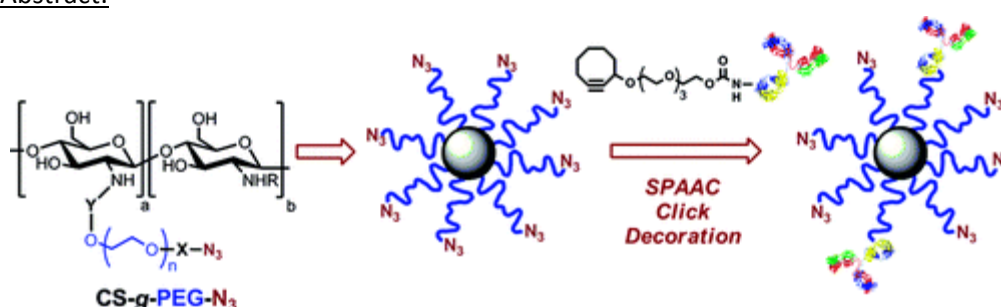
- Photoregulated Release of Caged Anticancer Drugs from Gold Nanoparticles
Agasti, S. S.; Chompoosor, A.; You, C.; Ghosh, P.; Kim, C.; Rotello, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 5728–5729.

Abstract:

An anticancer drug (5-fluorouracil) was conjugated to the surface of gold nanoparticles through a photocleavable o-nitrobenzyl linkage. In this system, the particle serves as both cage and carrier for the therapeutic, providing a nontoxic conjugate that effectively releases the payload upon long wavelength UV irradiation.

- Surpassing the Use of Copper in the Click Functionalization of Polymeric Nanostructures: A Strain-Promoted Approach

Lallana, E.; Fernandez-Megia, E.; Riguera, R. *J. Am. Chem. Soc.* **2009**, *131*, 5748–5750.

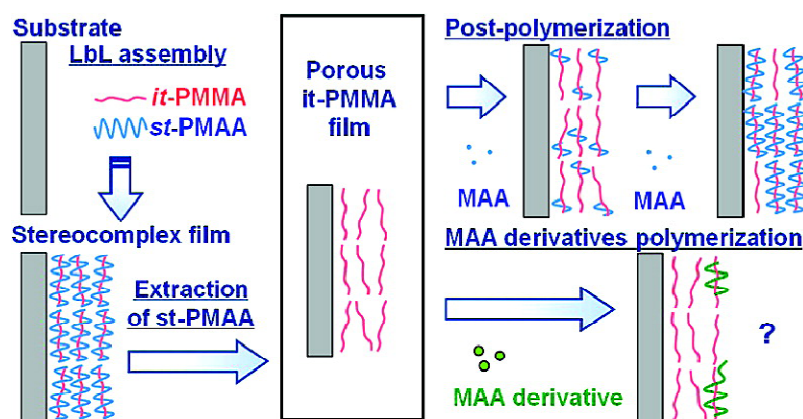
Abstract:

The limitations (depolymerization and Cu contamination) in the use of Cu(I)-catalyzed azide–alkyne [3 + 2] cycloadditions (CuAAC) for the selective click functionalization of polysaccharide-based systems have been efficiently surpassed using a strain-promoted approach (SPAAC). The SPAAC decoration of chitosan-g-poly(ethylene glycol) nanostructures with an immunoglobulin G under physiological conditions represents a step forward in the preparation of immunonanoparticles.

- Mechanistic Studies on Template Polymerization in Porous Isotactic Poly(methyl methacrylate) Thin Films by Radical Polymerization and Postpolymerization of Methacrylate Derivatives.

Ajiro, H.; Kamei, D.; Akashi, M. *Macromolecules* **2009**, *42*, 3019–3025.

Abstract:



The postpolymerization of various vinyl monomers was applied for mechanistic studies of the template polymerization of methacrylic acid (MAA) in porous isotactic (it-) poly(methyl methacrylate) (PMMA) thin films on quartz crystal microbalance (QCM) substrates and on silica gels, which were prepared by the alternative layer-by-layer (LbL) assembly of it-PMMA/syndiotactic- (st-) poly(methacrylic acid) (PMAA). In

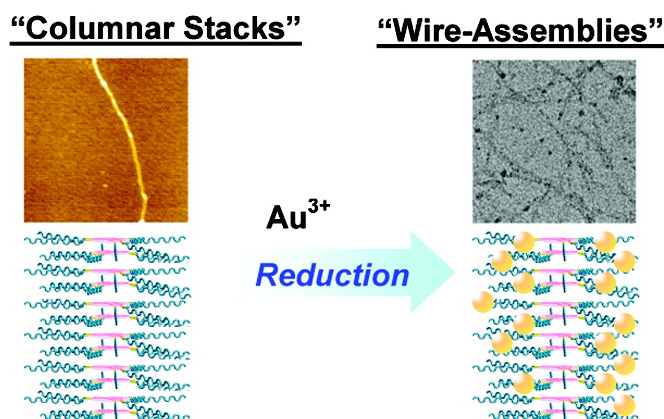
this study, QCM analyses, FT-IR/ATR spectra, ¹H NMR spectra, and SEC were employed to investigate the polymerization mechanism, and they highlighted the following points: (1) the livingness of polymer radicals by postpolymerization on a QCM, (2) substituent effects on the polymerizability in porous it-PMMA thin films, and

(3) partial stereocomplex formations of polymerized MMA with host it-PMMA. Stabilities of porous it-PMMA thin films on QCM substrates and on silica gels are also discussed herein.

- Columnar Stacks of Star- and Tadpole-Shaped Polyoxazolines Having Triphenylene Moiety and Their Applications for Synthesis of Wire-Assembled Gold Nanoparticles.

Ogoshi, T.; Hiramitsu, S.; Yamagishi, T.; Nakamoto, Y. *Macromolecules* **2009**, 42, 3042-3047.

Abstract:



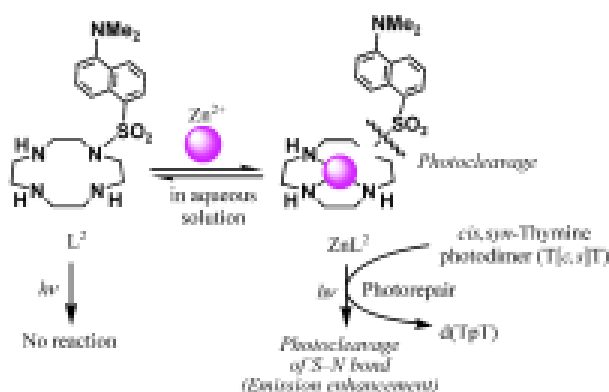
We report on synthesis, association behavior, and application of six-arm star-shaped and tadpole-shaped amphiphilic polyoxazolines from triphenylene initiators. We synthesized two kinds of novel triphenylene initiators: 2,3,6,7,10,11-hexa(6-bromohexyloxy)triphenylene (initiator for star-shaped polyoxazoline) and 2-(6-bromohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (initiator for tadpole-shaped polyoxazoline). Ring-opening cationic polymerization of 2-methyl-2-oxazoline from these initiators successfully produced star- and tadpole-shaped polyoxazolines. Both the star- and tadpole-shaped polyoxazolines formed supramolecular associations in aqueous media due to π - π stacking of hydrophobic triphenylene moiety. Critical micelle concentrations (CMCs) and amounts of π - π stacking of the star- and tadpole-shaped polyoxazolines in aqueous media were investigated by

¹H NMR and fluorescence measurements. From tapping mode atomic force microscopy (TM-AFM) measurements, the star-shaped polyoxazolines formed straight columnar stacks due to π - π stacking of hydrophobic disklike core of triphenylene moiety and symmetric star-shaped structure. In contrast, crooked nanowires were observed in the tadpole-shaped polyoxazoline. Tadpole shape was asymmetric, and thus ordered π - π stacking of hydrophobic triphenylene moiety was suppressed. Moreover, by using the columnar stacks of the star-shaped polyoxazoline as a template, we successfully synthesized wire-assembled gold nanoparticles.

- Photolysis of the Sulfonamide Bond of Metal Complexes of N-Dansyl-1,4,7,10-Tetraazacyclododecane in Aqueous Solution: A Mechanistic Study and Application to the Photorepair of *cis,syn*-Cyclobutane Thymine Photodimer

Aoki, S.; Tomiyama, Y.; Kageyama, Y.; Yamada, Y.; Shiro, M.; Kimura E. *Chem. Asian J.* **2009**, *4*, 561 – 573.

Abstract:



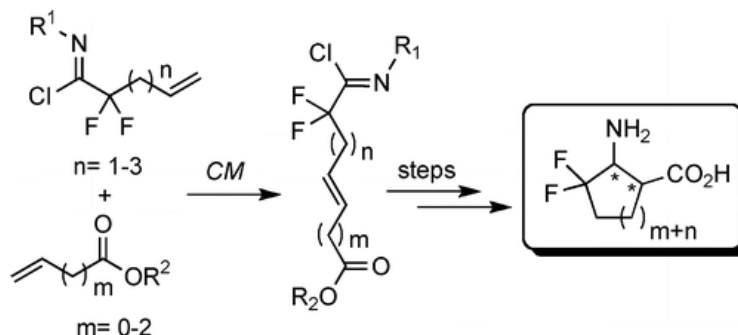
Conditional cleavage: Photochemical S — N bond cleavage of the Zn²⁺ complex of *N*-dansylcyclen (ZnL²) in aqueous solution was investigated. Moreover, photolysis of ZnL² (see scheme) facilitated photoreversion of *cis,syn*-thymine photodimer (T[c,s]T).

Sulfonamide constitutes a ubiquitous functional group that is frequently used in organic chemistry, analytical chemistry, and medicinal chemistry. We report herein on the photolysis of a dansylamide moiety of 1-dansyl-1,4,7,10-tetraazacyclododecane (*N*-dansylcyclen, L²) in the presence of a zinc(II) ion in aqueous solution. By potentiometric pH titrations, the complexation constant for the 1:1 complex of L² and Zn²⁺, log *K*_s(ZnL²), in aqueous solution at 25 °C with *I*=0.1 (NaNO₃) was determined to be 6.5±0.1. The structure of the ZnL² complex was confirmed by single-crystal X-ray diffraction analysis. During fluorescence titrations of L² with Zn²⁺ (irradiation at 308 or 350 nm) in aqueous solution at pH 7.4 (10 mM HEPES with *I*=0.1 (NaNO₃)) and 25 °C, considerable enhancement in fluorescence emission of the Zn²⁺ complex of L² (ZnL²) was observed, while metal-free L² exhibited only a negligible emission change upon UV irradiation. It was revealed that this emission enhancement arose from the photoinduced cleavage of a sulfonylamide moiety in ZnL², yielding the Zn²⁺-cyclen complex and 5-dimethylaminonaphthalene-1-sulfinic acid, which has a greater quantum yield (Φ) for fluorescence emission than that of L² and ZnL². For comparison, the photolysis of *N*-(1-naphthalenesulfonyl)cyclen (L³) and its Zn²⁺ complex (ZnL³) under the same conditions (irradiation at 313 nm) gave the corresponding sulfonate (1-naphthylsulfonate). We also describe the results of a photoreversion reaction of *cis,syn*-cyclobutane thymine photodimer (T[c,s]T) utilizing the photolysis of ZnL² and ZnL³.

- Cross-Metathesis Reactions as an Efficient Tool in the Synthesis of Fluorinated Cyclic β -Amino Acids

Fustero, S. ; Sanchez-Rosello, M. ; Acena, J. L.; Fernandez, B.; Asensio, A.; Sanz-Cervera, J. F.; del Pozo, C. J. *Org. Chem.* **2009**, 74, 3414-3423.

Abstract:

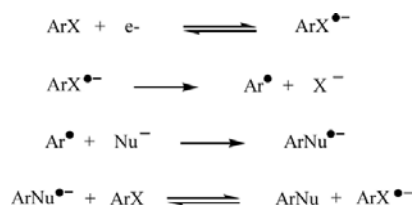


The synthesis of enantiomerically pure, cyclic, γ,γ -difluorinated β -amino acids with various ring sizes has been carried out with a cross-metathesis (CM) reaction being one of the key steps, followed by a Dieckmann-type condensation to bring about the cyclization. Subsequent catalytic hydrogenation under microwave irradiation with (-)-8-phenylmenthol as a chiral auxiliary led to the successful chemo- and diastereoselective chemical reduction of the resulting cyclic β -enamino esters. The efficiency and scope of the CM reaction with different types of fluorinated imidoyl chlorides and unsaturated esters has also been studied in order to determine the optimal reaction conditions with regard to selectivity and reactivity.

- Electron Transfer Initiated Reactions: Bond Formation and Bond Dissociation

Houmam, A. *Chem. Rev.* **2008**, 108, 2180-2237.

Abstract:



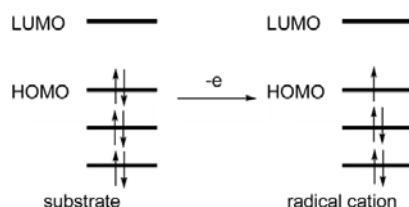
Electron transfer reactions are among the most elementary of all chemical reactions and play a fundamental role in many areas including organic synthesis, biological processes, novel energy sources, energy storage devices, amperometric sensors, etc. A field that has attracted considerable attention is that involving electron transfer to organic and bioorganic molecules. In such reactions, electron transfer is very often accompanied by the formation of new chemical bonds and/or the dissociation of existing ones. A wide variety of chemical transformations that are initiated by a single initial electron transfer are described in the literature and can be encountered under both oxidative and reductive conditions. Unraveling the nature of the fundamental steps involved in the electron transfer and the subsequent reactions has always been an essential step toward reaching a molecular understanding of these processes. In these multiple step reactions important questions arise concerning not only their mechanisms and the factors controlling them but also the associated energies and kinetics and any similarity to certain non-electron transfer processes. Extensive studies have already shed considerable new light on many of these important questions.

This review is intended to provide an up to date description of some of the important aspects and recent fundamental advances of these reactions including the chemistry, the techniques used, the principal mechanisms and their dichotomy with other polar mechanisms.

- Modern Strategies in Electroorganic Synthesis

Yoshida, J.-i.; Kataoka, K.; Horcajada, R.; Nagaki, A. *Chem. Rev.* **2008**, *108*, 2265-2299.

Abstract:



Electron transfer is one of the most important processes in organic chemistry, and many organic reactions are driven by electron-transfer processes. In an electron-transfer process, one electron is added to or removed from a substrate molecule. Such an electron transfer is reversible only when the resulting species is stable under those conditions. In other cases, an electron transfer triggers subsequent chemical processes, such as bond dissociation and bond formation.

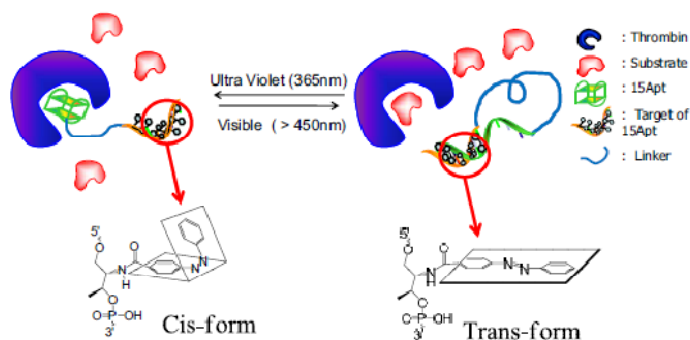
In organic synthesis, electron-transfer-driven reactions have been widely used for various transformations, although their potential has not yet been fully utilized. Among several methods for electron-transfer-driven reactions, the electrochemical method serves as a straightforward and powerful method. In fact, various carbon-carbon bond formations and functional group transformations can be accomplished by the electrochemical method. For example, the Kolbe reaction that involves the oxidation of carboxylate anions at an anode has been known for many years and still serves as a powerful tool for carbon-carbon bond formation in organic synthesis. In the Kolbe reaction, the initial electron transfer followed by the elimination of CO₂ generates carbon free radicals, which homocouple to make a new carbon-carbon bond. It is noteworthy that the electrochemical method serves as an excellent method for the generation of reactive species under mild conditions. In fact, radical cations and radical anions can be generated by electrochemical electron-transfer reactions of neutral organic compounds. Carbocations, carbon free radicals, and carbanions can also be generated by subsequent bond-dissociation or bond-forming processes. These reactive carbon species are utilized in various synthetic transformations, especially carbon-carbon bond formations. Oxidation and reduction of functional groups are also important transformations in organic synthesis, and the electrochemical method serves as "greener" procedures for such transformations. Therefore, electroorganic synthesis has received significant research interest from both academia and industry.

Because modern applications of traditional electrochemical methods have been recently reviewed, this article will provide an outline of principles and applications of new methods for effecting organic electrochemical reactions that have been developed in recent decades.

- Using photons to manipulate enzyme inhibition by an azobenzene-modified nucleic acid probe

Kim, Y.; Phillips, J. A.; Liu, H.; Kang, H.; Tan, W. *Proc. Nat. Acad. Sci.* **2009**, *106*, 6489-6494.

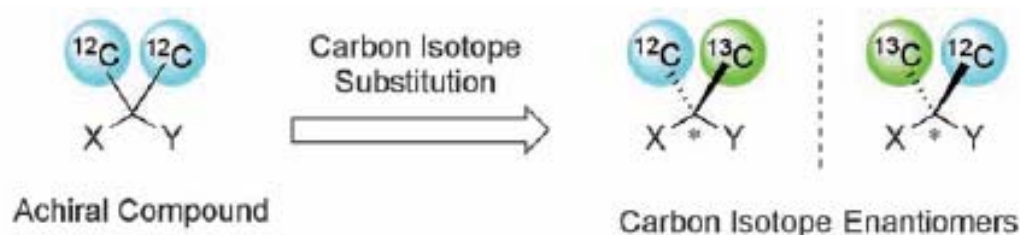
Abstract:



The ability to inhibit an enzyme in a specific tissue with high spatial resolution combined with a readily available antidote should find many biomedical applications. We have accomplished this by taking advantage of the *cis-trans* photoisomerization of azobenzene molecules. Specifically, we positioned azobenzene moieties within the DNA sequence complementary to a 15-base-long thrombin aptamer and then linked the azobenzene-modified cDNA to the aptamer by a polyethylene glycol (PEG) linker to make a unimolecular conjugate. During the photoisomerization of azobenzene by visible light, the inhibition of thrombin is disabled because the probe hybridizes with the cDNA in the *trans*-azobenzene conformation so that the aptamer cannot bind its target thrombin. However, when UV light is applied, melting of the hairpin structure (duplex) is induced via *trans*-to-*cis* conversion, thereby changing conformation of the aptamer and making the aptamer free to bind to and inhibit its target thrombin. By using standard clotting assays, we measured the IC₂₀₀ of various probe designs in both states and concluded the feasibility of using photon energy to temporally and spatially regulate these enzymatic reactions. Thus, we can report the development of DNA probes in the form of photon-controllable (thrombin) inhibitors, termed PCIs, and we expect that this approach will be highly beneficial in future biomedical and pharmaceutical applications.

- Asymmetric Autocatalysis Triggered by Carbon Isotope ($^{13}\text{C}/^{12}\text{C}$) Chirality
Kawasaki, T.; Matsumura, Y.; Tsutsumi, T.; Suzuki, K.; Ito, M.; Soai, K. *Science* **2009**, 324, 492 – 495.

Abstract:



Many apparently achiral organic molecules on Earth may be chiral because of random substitution of the 1.11% naturally abundant ^{13}C for ^{12}C in an enantiotopic moiety within the structure. However, chirality from this source is experimentally difficult to discern because of the very small difference between ^{13}C and ^{12}C . We have demonstrated that this small difference can be amplified to an easily seen experimental outcome using asymmetric autocatalysis. In the reaction between pyrimidine-5-carbaldehyde and diisopropylzinc, addition of chiral molecules in large enantiomeric excess that are, however, chiral only by virtue of isotope substitution causes a slight enantiomeric excess in the zinc alkoxide of the produced pyrimidyl alkanol. Asymmetric autocatalysis then leads to pyrimidyl alcohol

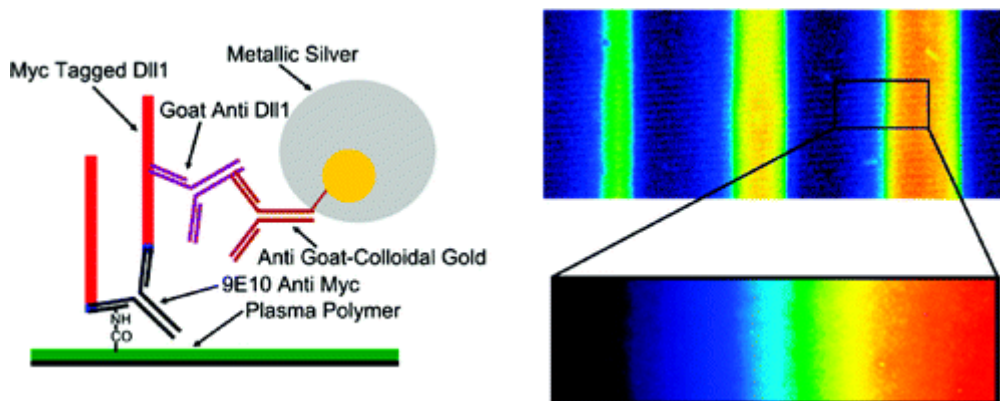
with a large enantiomeric excess. The sense of enantiomeric excess of the product alcohol varies consistently with the sense of the excess enantiomer of the carbon isotopically chiral compound.

11

- Submillimeter-Scale Surface Gradients of Immobilized Protein Ligands

Walker, R. A.; Cunliffe, V. T.; Whittle, J. D.; Steele, D. A.; Short, R. D. *Langmuir* **2009**, *25*, 4243-4246.

Abstract:

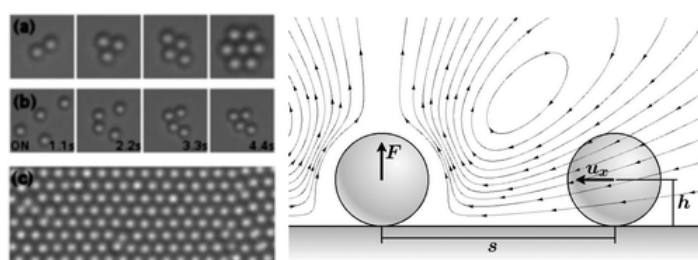


We describe a method to produce antibody-captured ligand gradients over biologically relevant distances (hundreds of micrometers) whereby the ligand density and gradient shape may be tailored. Separation of the ligand from the solid phase surface ensures that the biological activity of the ligand remains unaffected by immobilization. Our method involves the use of a plasma-masking method to generate a surface chemical gradient on a glass substrate to which the 9E10 antibody is covalently coupled. This antibody captures myc-tagged biomolecules. In our example, the antibody is then used to immobilize a gradient of the intercellular signaling molecule delta-like-1 (Dll1). To visualize the gradient of Dll1, we have used the multistep approach of binding with rabbit anti-Dll1 primary antibody and then adding colloidal-gold-conjugated secondary antibody.

- Colloidal Attraction Induced by a Temperature Gradient

Di Leonardo, R.; Ianni, F.; Ruocco, G. *Langmuir* **2009**, *25*, 4247-4250.

Abstract:

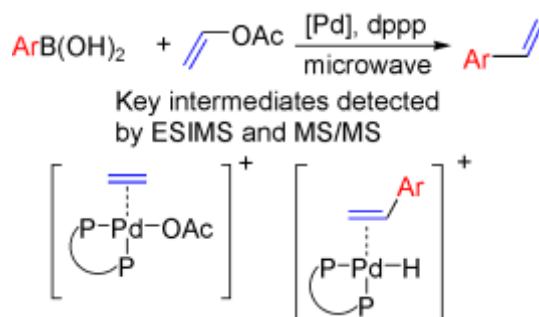


Colloidal crystals are of extreme importance for applied research and for fundamental studies in statistical mechanics. Long-range attractive interactions, such as capillary forces, can drive the spontaneous assembly of such mesoscopic ordered structures. However, long-range attractive forces are very rare in the colloidal realm. Here we report a novel strong, long-ranged attraction induced by a thermal gradient in the presence of a wall. By switching the thermal gradient on and off, we can rapidly and reversibly form stable hexagonal 2D crystals. We show that the observed attraction is hydrodynamic in nature and arises from thermally induced slip flow on particle surfaces. We used optical tweezers to measure the force law directly and compare it to an analytical prediction based on Stokes flow driven by Marangoni-like forces.

- Synthesis of Styrenes by Palladium(II)-Catalyzed Vinylation of Arylboronic Acids and Aryltrifluoroborates by Using Vinyl Acetate

Lindh, J.; Sävmarker, J.; Nilsson, P.; Sjöberg, P. J. R.; Larhed, M. *Chem.Eur.J.* **2009**, *15*, 4630-4636.

Abstract:



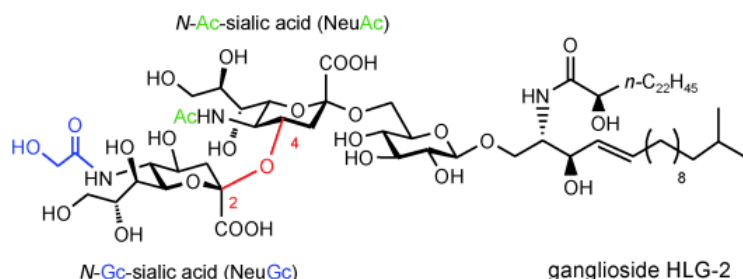
One Heck of a reaction: Treatment of arylboronic acids or aryltrifluoroborates with vinyl acetate by using a palladium(II) catalyst gives the corresponding styrenes (see scheme). No palladium reoxidant is needed and the vinylation is performed under non-inert conditions.

Reactions of aromatic and heteroaromatic boronic acids or aryltrifluoroborate salts with vinyl acetate in the presence of a palladium(II) catalyst give the corresponding styrenes in good yields. This Heck reaction proceeds with microwave heating in less than 30 min at 140 °C in the absence of base and tolerates a variety of substituents. No palladium reoxidant is needed and the vinylation is performed under non-inert conditions. Mass spectrometry (electrospray ionization mass spectrometry (ESIMS) and tandem mass spectrometry (MS/MS)) was used to identify cationic palladium-containing complexes in ongoing reactions. The key intermediates that have been detected, together with experiments that used deuterated vinyl acetate, support the existence of catalytically active palladium hydride species, and that it is the arylation of ethylene, not vinyl acetate, which generates the styrene product. The mechanism of the reaction is discussed in terms of the palladium(II) intermediates mentioned above.

- A First Total Synthesis of Ganglioside HLG-2

Iwayama, Y.; Ando, H.; Ishida, H.; Kiso, M. *Chem.Eur.J.* **2009**, *15*, 4637-4648.

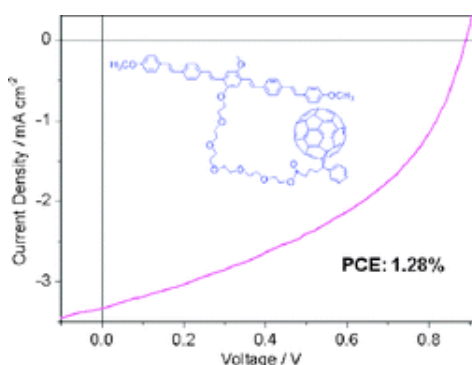
Abstract:



A neuritegenic ganglioside from sea cucumber, HLG-2 (see figure), has been synthesized for the first time. The unique tandem of sialic acids, Neu5Gc- α -(2,4)-NeuAc, was established by the combination of a reactive *N*-Troc sialyl donor and a 1,5-lactamized sialyl acceptor. The ceramide counterpart was assembled in a stereoselective manner. Direct connection of the trisaccharide and the ceramide successfully afforded a precursor of HLG-2, which was converted to ganglioside HLG-2 in pure form.

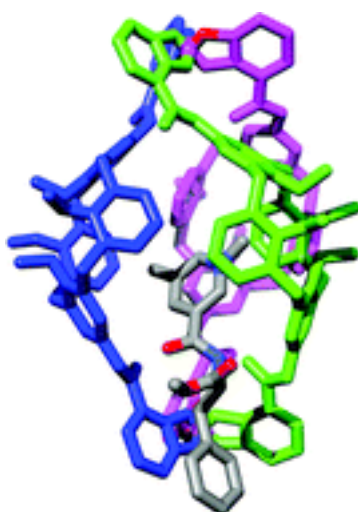
A first synthesis of the neuritegenic ganglioside HLG-2, which was identified in extracts of the sea cucumber *Holothuria leucospilota*, is described. The characteristic sequence of the trisaccharide part, α -N-glycolylsialyl-(2,4)- α -N-acetylsialyl-(2,6)-glucoside, was efficiently assembled by coupling of a highly active *N*-2,2,2-trichloroethoxycarbonyl (Troc)-protected sialyl donor and a 1,5-lactamized sialyl acceptor with high stereoselectivity. The corresponding trisaccharyl imidate donor was directly glycosidated with the primary hydroxyl group of the ceramide part, producing protected HLG-2 in relatively high yield, global deprotection of which furnished ganglioside HLG-2 in highly pure form.

- Efficient dyad-based organic solar cells with a highly crystalline donor group.
Nishizawa, T.; Kesuma Lim, H.; Tajima, K.; Hashimoto, K. *Chem. Commun.* **2009**, 2469 – 2471.
Abstract:



A novel oligo(p-phenylenevinylene)(OPV)-fullerene dyad, with strong intermolecular – interactions between the donor groups, led to improvements in the fill factor and power conversion efficiency of dyad-based solar cells of up to 0.44 and 1.28%, respectively, which are the highest values reported for dyad-based solar cells to date.

- Asymmetric induction of supramolecular helicity in calix[4]arene-based triple-stranded helicate.
Haino, A.; Shio, H.; Takano, R.; Fukazawa, Y. *Chem. Commun.* **2009**, 2481 – 2483.
Abstract :

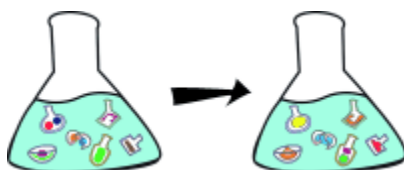


Calix[4]arene-based triple helicates take up an achiral part of chiral guests; the chiral center outside the cavity causes the asymmetric induction of their supramolecular helicity.

- Functional Molecular Flasks: New Properties and Reactions within Discrete, Self-Assembled Hosts

Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3418-3438.

Abstract:



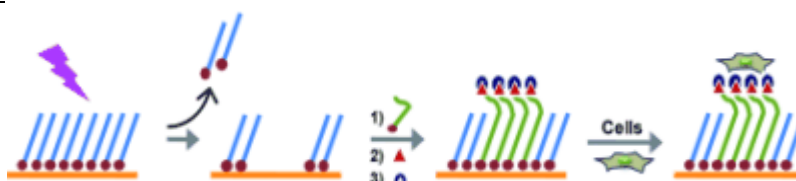
Insider dealing: Self-assembled hosts applied as “molecular flasks” can alter and control the reactivity and properties of molecules encapsulated within their well-defined, confined spaces. A variety of functional hosts of differing sizes, shapes, and utility have been prepared by using the facile and modular concepts of self-assembly.

The application of self-assembled hosts as “molecular flasks” has precipitated a surge of interest in the reactivity and properties of molecules within well-defined confined spaces. The facile and modular synthesis of self-assembled hosts has enabled a variety of hosts of differing sizes, shapes, and properties to be prepared. This Review briefly highlights the various molecular flasks synthesized before focusing on their use as functional molecular containers - specifically for the encapsulation of guest molecules to either engender unusual reactions or unique chemical phenomena. Such self-assembled cavities now constitute a new phase of chemistry, which cannot be achieved in the conventional solid, liquid, and gas phases.

- Mass Spectrometry Assisted Lithography for the Patterning of Cell Adhesion Ligands on Self-Assembled Monolayers

Kim, Y.-K.; Ryoo, S.-R.; Kwack, S.-J.; Min, D.-H. *Angew. Chem. Int. Ed.* **2009**, *48*, 3507-3511.

Abstract:



Pattern of events: A simple and flexible method has been developed for patterning cell adhesion ligands. Locally erasing self-assembled monolayers with tri(ethyleneglycol) groups on a gold substrate by using a MALDI-TOF MS nitrogen laser and filling the exposed gold surface with an alkanethiol presenting carboxylic acid groups enables subsequent immobilization of maleimide and a cell adhesion peptide, which can then recognize cells (see scheme).