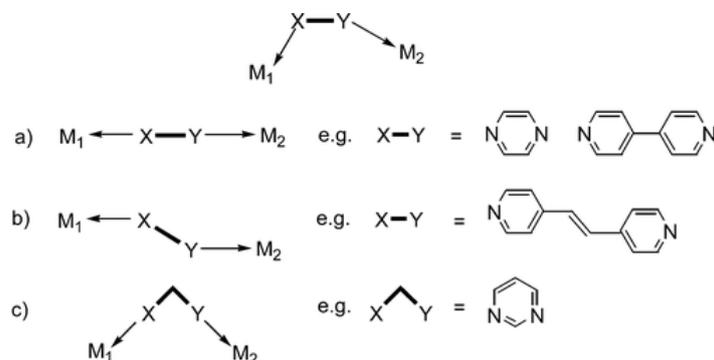


- Trinuclear Metallacycles: Metallatriangles and Much More
Zangrando, E.; Casanova, M.; Alessio, E. *Chem. Rev.* **2008**, *108*, 4979-5013.

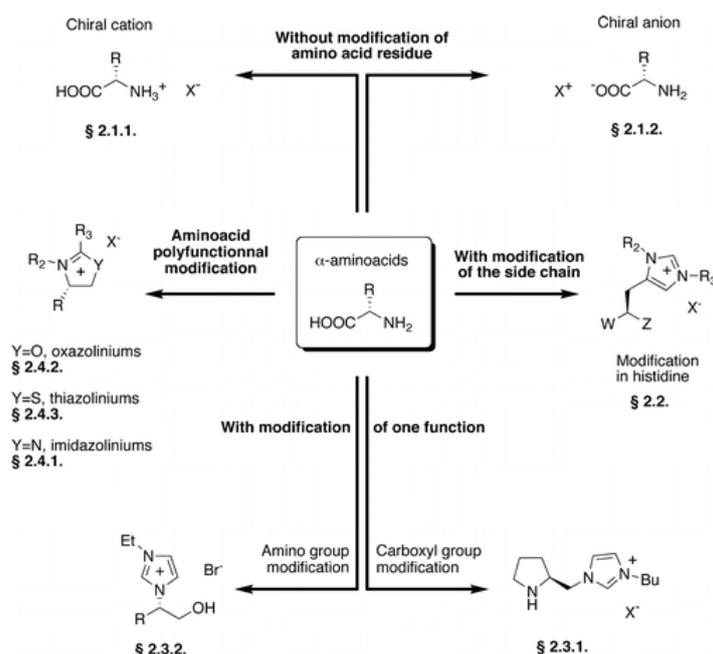
Abstract:



In 1990, Fujita and co-workers described the first example of a rationally designed metallacycle, the molecular square $\{[Pd(en)(\mu\text{-}4,4'\text{-bipy})]_4\}(\text{NO}_3)_8$, prepared by self-assembly of the *cis*-protected square-planar Pd(II) precursor with two adjacent labile ligands $[Pd(en)(\text{ONO}_2)_2]$ (*en* = ethylenediamine) with the linear linker 4,4'-bipyridine (4,4'-bipy). Since then, supramolecular chemistry has produced an amazing number of fascinating 2D and 3D metal-mediated molecular architectures, including many macrocycles and cages. Several review articles have thoroughly covered this thriving field in recent years. Beside their shared structural beauty, some of these assemblies are finding applications as receptors and molecular vessels for trapping reactive intermediates, as well as for stoichiometric and catalytic reactions. The smallest and simplest of the metal-mediated molecular polygons, the trinuclear metallacycles, are typically defined in the papers as *rare* or *seldom found*, but a search of the literature demonstrates that, indeed, they are not particularly rare. Instead, it is perhaps fair to say that very often their isolation was totally unexpected, or serendipitous at best, typically from reactions aimed at the preparation of larger metallacycles. In other words, the formation of trinuclear metallacycles is frequently in contrast with the paradigms of the *directional-bonding approach* as defined by Mirkin and Holliday (originally called the *molecular library model* by Stang and co-workers), that rationalizes the metal-mediated construction of supramolecular architectures. Thus, in their apparent simplicity, trinuclear metallacycles pose a number of questions, both practical and theoretical, to the chemists involved in metal-mediated supramolecular chemistry.

- Ionic Liquids: New Targets and Media for α -Amino Acid and Peptide Chemistry
Plaquevent, J.-C.; Levillain, J.; Guillen, F.; Malhiac, C.; Gaumont, A.-C. *Chem. Rev.* **2008**, *108*, 5035-5060.

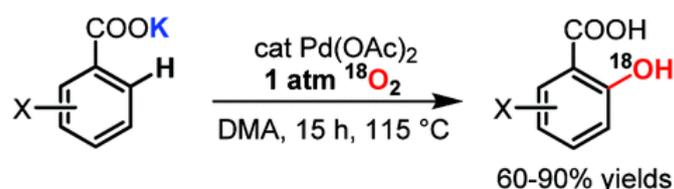
Abstract:



Owing to their unique properties, ionic liquids nowadays are very fascinating for chemists in various fields. Besides their potential for green chemistry, mainly due to their low vapor pressure, reexamination of organic synthesis in these new media led to a shining series of convincing examples of increases in chemical yields, chemo-, regio-, and stereoselectivity, as well as recycling of catalysts. Most of these studies have been recently reviewed by prominent scientists in the field. Beyond this impressive series of successes it can be noted that most organic syntheses can be performed at least with equal efficiency in ionic solvents as in molecular solvents. Nevertheless, a new question emerges: in which chemistry could ionic liquids afford more than an alternative reaction medium? In other words, could ionic solvents be used for doing what is either impossible or extremely difficult in molecular solvents? In this context, two new fields emerge: first, the field of ionic liquids and chirality, including the search for new chiral ionic liquids (CIL) and their use in various applications, and second, the synthesis and behavior of biomolecules in ionic liquids. Most of the literature summarized below has only been published during the last few years, emphasizing the novelty of these approaches and the interest of chemists in this new research field. This review has the ambition to give an exhaustive overview of published literature up to 2007. "Amino acids for ionic liquids and ionic solvents for peptide chemistry": a new emergent paradigm?

- Pd(II)-Catalyzed Hydroxylation of Arenes with 1 atm of O₂ or Air
 Zhang, Y. H.; Yu, J. Q. *J. Am. Chem. Soc.* **2009**, *131*, 14654–14655.

Abstract:



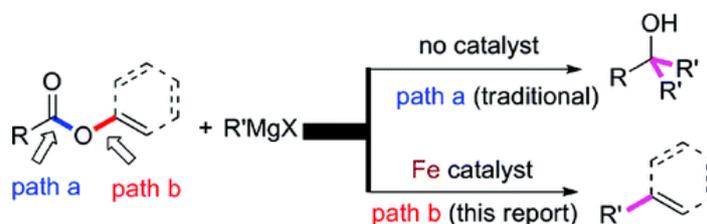
X = Me, OMe, NHAc, Cl, F, CF₃, COPh, COMe, NO₂, CN

Pd(II)-catalyzed ortho-hydroxylation of variously substituted benzoic acids under 1 atm of O₂ or air is achieved under nonacidic conditions. Extensive labeling studies support a direct oxygenation of aryl C–H bonds with molecular oxygen.

- Cross-Coupling of Alkenyl/Aryl Carboxylates with Grignard Reagent via Fe-Catalyzed C–O Bond Activation

Li, B. J.; Xu, L.; Wu, Z. H.; Guan, B. T.; Sun, C. L.; Wang, B. Q.; Shi, Z. J. *J. Am. Chem. Soc.* **2009**, *131*, 14656–14657.

Abstract:

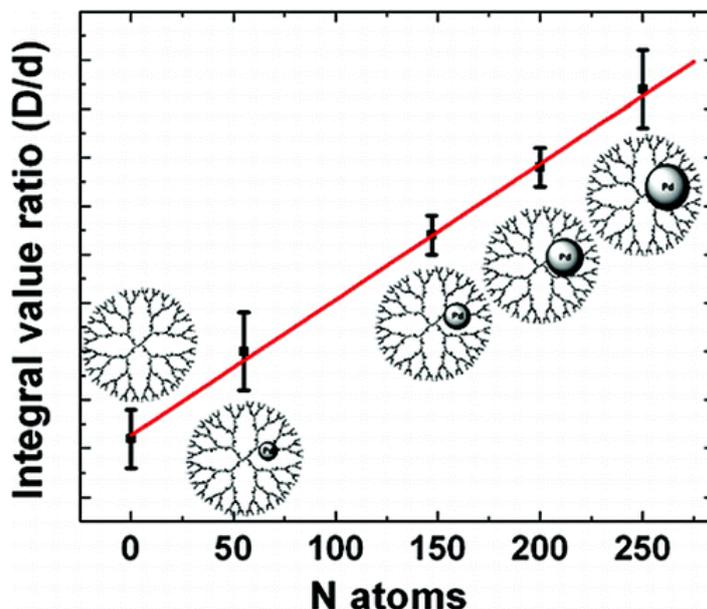


Iron-catalyzed cross-coupling of alkenyl/aryl carboxylates with primary alkyl Grignard reagent was described. This reaction brought a new family of electrophiles to iron catalysis. The combination of an inexpensive carboxylate electrophile and an iron catalyst would generate ample advantages.

- Nanoparticle Size Determination by ^1H NMR Spectroscopy

Gomez, M. V.; Guerra, J.; Myers, V. S.; Crooks, R. M.; Velders, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 14634–14635.

Abstract:



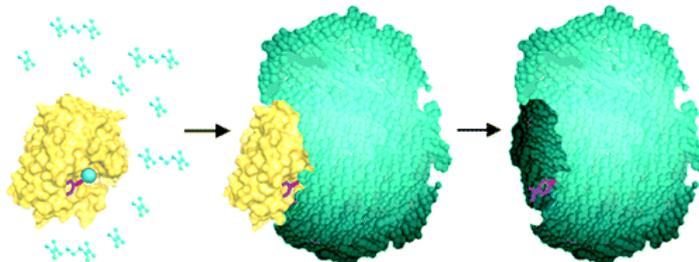
High-resolution solution ^1H NMR spectroscopy has been used to characterize the size of Pd dendrimer-encapsulated nanoparticles (DENs). The Pd nanoparticles measured by this technique contain 55, 147, 200, or 250 atoms, and they are encapsulated within sixth-generation, hydroxyl-terminated poly(amidoamine) PAMAM dendrimers (G6-OH). Detailed analysis of the NMR data shows that signals arising from the innermost protons of G6-OH(Pd_n) decrease significantly as the size of the encapsulated nanoparticles increase. A mathematical correlation between this decrease in the integral value and the theoretical number of Pd atoms in the nanoparticle is extracted. It enables the elucidation of the size of Pd DENs by ^1H NMR spectroscopy. NMR pulse-field gradient spin-echo experiments demonstrate that G6-OH with and without DENs have identical hydrodynamic radii, which excludes the presence of dendrimer/nanoparticle aggregates.

- Molecularly Imprinted Microgels as Enzyme Inhibitors

Cutivet, A.; Schembri, C.; Kovensky, J.; Haupt, K. *J. Am. Chem. Soc.* **2009**, *131*, 14699–14702.

4

Abstract:

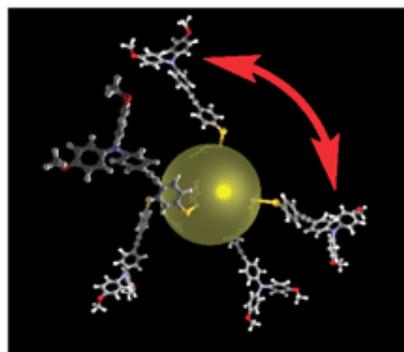


We demonstrate, on the example of trypsin, the use of water-soluble molecularly imprinted polymer microgels as specific enzyme inhibitors. Using a strong anchoring monomer, methacryloylaminobenzamidine, the growing polymer chains are confined to close proximity of the substrate recognition site of our model enzyme. The microgels bind selectively trypsin over other proteins of similar size and molecular weight, and show competitive inhibition of trypsin with an inhibition constant K_i of 79 nM, making them more potent inhibitors than the low molecular-weight competitive inhibitor benzamidine by almost 3 orders of magnitude. We believe that these tailor-made materials with biological activity have potential for future drug development that extends beyond enzyme inhibition.

- Mixed-valence interactions in triarylamine–gold–nanoparticle conjugates.

Müller, C. I.; Lambert, C.; Steeger, M.; Forster, F.; Wiessner, M.; Schöll, A.; Reinert, F.; Kamp, M. *Chem. Commun.* **2009**, 6213 – 6215.

Abstract:

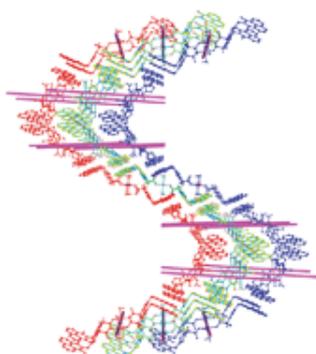


Optical and electrochemical investigations of triarylamine redox centres attached to gold nanoparticles via a π -conjugated bridge show intervalence charge-transfer bands which prove to be surprisingly strong interchromophore interactions.

- Homochiral, helical metal–organic framework structures organized by strong, non-covalent – stacking interactions

Reger, D. L.; Horger, J.; Smith, M. D.; Long, G. L. *Chem. Commun.* **2009**, 6219 – 6221.

Abstract:

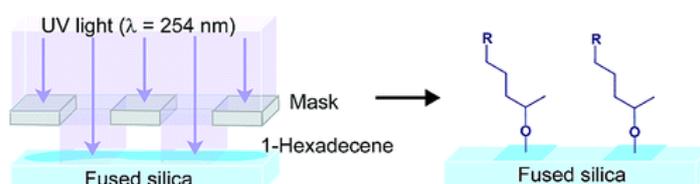


A new trifunctional ligand, L_{ala} , containing a carboxylate donor group, a homochiral center derived from L-alanine and a strong π -stacking, 1,8-naphthalimide synthon, has been used to prepare the copper(II) complex $[Cu(L_{ala})_2(4,4\text{-bipy})(H_2O)_2] \cdot 4.25H_2O$ that has a homochiral, helical, supramolecular metal-organic framework 3-D structure, organized in one dimension solely by strong non-covalent forces.

- Photochemical Covalent Attachment of Alkene-Derived Monolayers onto Hydroxyl-Terminated Silica

Maat, J.; Regeling, R.; Yang, M.; Mullings, M. N.; Bent, S. F.; Zuilhof, H. *Langmuir* **2009**, *25*, 11592–11597.

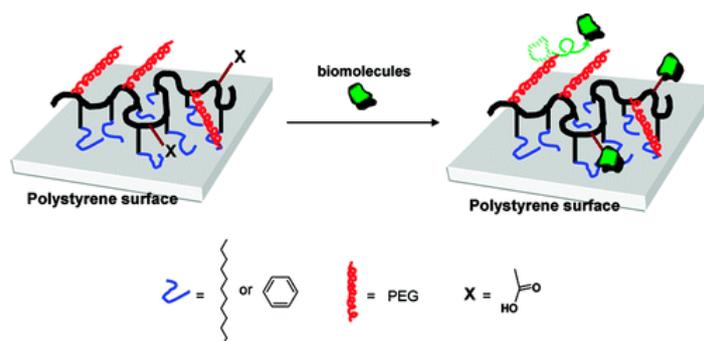
Abstract:



The functionalization of optically transparent substrates is of importance, for example, in the field of biosensing. In this article, a new method for modification of silica surfaces is presented that is based on a photochemical reaction of terminal alkenes with the surface. This yields highly hydrophobic surfaces, which are thermally stable up to at least 400 °C. The formed monolayer provides chemical passivation of the underlying surface, according to studies showing successful blocking of platinum atomic layer deposition (ALD). The reaction is photochemically initiated, requiring light with a wavelength below 275 nm. X-ray photoelectron spectroscopy and infrared spectroscopy studies show that the alkenes initially bind to the surface hydroxyl groups in Markovnikov fashion. At prolonged reaction times (>5 h), however, oligomerization occurs, resulting in layer growth normal to the surface. The photochemical nature of the reaction enables the use of photolithography as a tool to constructively pattern silica surfaces. Atomic force microscopy shows that the features of the photomask are well transferred. The newly developed method can complement existing patterning methods on silica that are based on soft lithograph

- Facile Method for Selective Immobilization of Biomolecules on Plastic Surfaces
Sung, D.; Park, S.; Jon, S. *Langmuir* **2009**, *25*, 11289–11294.

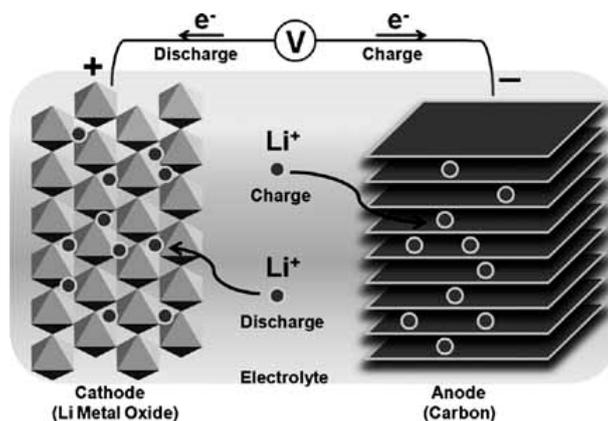
Abstract:



A key aspect of biochip and biosensor preparation is optimizing surface attachment of biomolecules. Here, we report a facile approach for selectively immobilizing biomolecules on amphiphilic polymer-coated plastic surfaces with antibiofouling properties. To modify plastic surfaces, we synthesized two types of random copolymers by radical polymerization, which consisted of three parts: an anchoring group; a PEG component, which acted as a repellent of nonspecific biomolecules; and a functional group, to which biomolecules were conjugated. Dodecyl- and benzyl-based copolymers were highly soluble in water, presumably due to the presence of multiple PEG groups, and could easily coat the model plastic surface (polystyrene) in an aqueous environment. The antibiofouling property of each polymer-coated plastic surface was examined by measuring the extent of nonspecific protein adsorption using bovine serum albumin (BSA). Both polymer-coated plastic surfaces showed a very low level of BSA adsorption relative to that of an uncoated plastic surface (control). Finally, we showed that streptavidin and antibodies, as representative biomolecules, could be selectively immobilized on the polymer-coated plastic surfaces imprinted with biotin and protein A, respectively, by microcontact printing, exhibiting an intense signal with low background.

- Nanostructured Silicon Anodes for Lithium Ion Rechargeable Batteries
Teki, R.; Datta, M. K.; Krishnan, R.; Parker, T. C.; Lu, T.-M.; Kumta, P. N.; Koratkar, N. *Small* **2009**, 5, 2236-2242.

Abstract:



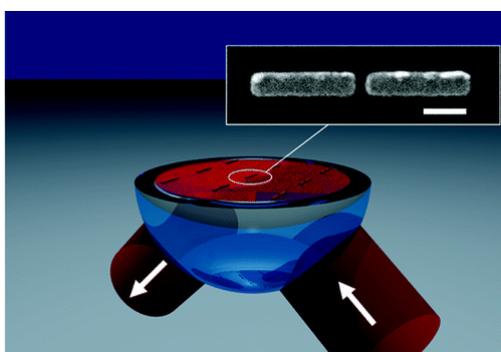
Rechargeable lithium ion batteries are integral to today's information-rich, mobile society. Currently they are one of the most popular types of battery used in portable electronics because of their high energy density and flexible design. Despite their increasing use at the present time, there is great continued commercial interest in developing new and improved electrode materials for lithium ion batteries that would lead to dramatically higher energy capacity and longer cycle life. Silicon is one of the most promising anode materials because it has the highest known theoretical charge capacity and is the second most abundant element on earth. However, silicon anodes have limited

applications because of the huge volume change associated with the insertion and extraction of lithium. This causes cracking and pulverization of the anode, which leads to a loss of electrical contact and eventual fading of capacity. Nanostructured silicon anodes, as compared to the previously tested silicon film anodes, can help overcome the above issues. As arrays of silicon nanowires or nanorods, which help accommodate the volume changes, or as nanoscale compliant layers, which increase the stress resilience of silicon films, nanoengineered silicon anodes show potential to enable a new generation of lithium ion batteries with significantly higher reversible charge capacity and longer cycle life.

- Nano-optical Trapping of Rayleigh Particles and *Escherichia coli* Bacteria with Resonant Optical Antennas

Righini, M.; Ghenuche, P.; Cherukulappurath, S.; Myroshnychenko, V.; Garcia de Abajo, F. J.; Quidant, R. *Nano Lett.* **2009**, *9*, 3387–3391.

Abstract:

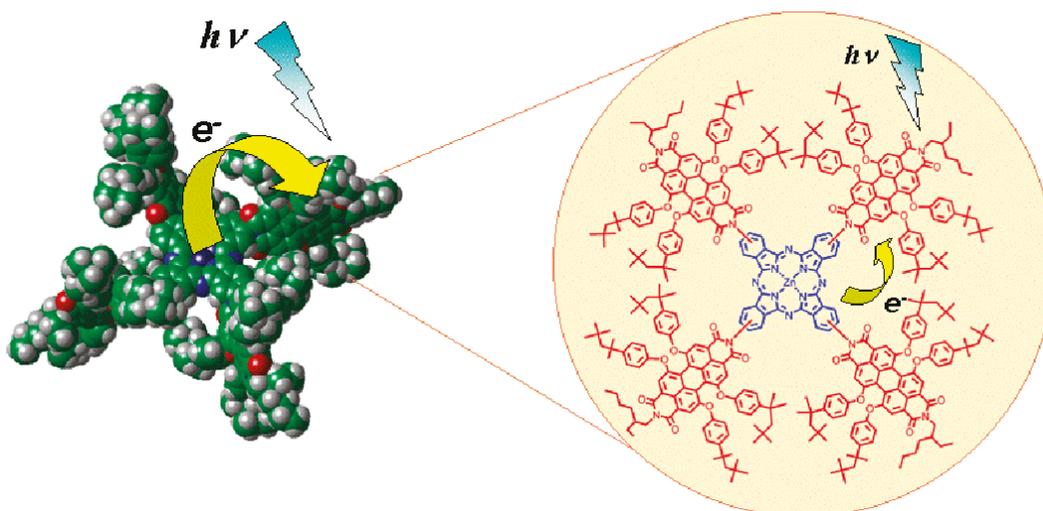


Immobilizing individual living microorganisms at designated positions in space is important to study their metabolism and to initiate an in situ scrutiny of the complexity of life at the nanoscale. While optical tweezers enable the trapping of large cells at the focus of a laser beam, they face difficulties in maintaining them steady and can become invasive and produce substantial damage that prevents preserving the organisms intact for sufficient time to be studied. Here we demonstrate a novel optical trapping scheme that allows us to hold living *Escherichia coli* bacteria for several hours using moderate light intensities. We pattern metallic nanoantennas on a glass substrate to produce strong light intensity gradients responsible for the trapping mechanism. Several individual bacteria are trapped simultaneously with their orientation fixed by the asymmetry of the antennas. This unprecedented immobilization of bacteria opens an avenue toward observing nanoscopic processes associated with cell metabolism, as well as the response of individual live microorganisms to external stimuli, much in the same way as pluricellular organisms are studied in biology.

- Synthesis and Photoinduced Electron Transfer of Phthalocyanine-Perylenebisimide Pentameric Arrays

Céspedes-Guirao, F. J.; Ohkubo, K.; Fukuzumi, S.; Sastre-Santos, A.; Fernández-Lázaro, F. J. *Org. Chem.* **2009**, *74*, 5871–5880.

Abstract:

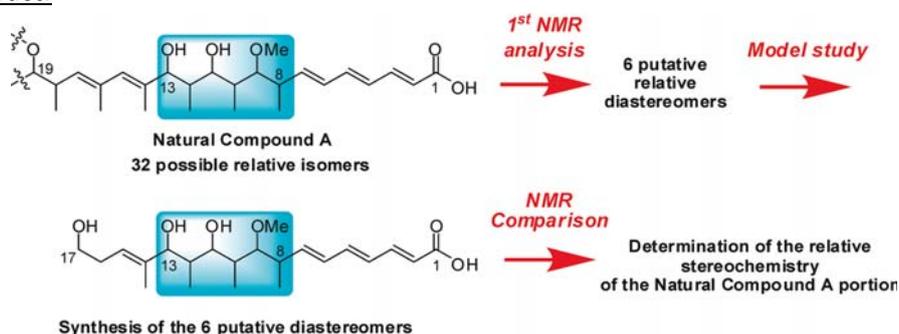


Zinc phthalocyanine–perylenebisimide pentameric arrays, $\text{ZnPc}(\text{PDI})_4$ **1** and **2**, have been synthesized. $\text{ZnPc}(\text{PDI})_4$ **1** has no substituents in the PDI bay positions, while $\text{ZnPc}(\text{PDI})_4$ **2** presents four phenoxy groups in the bay positions of each perylene. In both cases, the PDI moieties are directly connected to the ZnPc. As a consequence of aggregation, photoexcitation of **1** affords the intermolecular exciplex rather than the charge-separated state. In contrast to **1**, photoexcitation of **2**, which contains sterically demanding substituents in the PDI moieties, affords the charge-separated (CS) state, which was clearly detected by its transient absorption spectrum in femtosecond laser flash photolysis measurements. The CS lifetime was determined to be 26 ps. The addition of $\text{Mg}(\text{ClO}_4)_2$ to a benzonitrile solution of **2** and the photoexcitation affords the long-lived CS state with the lifetime of 480 μs , whereas no such long-lived CS state was formed in the case of **1** under such conditions. The remarkable elongation of the CS lifetime results from the strong binding of Mg^{2+} to the $\text{PDI}^{\bullet-}$ moiety in the CS state.

- Relative Stereochemical Determination and Synthesis of the C1-C17 Fragment of a New Natural Polyketide

Fleury, E.; Lannou, M.-I.; Bistri, O.; Sautel, F.; Massiot, G.; Pancrazi, A.; Ardisson, J. *J. Org. Chem.* **2009**, *74*, 7034–7045.

Abstract:

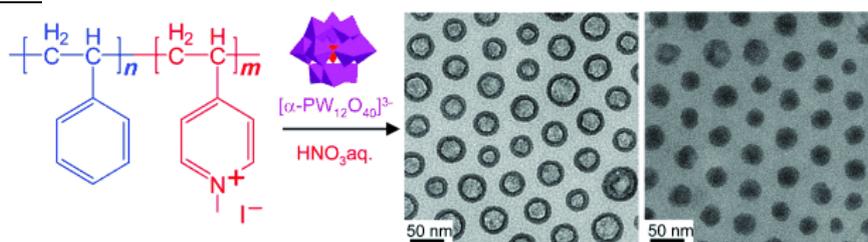


The challenging determination of the relative stereochemistry of a complex natural polyketide portion was achieved. After careful NMR analysis, a concise synthesis of a set of possible relative diastereomers (only 6 diastereomers out of the 32 initially envisioned) has been carried out using a common strategy based on enantioselective aldol reactions. With a high predictability, final NMR comparison established the relative stereochemistry of the C1–C17 fragment of this natural product.

- Micelles and Vesicles Formed by Polyoxometalate–Block Copolymer Composites

Bu, W.; Uchida, S.; Mizuno, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 8281–8284.

Abstract:

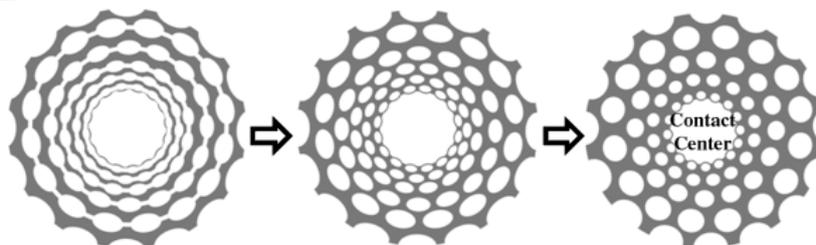


Core-corona composites were prepared by incorporating a hydrophilic polyoxometalate (POM) into poly(styrene-*b*-4-vinyl-*N*-methylpyridinium iodide) matrices in acidic aqueous solution (see scheme). On dispersal in toluene they self-assemble into micellar and vesicular morphologies (see TEM images), which can be controlled by means of the weight fraction of POM.

- Evolution of Ordered Block Copolymer Serpentine into a Macroscopic, Hierarchically Ordered Web

Hong, S. W.; Wang, J.; Lin, Z. *Angew. Chem. Int. Ed.* **2009**, *48*, 8356–8360.

Abstract:

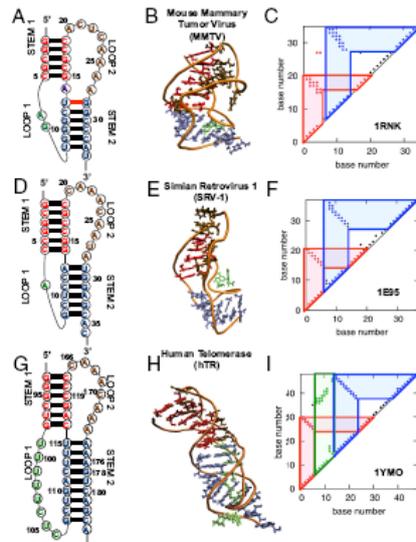


Polymer coffee rings: Evaporation of diblock copolymer solutions confined in a sphere-on-flat geometry yields concentric serpentine microstructures over large areas (see picture, left). Selective solvent vapor annealing then transforms these microstructures into a macroscopic pattern of regularly arranged microporous mesh arrays (see picture, right) while at the same time forming domains of nanoscopic cylinders of diblock copolymer.

- Assembly mechanisms of RNA pseudoknots are determined by the stabilities of constituent secondary structures

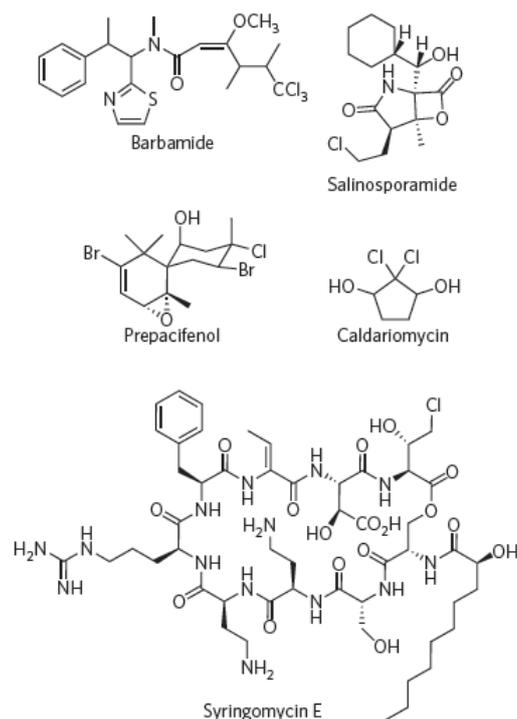
Cho, S. S.; Pincus, D. L.; Thirumalai, D. *Proc. Nat. Acad. Sci.* **2009**, *106*, 17349–17354.

Abstract:



Understanding how RNA molecules navigate their rugged folding landscapes holds the key to describing their roles in a variety of cellular functions. To dissect RNA folding at the molecular level, we performed simulations of three pseudoknots (MMTV and SRV-1 from viral genomes and the hTR pseudoknot from human telomerase) using coarse-grained models. The melting temperatures from the specific heat profiles are in good agreement with the available experimental data for MMTV and hTR. The equilibrium free energy profiles, which predict the structural transitions that occur at each melting temperature, are used to propose that the relative stabilities of the isolated helices control their folding mechanisms. Kinetic simulations, which corroborate the inferences drawn from the free energy profiles, show that MMTV folds by a hierarchical mechanism with parallel paths, i.e., formation of one of the helices nucleates the assembly of the rest of the structure. The SRV-1 pseudoknot, which folds in a highly cooperative manner, assembles in a single step in which the preformed helices coalesce nearly simultaneously to form the tertiary structure. Folding occurs by multiple pathways in the hTR pseudoknot, the isolated structural elements of which have similar stabilities. In one of the paths, tertiary interactions are established before the formation of the secondary structures. Our work shows that there are significant sequence-dependent variations in the folding landscapes of RNA molecules with similar fold. We also establish that assembly mechanisms can be predicted using the stabilities of the isolated secondary structures.

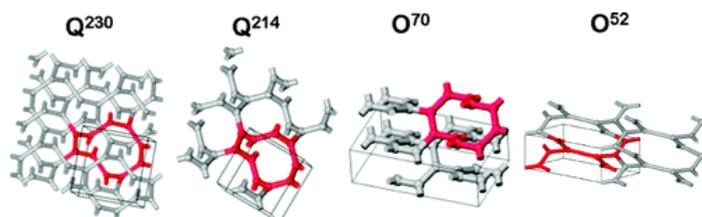
- Mechanistic considerations of halogenating enzymes
Butler, A.; Sandy, M. *Nature* **2009**, *460*, 848-854.
Abstract:



In nature, halogenation is a strategy used to increase the biological activity of secondary metabolites, compounds that are often effective as drugs. However, halides are not particularly reactive unless they are activated, typically by oxidation. The pace of discovery of new enzymes for halogenation is increasing, revealing new metalloenzymes, flavoenzymes, *S*-adenosyl-*l*-methionine (SAM)-dependent enzymes and others that catalyse halide oxidation using dioxygen, hydrogen peroxide and hydroperoxides, or that promote nucleophilic halide addition reactions.

- Ordered Network Mesostructures in Block Polymer Materials
Meuler, A. J.; Hillmyer, M. A.; Bates, F. S. *Macromolecules* **2009**, *42*, 7221–7250.

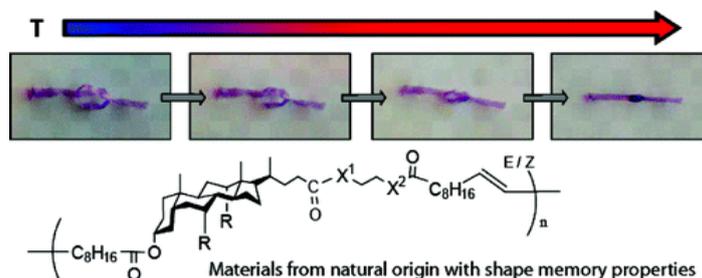
Abstract:



Block polymers are formed by the covalent union of two or more chemically distinct homopolymers. These composite macromolecules self-assemble into a variety of ordered morphologies with features on the nanometer length scale, a phenomenon that has interested researchers for roughly four decades. The known ordered morphologies include numerous multiply continuous network mesostructures, the focus of this review. Multiply continuous network morphologies contain two or more chemically distinct domains that continuously percolate through the specimen in all three dimensions. They have captivated researchers because of their superior mechanical properties and could potentially find utility in technologies such as catalysis, photonic materials, solar cells, and separations. This review summarizes experimental and theoretical investigations of the structures and properties of network morphologies in AB block copolymer and ABC block terpolymer systems and includes a discussion of some proposed technological applications of these intriguing mesostructures.

- Shape Memory Polymers Based on Naturally-Occurring Bile Acids
Gautrot, J. E.; Zhu, X. X. *Macromolecules* **2009**, *42*, 7324–7331.

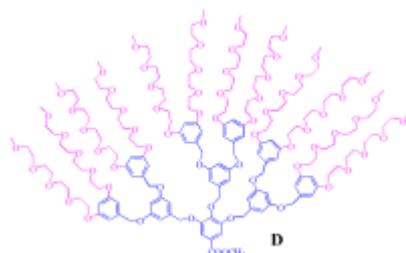
Abstract:



Naturally occurring bile acids are ideal building blocks for a new generation of biomaterials displaying low systemic toxicity and engineered properties. Herein we report the synthesis of bile acid-based polyesters using entropy-driven ring-opening metathesis polymerization (ED-ROMP) and characterization of the structure of the resulting polymers. The materials synthesized display high molecular weights (M_n above 100000), typical of ED-ROMPs. The mechanical and responsive behavior of these bile acid-based polyesters (BAPs) is studied by dynamic mechanical analysis (DMA) and thermomechanical cycling. Although BAPs are amorphous thermoplastics, they display typical rubber-like elasticity with tunable mechanical behavior, glass transitions close to body temperature, and outstanding shape memory properties. By introducing small changes in the chemical structure of BAPs (amide bonds or additional hydroxyl groups), we were able to correlate the materials' stiffness, their T_g and shape recovery temperature to their structure. In addition, we show that BAPs can be deformed to high strains even at low temperature and still display shape recovery.

- Single-Molecule Behavior of Dendritic Poly(ethylene glycol) Structures towards Lithium Ions
Tang, D.; Wu, D.; Luo, Q.; Hu, W.; Wang, F.; Liu, S.; Liu, X.; Fan, Q. *Chem. Eur. J.* **2009**, *15*, 10352-10355.

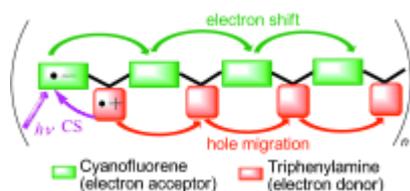
Abstract:



PEG-ged out: Dendritic poly(ethylene glycol) (PEG) **D** exhibits excellent single-molecule behavior to lithium ions, and has been characterized by MALDI-TOF-MS and TOF-ESI-MS. Since commercially available linear PEG structures are not monocomponent, constructing dendritic structures may become a good strategy to achieve higher molecular-weight PEG moieties.

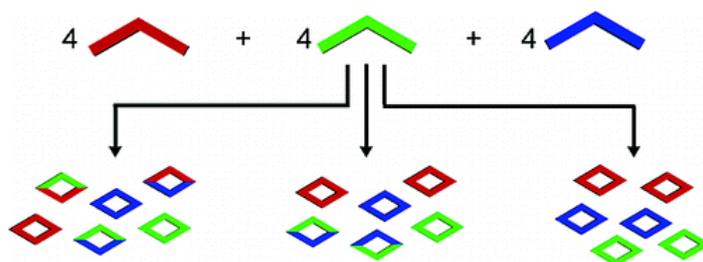
- A New Cyanofluorene–Triphenylamine Copolymer: Synthesis and Photoinduced Intramolecular Electron Transfer Processes
Lin, Y.; El-Khouly, M. E.; Chen, Y.; Supur, M.; Gu, L.; Li, Y.; Fukuzumi, S. *Chem. Eur. J.* **2009**, *15*, 10818-10824.

Abstract:



A new π -conjugated copolymer, namely, poly{cyanofluore-*alt*-[5-(*N,N'*-diphenylamino)phenylenevinylene]} ((CNF-TPA)_n), was synthesized by condensation polymerization of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)diacetonitrile and 5-(*N,N'*-diphenylamino)-benzene-1,3-dicarbaldehyde by using the Knoevenagel reaction. By design, diphenylamine, alkylfluorene and poly(*p*-phenylenevinylene) linkages were combined to form a (CNF-TPA)_n copolymer which exhibits high thermal stability and glass-transition temperature. Photodynamic measurements in polar benzonitrile indicate fast and efficient photoinduced electron transfer ($\approx 10^{11} \text{ s}^{-1}$) from triphenylamine (TPA) to cyanofluorene (CNF) to produce the long-lived charge-separated state (90 μs). The finding that the charge-recombination process of (CNF⁻-TPA⁺)_n is much slower than the charge separation in polar benzonitrile suggests a potential application in molecular-level electronic and optoelectronic devices.

- Self-Organization in Coordination-Driven Self- Assembly
Northrop, B. H.; Zheng, Y.-R.; Chi, K.-W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554–1563.
Abstract:



Self-assembly allows for the preparation of highly complex molecular and supramolecular systems from relatively simple starting materials. Typically, self-assembled supramolecules are constructed by combining complementary pairs of two highly symmetric molecular components, thus limiting the chances of forming unwanted side products. Combining asymmetric molecular components or multiple complementary sets of molecules in one complex mixture can produce myriad different ordered and disordered supramolecular assemblies. Alternatively, spontaneous self-organization phenomena can promote the formation of specific product(s) out of a collection of multiple possibilities. Self-organization processes are common throughout much of nature and are especially common in biological systems. Recently, researchers have studied self-organized self-assembly in purely synthetic systems.

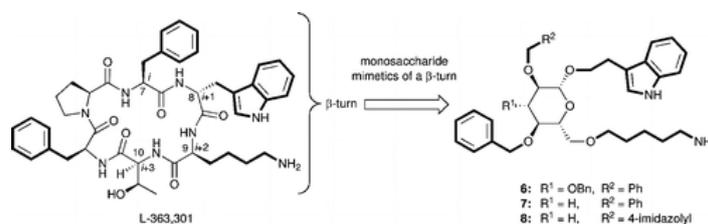
This Account describes our investigations of self-organization in the coordination-driven self-assembly of platinum(II)-based metallasupramolecules. The modularity of the coordination-driven approach to self-assembly has allowed us to systematically study a wide variety of different factors that can control the extent of supramolecular self-organization. In particular, we have evaluated the effects of the symmetry and polarity of ambidentate donor subunits, differences in geometrical parameters (e.g., the size, angularity, and dimensionality) of Pt(II)-based acceptors and organic donors, the influence of temperature and solvent, and the effects of intermolecular steric interactions and hydrophobic interactions on self-organization.

Our studies have shown that the extent of self-organization in the coordination-driven self-assembly of both 2D polygons and 3D polyhedra ranges from no organization (a statistical mixture of multiple products) to amplified organization (wherein a particular product or products are favored over others) and all the way to the absolute self-organization of discrete supramolecular assemblies. In many cases, inputs such as dipolar interactions, steric interactions, and differences in the geometric parameters of subunits, used either alone or as multiple factors simultaneously, can achieve absolute self-organization of discrete supramolecules. We have also observed instances where self-organization is not absolute and varies in its deviation from statistical results. Steric interactions are particularly useful control factors for driving such amplified self-organization because they can be subtly tuned through small structural variations.

Having the ability to fully understand and control the self-organization of complex mixtures into specific synthetic supramolecules can provide a better understanding of analogous processes in biological systems. Furthermore, self-organization may allow for the facile synthesis of complex multifunctional, multicomponent systems from simply mixing a collection of much simpler, judiciously designed individual molecular components.

- The β -d-Glucose Scaffold as a β -Turn Mimetic
Hirschmann, R. F.; Nicolaou, K. C.; Angeles, A. R.; Chen, J. S.; Smith, III, A. B. *Acc. Chem. Res.* **2009**, *42*, 1511–1520.

Abstract:



Activity and selectivity are typically the first considerations when designing a drug. However, absorption, distribution, metabolism, excretion, and toxicity (ADMET) are equally important considerations. Peptides can provide a combination of potent binding and exquisite selectivity, as evidenced by their pervasive use as enzymes, hormones, and signaling agents within living systems. In particular, peptidic turn motifs are key elements of molecular recognition. They may be found at the exposed surfaces of globular proteins, where they are available for binding interactions with other peptides and small molecules.

However, despite these advantages, peptides often make poor drugs. The amide backbone is subject to rapid enzymatic proteolysis, resulting in short half-lives. Furthermore, the ability of the amide backbone to hydrogen bond with water restricts its ability to cross membranes and, consequentially, results in poor oral bioavailability. Accordingly, the development of nonpeptidic scaffolds that mimic peptidic turn motifs represents a promising means of converting peptidic agents into more drugable molecules. In this Account, we describe the design and synthesis of β -turn mimetics that use a β -d-glucose scaffold, the first use of a sugar scaffold for this purpose.

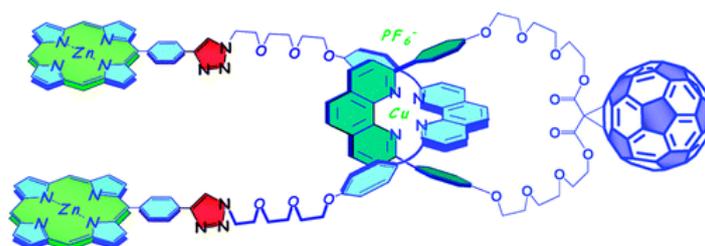
Somatostatin (SRIF) is a small protein (14 amino acid residues) human hormone; a shorter (6 amino acid residues) synthetic peptide, L-363,301, is a fully peptidal agonist. These two cyclic peptides share the β -turn motif comprising Phe⁷-Trp⁸-Lys⁹-Thr¹⁰ (d-Trp⁸ in the case of L-363,301), of which the tryptophan and lysine residues in the $i + 1$ and $i + 2$ positions, respectively, are critical for binding. In 1988, we initiated a program that tested and validated the then-novel proposition that the β -d-glucose scaffold can mimic the β -turn in L-363,301. The β -d-glucose scaffold proved to be an

attractive mimic of a β -turn in part because it permits the convenient attachment of amino acid side chains via facile etherification reactions, rather than carbon–carbon bond formations; it is also an inexpensive starting material with well-defined stereochemistry. From the beginning, biological assays were used alongside physical measurements to assess the relevance of the design. Our first two synthetic targets, compounds **6** and **7**, bound the SRIF receptors on benchmark (AtT-20) cells, albeit weakly, consistent with the objective of the design. Subsequently, a better ligand (**8**) and two congeners were found to be agonists at the SRIF receptors, providing convincing evidence that the peptide backbone is not required for receptor binding or signal transduction.

The unexpectedly high level of receptor affinity of selected analogs, as well as the fortuitous discovery that our peptidomimetics were active against several chemically distinct receptors, led us to hypothesize that these monosaccharides could access multiple potential binding modes. Our later studies of this sugar scaffold confirmed this property, which we termed pseudosymmetry, whereby multiple similar but nonidentical motifs are displayed within a single analog. We propose the presence of pseudosymmetry to be an element of privilege and an advantage for lead discovery.

- Efficient One-Pot Synthesis of Rotaxanes Bearing Electron Donors and [60]Fullerene
Megiatto, Jr., J. D.; Spencer, R.; Schuster, D. I. *Org. Lett.* **2009**, *11*, 4152–4155.

Abstract:

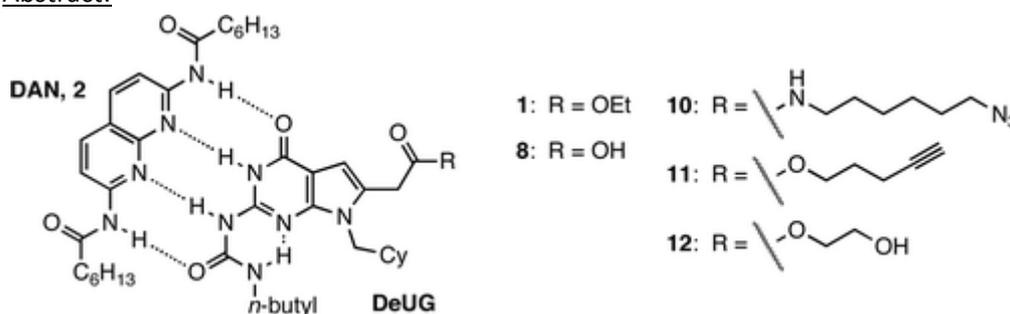


An easy one-pot procedure to synthesize rotaxanes bearing electron donors and C₆₀ is described. The straightforward strategy, based on copper(I)-templated synthesis and “click” chemistry, proved to be very efficient and versatile, allowing the preparation of porphyrin- and ferrocene-stoppered fullerene–rotaxanes in high yields. As revealed by NMR analysis and computational studies, the highly flexible porphyrin–fullerene rotaxane can assume different conformations, which are most likely driven by attractive interactions between porphyrin and fullerene moieties.

- Hydrogen-Bonded DeUG·DAN Heterocomplex: Structure and Stability and a Scalable Synthesis of DeUG with Reactive Functionality

Kuykendall, D. W.; Anderson, C. A.; Zimmerman, S. C. *Org. Lett.* **2009**, *11*, 61–64.

Abstract:

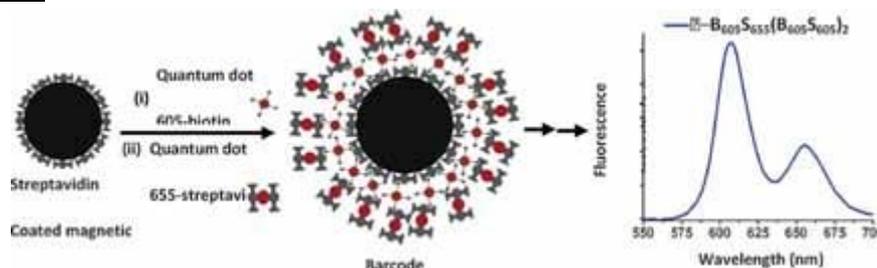


A convenient, scalable synthesis of the supramolecular building block 7-deazaguanine-based urea (DeUG) is reported. Incorporation of reactive moieties (DeUG azide **10** and alkyne **11** for copper-

catalyzed azide-alkyne cycloadditions, “click chemistry”) and a demonstration of transesterification (DeUG glycol, **12**) highlights the versatility. X-ray structures of DeUG and a DeUG·DAN heterocomplex were obtained. K_{assoc} for the **1·2** heterocomplex was estimated to be $2 \times 10^8 \text{M}^{-1}$ in chloroform.

- Production of Quantum Dot Barcodes Using Biological Self-Assembly
Rauf, S.; Glidle, A.; Cooper J. M. *Adv. Mater.* **2009**, 4020-4024.

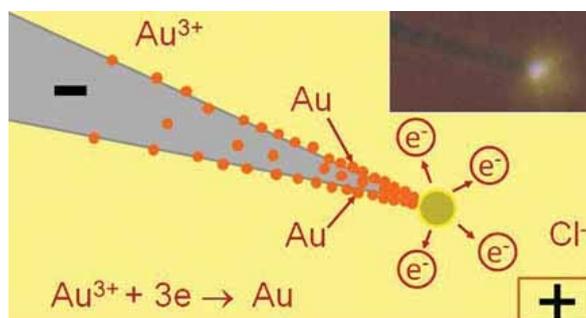
Abstract:



A new strategy to produce stable barcodes using biological self-assembly of streptavidin- and biotin-functionalized quantum dots is reported. Such systems are of potential use in multiplexed immunoassay and nucleic acid hybridization assays.

- Localized Synthesis of Metal Nanoparticles Using Nanoscale Corona Discharge in Aqueous Solutions
Bhattacharyya, S.; Staack, D.; Vitol, E. A.; Singhal, R.; Fridman, A.; Friedman, G.; Gogotsi, Y. *Adv. Mater.* **2009**, 4039-4044.

Abstract:



Highly localized and controlled metal nanoparticle synthesis using nanoscale corona discharge in aqueous solutions is illustrated. As a case study, gold nanoparticles are successfully deposited at the very tip of carbon nanopipettes to act as surface-enhanced Raman spectroscopy (SERS) probes.