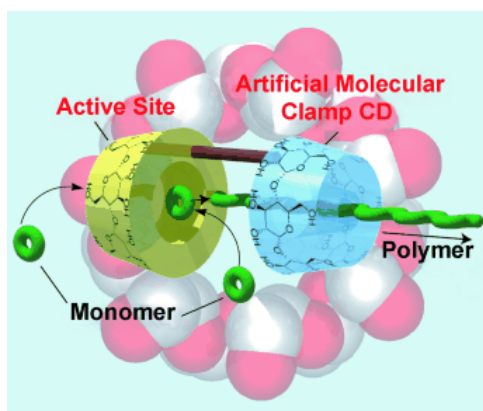


- Artificial Molecular Clamp: A Novel Device for Synthetic Polymerases

Takashima, Y.; Osaki, M.; Ishimaru, Y.; Yamaguchi, H.; Harada, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 7524–7528.

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Abstract:

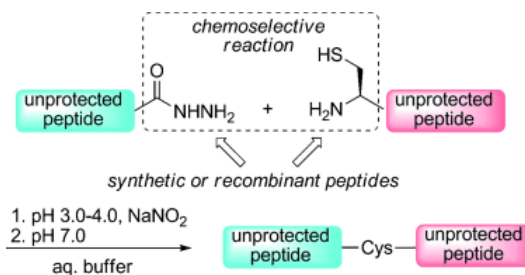


Synthetic polymerases composed of a cyclodextrin (CD) dimer yield high-molecular-weight polymers of cyclic esters without using solvents and co-catalysts. One CD moiety is attached to the active site of a supramolecular catalyst and propagates the polymerization by serving as artificial molecular clamp (see picture). The other CD moiety initiates the ring-opening polymerization.

- Protein Chemical Synthesis by Ligation of Peptide Hydrazides

Fang, G.-M.; Li, Y.-M.; Shen, F.; Huang, Y.-C.; Li, J.-B.; Lin, Y.; Cui, H.-K.; Liu, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 7645–7649.

Abstract:

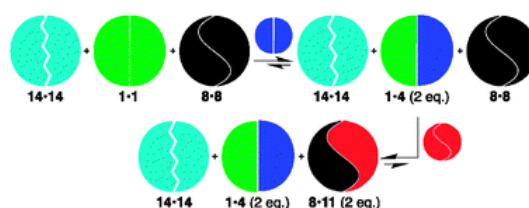


pH determines selectivity: The ligation of peptide hydrazides is a new method for protein chemical synthesis that is complementary to native chemical ligation. Peptide hydrazides may be the long-sought reagent equivalent to a “thioester synthon”, one that is stable to the conditions of native chemical ligation.

- Reassembly self-sorting triggered by heterodimerization

Cao, L.-P.; Wang, J.-G.; Ding, J.-Y.; Wu, A.-X.; Isaacs, L. *Chem. Commun.* **2011**, *47*, 8548-8550.

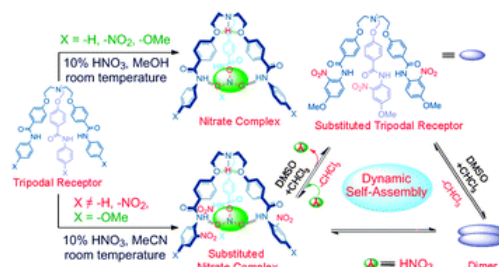
Abstract:



The self-sorting mixture comprising three homodimers undergoes stepwise reassembly self-sorting triggered by selective heterodimerization.

- Dynamic self-assembly of molecular capsules *via* solvent polarity controlled reversible binding of nitrate anions with C_3 symmetric tripodal receptors
Singh, A. S.; Sun, S.-S. *Chem. Commun.* **2011**, 47, 8563-8565.

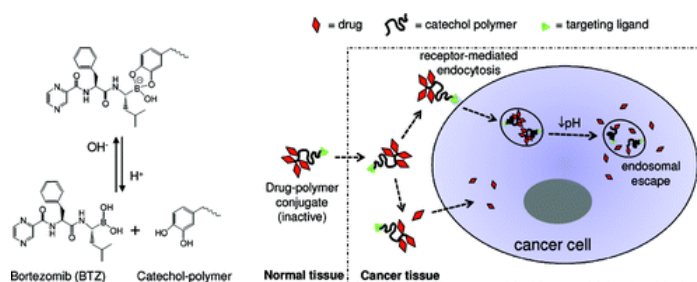
Abstract:



A series of N-bridgehead tripodal receptors bearing amide functionality is reported which displays reversible binding of nitrate anions *via* solvent polarity controlled molecular capsule formation through a dynamic self-assembly process.

- Catechol Polymers for pH-Responsive, Targeted Drug Delivery to Cancer Cells
Su, J.; Chen, F.; Cryns, V. L.; Messersmith, P. B. *J. Am. Chem. Soc.* **2011**, 133, 11850–11853.

Abstract:



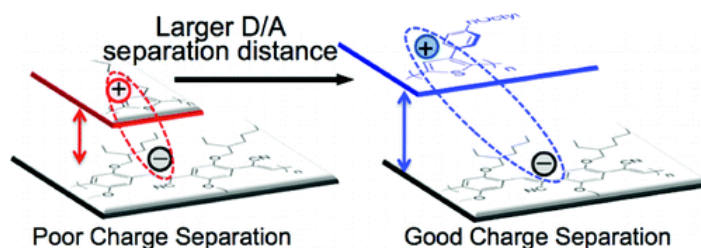
A novel cell-targeting, pH-sensitive polymeric carrier was employed in this study for delivery of the anticancer drug bortezomib (BTZ) to cancer cells. Our strategy is based on facile conjugation of BTZ to catechol-containing polymeric carriers that are designed to be taken up selectively by cancer cells through cell surface receptor-mediated mechanisms. The polymer used as a building block in this study was poly(ethylene glycol), which was chosen for its ability to reduce nonspecific interactions with proteins and cells. The catechol moiety was exploited for its ability to bind and release borate-containing therapeutics such as BTZ in a pH-dependent manner. In acidic environments, such as in cancer tissue or the subcellular endosome, BTZ dissociates from the polymer-bound catechol groups to liberate the free drug, which inhibits proteasome function. A cancer-cell-targeting ligand, biotin, was presented on the polymer carriers to facilitate targeted entry of drug-loaded polymer carriers into cancer cells. Our study demonstrated that the cancer-targeting drug-polymer conjugates dramatically enhanced cellular uptake, proteasome inhibition, and cytotoxicity toward breast carcinoma cells in comparison with nontargeting drug-polymer conjugates. The pH-sensitive catechol-boronate binding mechanism provides a chemoselective approach for controlling the release of BTZ in targeted cancer cells, establishing a concept that may be applied in the future toward other boronic acid-containing therapeutics to treat a broad range of diseases.

- Steric Control of the Donor/Acceptor Interface: Implications in Organic Photovoltaic Charge Generation

Holcombe, T. W.; Norton, J. E.; Rivnay, J.; Woo, C. H.; Goris, L.; Piliago, C.; Griffini, G.; Sellinger, A.; Brédas, J.; Salleo, A.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2011**, *133*, 12106–12114.

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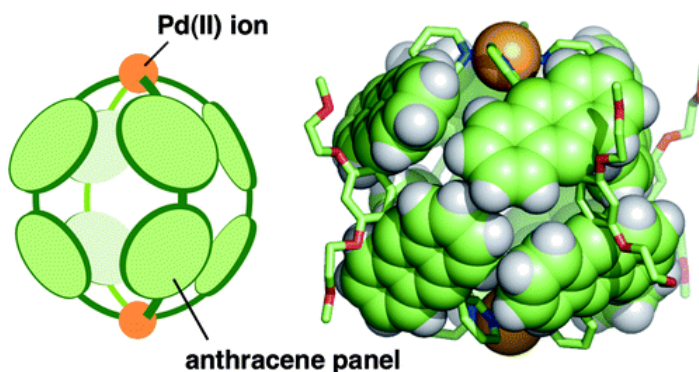
Abstract:



The performance of organic photovoltaic (OPV) devices is currently limited by modest short-circuit current densities. Approaches toward improving this output parameter may provide new avenues to advance OPV technologies and the basic science of charge transfer in organic semiconductors. This work highlights how steric control of the charge separation interface can be effectively tuned in OPV devices. By introducing an octylphenyl substituent onto the investigated polymer backbones, the thermally relaxed charge-transfer state, and potentially excited charge-transfer states, can be raised in energy. This decreases the barrier to charge separation and results in increased photocurrent generation. This finding is of particular significance for nonfullerene OPVs, which have many potential advantages such as tunable energy levels and spectral breadth, but are prone to poor exciton separation efficiencies. Computational, spectroscopic, and synthetic methods were combined to develop a structure–property relationship that correlates polymer substituents with charge-transfer state energies and, ultimately, device efficiencies.

- An M₂L₄ Molecular Capsule with an Anthracene Shell: Encapsulation of Large Guests up to 1 nm
Norifumi, K.; Li, Z.; Yoza, K.; Akita, M. *J. Am. Chem. Soc.* **2011**, *133*, 11438–11441.

Abstract:

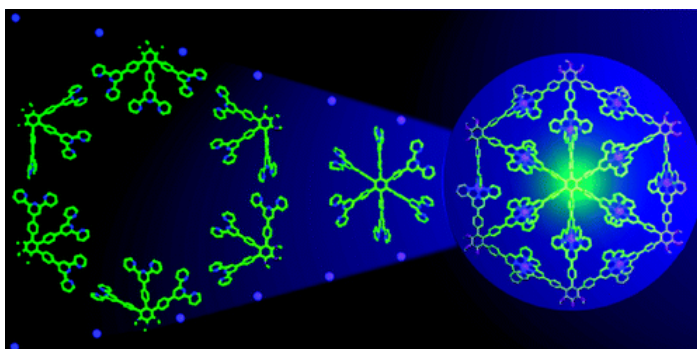


A new M₂L₄ molecular capsule with an aromatic shell was prepared using two Pd(II) ions and four bisanthracene ligands. The self-assembled capsule possesses a cavity with a diameter of 1 nm that can encapsulate medium-sized spherical and planar molecules as well as a very large molecule (C₆₀) in quantitative yields. The encapsulated guests are fully segregated and shielded from the external environment by the large anthracene panels.

- Stoichiometric Self-Assembly of Shape-Persistent 2D Complexes: A Facile Route to a Symmetric Supramacromolecular Spoked Wheel
Wang, J.-L.; Li, X.; Lu, X.; Hsieh, I.-F.; Cao, Y.; Moorefield, C. N.; Wesdemiotis, C.; Cheng, S. Z. D.; Newkome, G. R. *J. Am. Chem. Soc.* **2011**, *133*, 11450–11453.

Abstract:

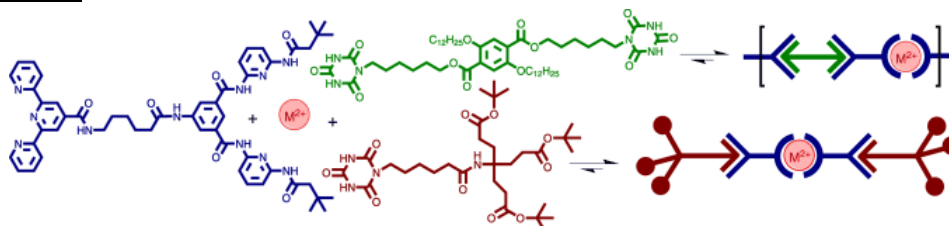
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An approach to multicomponent coordination-driven self-assembly of the first terpyridine-based, shape-persistent, giant two-dimensional D_{6h} supramacromolecular spoked wheel is reported. Mixing core T6, rim T3, and Zn^{II} or Cd^{II} ions in a stoichiometric ratio (1:6:12) permitted the selective generation of a highly symmetric spoked wheel in 94% isolated yield via geometric and thermodynamic control. The products were characterized by a combination of traveling-wave ion mobility mass spectrometry and NMR techniques together with TEM imaging, which agreed with computational simulations.

- Self-Assembly of Supramolecular Architectures and Polymers by Orthogonal Metal Complexation and Hydrogen-Bonding Motifs

Grimm, F.; Ulm, N.; Gröhn, F.; Düring, J.; Hirsch, A. *Chem. Eur. J.* **2011**, *17*, 9478-9488.

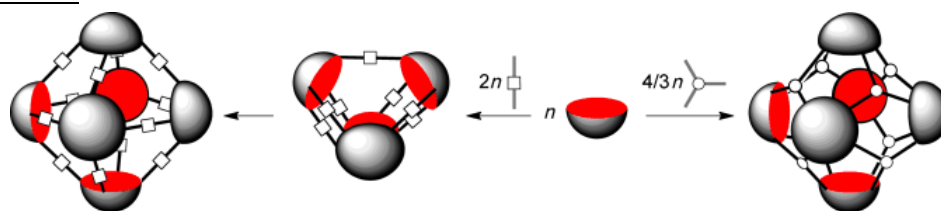
Abstract:

A modular construction kit with two orthogonal noncovalent binding sites for self-assembly of supramolecular architectures is presented. The heteroditopic building blocks contain a terpyridine (tpy) unit for coordination of metal ions and a Hamilton receptor for multiple H-bonding of cyanuric acid derivatives. The association constants of ligand binding of M^{III} complexes (M=Ru, Zn, Fe, and Pt) with a dendritic end cap were determined to be in the range of 10² and 10⁴ L mol⁻¹ in chloroform. The capabilities for binding of metal ions were investigated by ¹H NMR and UV/Vis spectroscopy. The Fe complexes are most appropriate for the generation of discrete and high-ordered architectures due to their strong tendency to form FeL₂ complexes. Superstructures are readily formed in a one-pot procedure at room temperature. No mutual interactions between the orthogonal binding motifs were observed, and this demonstrates the highly specific nature of each binding process. Decomplexation experiments were carried out to examine the reversibility of Fe–tpy coordination. Substitution of the terminal end cap with a homoditopic bis-cyanurate linkage leads to formation of an iron-containing supramolecular strand. Formation of coordination polymers was confirmed by viscosity measurements. The supramolecular polymer strands can be reversibly cleaved by addition of a terminating cyanuric acid building block, and this proves the dynamic nature of this noncovalent polymerization process.

- Multicomponent Assembly of Cavitand-Based Polyacylhydrazone Nanocapsules

Lin, Z.; Emge, T. J.; Warmuth, R. *Chem. Eur. J.* **2011**, *17*, 9395-9405.

Abstract:

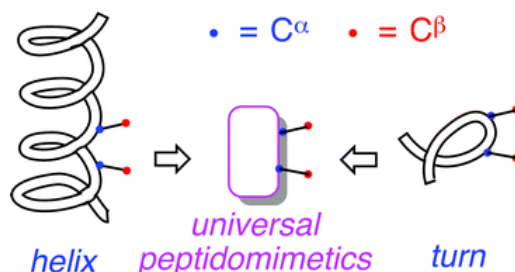


The thermodynamically controlled syntheses of different di-, tetra-, and hexacavitand polyacylhydrazone nanocapsules are reported. [2+4]-, [4+8]-, and [6+12]-nanocapsules assemble upon reacting a tetraformyl cavitand with two equivalents of isophthalic dihydrazide, or terephthalic dihydrazide in the presence of trifluoroacetic acid, whereby the building blocks are linked together through 8, 16, or 24 newly formed acylhydrazone bonds. Furthermore, the reaction of the tetraformylcavitands with different trigonal planar trihydrazides, simultaneously leads to the formation of [2+4]- and [6+8]-nanocapsules in varying ratios that depend on the cavitand to trihydrazide ratio and the nature of the cavitand and trihydrazide building blocks. The product ratios are rationalized with the different conformational strain of the acylhydrazone linkages in these nanocapsules. Diffusion NMR experiments with the hexacavitand polyacylhydrazone nanocapsules yield solvodynamic radii that range from 1.6 to 2.5 nm, consistent with estimates from force field calculations, and support, that these capsules have solvent filled, spherical interiors, the sizes of which approaches those of smaller proteins.

- Minimalist and universal peptidomimetics

Ko, E.; Liu, J.; Burgess, K. *Chem. Soc. Rev.* **2011**, *40*, 4411–4421.

Abstract:



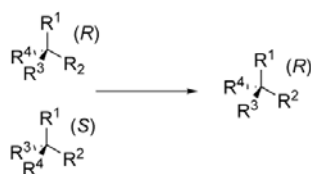
Many “new generation” peptidomimetics are designed to present amino acid side chains *only*; they do not have structural features that resemble peptide main chains. These types of molecules have frequently been presented in the literature as mimics of *specific* secondary structures. However, many “side-chain only” peptidomimetics do *not* rest in single conformational states, but exist in a limited number of freely interconverting forms. These different conformations may resemble different secondary structures, so referring to them as, for instance, turn- or helical-mimics understates the ways they could adapt to various binding situations. Sets of scaffolds that can be used to mimic aspects of nearly every secondary structure, *i.e.* universal peptidomimetics, can be constructed. These may assume a privileged place in library design, particularly in high throughput screening for pharmacological probes for which binding conformations, or even the target itself, is unknown at the time the library is designed (*critical review*, 101 references).

- Enantioenriched Compounds via Enzyme-Catalyzed Redox Reactions

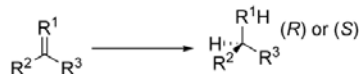
Hall, M.; Bommarium, A. S. *Chem. Rev.* **2011**, *111*, 4088–4110.

Abstract:

a) Deracemization



b) Asymmetric synthesis using dehydrogenases



Redox reactions are essential to any currently known form of life and are at the core of a majority of metabolic processes, such as cellular respiration or photosynthesis. As about 25% of known enzymes are oxidoreductases, it is no wonder that chemists have taken advantage of redox reactions occurring in Nature to serve synthesis purposes.

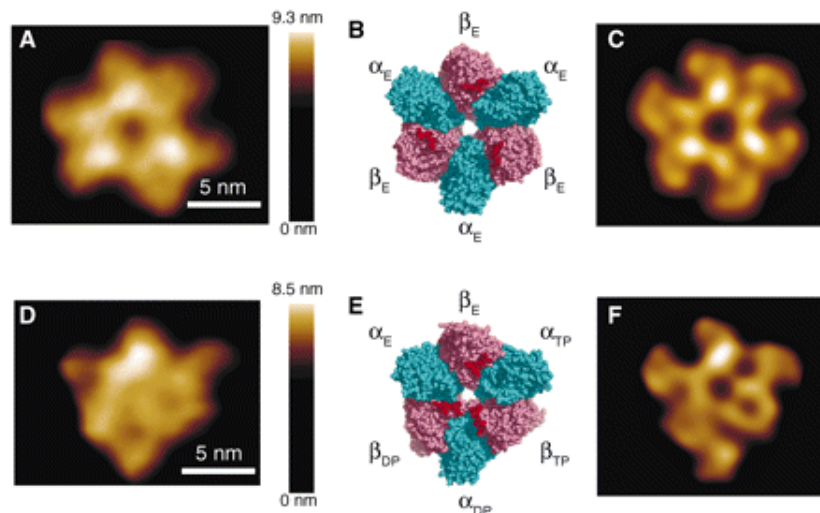
While the pharma industry is driven by the need for enantiopure drugs (the majority of small molecule active pharmaceutical ingredients (APIs) having at least one chiral center are developed as single enantiomers), there is still a lack for broad synthesis methods that would generate both enantiomeric forms of a target compound in high purity. Homogeneous catalysis and organocatalysis recently have shown great progress toward this goal, but the past decade has seen even more advances from biocatalysis. Enzymes are biological catalysts and their use is less subjected to environmental regulations and societal scrutiny. Biocatalysts not only commonly work under ambient conditions of temperature, pH value, and pressure in aqueous solutions, a greener approach to chemistry but, most importantly, are highly chemo-, regio-, and stereoselective and therefore of great interest in fine chemical synthesis.

Oxidoreductases constitute EC class number 1 and are classified into 22 subclasses. They allow the creation of stereogenic centers or the enantioenrichment of existing ones. While abundant literature has been published on biocatalyzed redox reactions, it is essential to stress their applicability in asymmetric synthesis. Thus, this review highlights the tremendous progress achieved over the last 10 years in the application of biocatalysts in the synthesis of enantiomerically pure compounds (EPCs), whether in purified form or as whole-cell biocatalysts, while specifically emphasizing on applications for the pharma industry. Advances in protein engineering are the main cause of that progress. It is now common to encounter enzymes with a broad substrate spectrum on non-natural substrates while displaying high chemo-, regio-, and stereoselectivity.

This review summarizes major advances dealing with reductases and oxidases and is organized according to important concepts in asymmetric biosynthesis. Therefore, advances that do not employ oxidoreductases, such as the transaminase-catalyzed synthesis of sitagliptin, the active ingredient of Januvia and Janumet, are not covered by this review. The review highlights specific examples where the use of redox biocatalysts has allowed the development of synthetic routes to pharmaceutically relevant molecules by enhancing the optical purity of the product, giving access to previously nonaccessible enantiomers, or increasing space-time yields and industrial applicability.

- High-Speed Atomic Force Microscopy Reveals Rotary Catalysis of Rotorless F1-ATPase Uchihashi, T.; Iino, R.; Ando, T.; Noji, H. *Science* **2011**, *333*, 755-758.

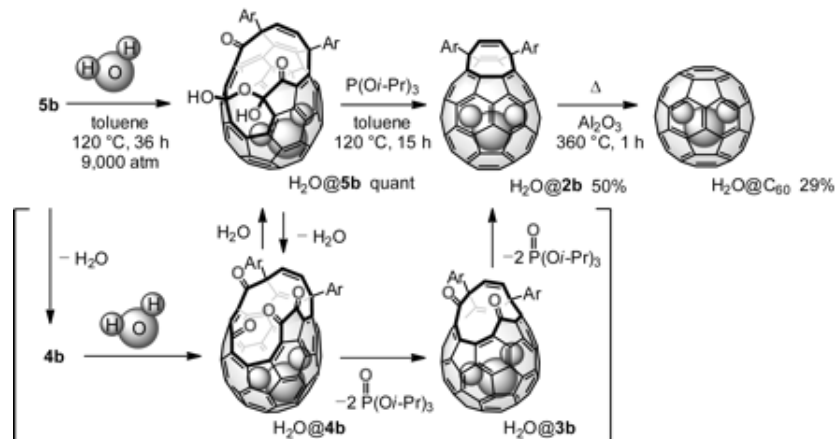
Abstract:



F_1 is an adenosine triphosphate (ATP)–driven motor in which three torque-generating β subunits in the $\alpha_3\beta_3$ stator ring sequentially undergo conformational changes upon ATP hydrolysis to rotate the central shaft γ unidirectionally. Although extensive experimental and theoretical work has been done, the structural basis of cooperative torque generation to realize the unidirectional rotation remains elusive. We used high-speed atomic force microscopy to show that the rotorless F_1 still “rotates”; in the isolated $\alpha_3\beta_3$ stator ring, the three β subunits cyclically propagate conformational states in the counterclockwise direction, similar to the rotary shaft rotation in F_1 . The structural basis of unidirectionality is programmed in the stator ring. These findings have implications for cooperative interplay between subunits in other hexameric ATPases.

- A Single Molecule of Water Encapsulated in Fullerene C_{60}
Kurotobi, K.; Murata, Y. *Science* **2011**, 333, 613-616.

Abstract:



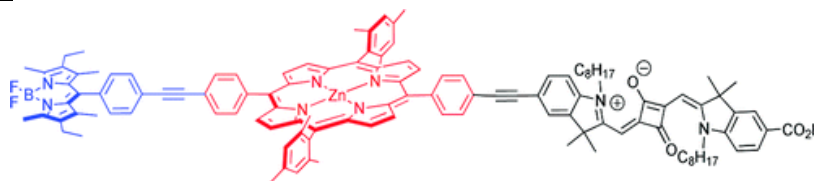
Water normally exists in hydrogen-bonded environments, but a single molecule of H_2O without any hydrogen bonds can be completely isolated within the confined subnano space inside fullerene C_{60} . We isolated bulk quantities of such a molecule by first synthesizing an open-cage C_{60} derivative whose opening can be enlarged in situ at 120°C that quantitatively encapsulated one water molecule under the high-pressure conditions. The relatively simple method was developed to close the cage and encapsulate water. The structure of $H_2O@C_{60}$ was determined by single-crystal x-ray analysis, along with its physical and spectroscopic properties.

- Panchromatic Trichromophoric Sensitizer for Dye-Sensitized Solar Cells Using Antenna Effect

Warnan, J.; Buchet, F.; Pellegrin, Y.; Blart, E.; Odobel, F. *Org. Lett.* **2011**, *13*, 3944-3947.

Abstract:

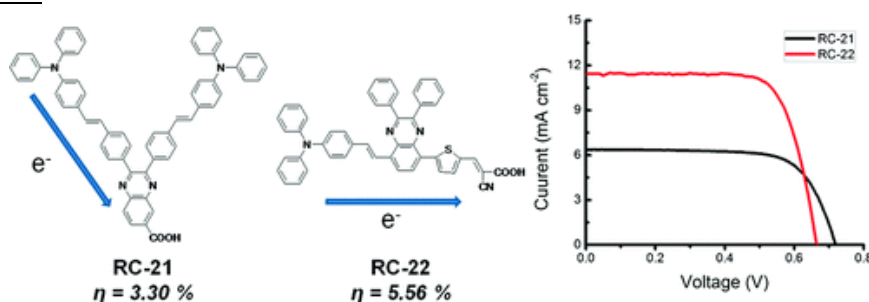
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The first trichromophoric sensitizer, consisting of covalently linked boradiazaindacene (BODIPY), zinc porphyrin (ZnP), and squaraine (SQ) units, has been synthesized by Heck alkylation to obtain a panchromatic dye, for dye sensitized solar cells (DSSCs). Efficient intramolecular energy transfers (ET) were observed between all chromophoric subunits and enhance the overall conversion efficiency by 25%. The antenna effect is demonstrated by the photoaction spectrum which features all of a chromophore's absorption bands.

- Novel Quinoxaline-Based Organic Sensitizers for Dye-Sensitized Solar Cells
Chang, D. W.; Lee, H. J.; Kim, J. H.; Park, S. Y.; Park, S.-M.; Dai, L.; Baek, J. B. *Org. Lett.* **2011**, *13*, 3880-3883.

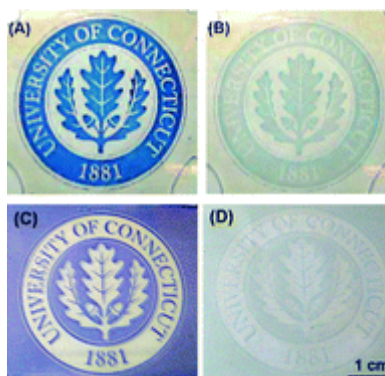
Abstract:



Novel quinoxaline-based organic sensitizers using vertical (RC-21) and horizontal (RC-22) conjugation between an electron-donating triphenylamine unit and electron-accepting quinoxaline unit have been synthesized and used for dye-sensitized solar cells (DSSCs), leading to the relatively high power conversion efficiencies of 3.30 and 5.56% for RC-21 and RC-22, respectively. This result indicates that the quinoxaline electron-accepting unit is quite a promising candidate in organic sensitizers.

- A simple, low waste and versatile procedure to make polymer electrochromic devices
Ding, Y.; Invernale, M. A.; Mamangun, D. M. D.; Kumar, A.; Sotzing, G. A. *J. Mater. Chem.* **2011**, *21*, 11873-11878.

Abstract:

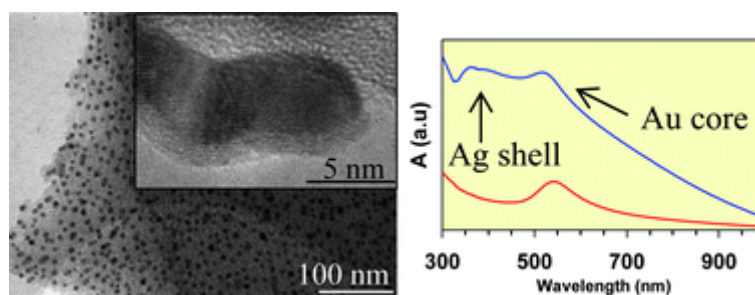


Herein we present a simple and elegant method for the creation of solid-state conjugated polymer devices. Their electrochromic properties were fully explored in this study, but one could envision the extension of this method to displays, solar cells, OLEDs, transistors, or many other applications. We prepared conductive polymer composites or blends within a polymer electrolyte using electrochemical polymerization of these monomers inside an assembled solid-state device. This method will work for any monomer that can be dissolved in the gel electrolyte. This technique offers simplicity in device construction, is easily adapted to patterned systems and comprises a low-waste assembly process. Our novel approach of assembling polymer electrochromic devices avoids the tedious cleaning process of the substrates, produces almost no waste, and by inkjetting insulating materials to mask the substrates, letters and high-resolution images could be achieved inside the converted polymer devices. Electrochromic devices utilizing PEDOT assembled by our method showed compatible switching speed and durability with a slightly higher contrast ratio.

- Elaboration and characterization of bimetallic gold–silver nanoparticles supported on mesostructured silica films

Chassagneux, F. ; Bois, L. ; Simon, J.-P. ; Desroches, C. ; Brioude, A. *J. Mater. Chem.*, **2011**, *21*, 11947-11955.

Abstract:



Silver–gold nanoparticles are grown inside mesostructured silica films obtained from block copolymers, using two successive steps: the first one involves silver nanoparticle growth. The second step consists of the replacement of the silver with gold. Using two commercial block copolymers, containing polyethylene oxide and polypropylene oxide blocks, mesostructured silica films are suitable “soft” templates for elaborating either spherical gold nanoparticles or nanorods array. Then, a third step involving soft silver reduction allows the preparation of core–shell gold–silver nanostructures. Grazing incidence small-angle X-ray scattering (GISAXS) and Anomalous GISAXS (AGISAXS) analysis are performed using synchrotron radiation on a bimetallic nanoparticles-containing film.