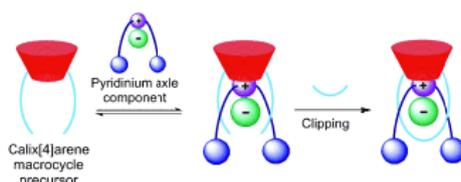


- Calix[4]arene-Based Rotaxane Host Systems for Anion Recognition
McConnell, A. J.; Serpell, C. J.; Thompson, A. L.; Allan, D. A.; Beer, P. D. *Chem. Eur. J.* **2010**, *16*, 1256-1264.

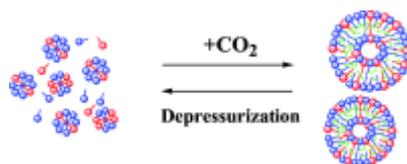
Abstract:



The synthesis, structure and anion binding properties of the first calix[4]arene-based [2]rotaxane anion host systems are described. Rotaxanes 9-Cl and 12-Cl, consisting of a calix[4]arene functionalised macrocycle wheel and different pyridinium axle components, are prepared via adaption of an anion templated synthetic strategy to investigate the effect of preorganisation of the interlocked host's binding cavity on anion binding. Rotaxane 12-Cl contains a conformationally flexible pyridinium axle, whereas rotaxane 9-Cl incorporates a more preorganised pyridinium axle component. The X-ray crystal structure of 9-Cl and solution phase ^1H NMR spectroscopy demonstrate the successful interlocking of the calix[4]arene macrocycle and pyridinium axle components in the rotaxane structures. Following removal of the chloride anion template, anion binding studies on the resulting rotaxanes 9- PF_6 and 12- PF_6 reveal the importance of preorganisation of the host binding cavity on anion binding. The more preorganised rotaxane 9- PF_6 is the superior anion host system. The interlocked host cavity is selective for chloride in 1:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$ and remains selective for chloride and bromide in 10 % aqueous media over the more basic oxoanions. Rotaxane 12- PF_6 with a relatively conformationally flexible binding cavity is a less effective and discriminating anion host system although the rotaxane still binds halide anions in preference to oxoanions.

- Reversible Switching of a Micelle-to-Vesicle Transition by Compressed CO_2
Li, W.; Zhang, J.; Zhao, Y.; Hou, M.; Han, B.; Yu, C.; Ye, J. *Chem. Eur. J.* **2010**, *16*, 1296-1305.

Abstract:

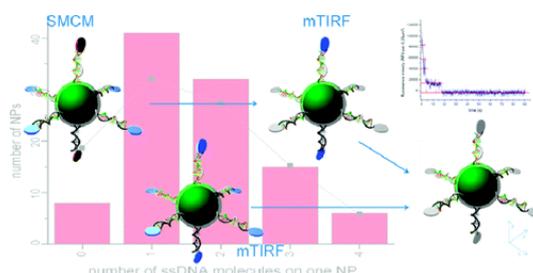


The study of the micelle-to-vesicle transition (MVT) is of great importance from both theoretical and practical points of view. Herein, we studied the effect of compressed CO_2 on the aggregation behavior of dodecyltrimethylammonium bromide (DTAB)/sodium dodecyl sulfate (SDS) mixed surfactants in aqueous solution by means of direct observation, turbidity and conductivity measurements, steady-state fluorescence, time-resolved fluorescence quenching (TRFQ), fluorescence quantum yield, and template methods. Interestingly, all these approaches showed that compressed CO_2 could induce the MVT in the surfactant system, and the vesicles returned to the micelles simply by depressurization; that is, CO_2 can be used to switch the MVT reversibly by controlling pressure. Some other gases, such as methane, ethylene, and ethane, could also induce the MVT of the surfactant solution. A possible mechanism is proposed on the basis of the packing-parameter theory and thermodynamic principles. It is shown that the mechanism of the MVT induced by a nonpolar gas is different from the MVT induced by polar and electrolyte additives.

- Improved Method for Counting DNA Molecules on Biofunctionalized Nanoparticles
Delpont, F.; Deres, A.; Hotta, J.-I.; Pollet, J.; Verbruggen, B.; Sels, B.; Hofkens, J.; Lammertyn, J. *Langmuir* **2010**, *26*, 1594–1597.

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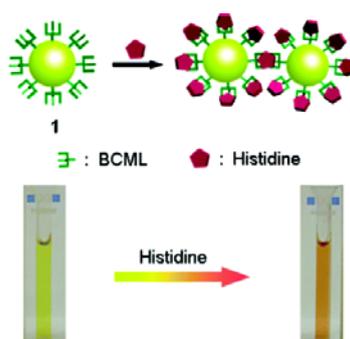
Abstract:



In order to accurately determine low numbers (1–100) of immobilized ssDNA molecules at a single, silica 250 nm nanoparticle surface, we hereby propose an integrated approach combining classic single molecule confocal microscopy (SMCM), that is, stepwise photobleaching of labeled ssDNA, with modified total internal reflection fluorescence microscopy (mTIRF). We postulate that SMCM alone is unable to exactly account for all labeled ssDNA because of inherent laser polarization effects; that is, perpendicularly oriented molecules to the sample surface are not (or are only slightly) susceptible to laser excitation and thus are invisible in a classic photobleaching experiment. The SMCM method accounts for at best two-thirds (68%) of the present ssDNA molecules. The principle of the mTIRF technique, which relies on the creation of highly inclined illumination combined with part of the laser remaining in normal Köhler illumination, enables accurate counting of SMCM invisible molecules. The combined approach proposed here circumvents the polarization issue and allows a complete single molecule counting on individual nanoparticles, fully in line with bulk measurements, as will be demonstrated.

- Lysine-Functionalized Silver Nanoparticles for Visual Detection and Separation of Histidine and Histidine-Tagged Proteins
Bae, D. R.; Han, W. S.; Lim, J. M.; Kang, S.; Lee, J. Y.; Kang, D.; Jung, J. H. *Langmuir* **2010**, *26*, 2181–2185.

Abstract:

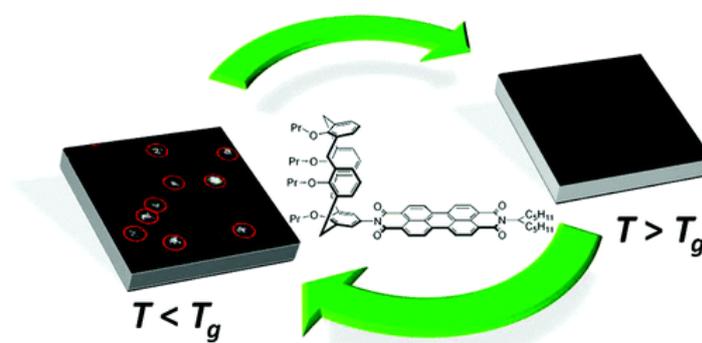


A new chromogenic chemosensor based on lysine-functionalized silver nanoparticles **1** was prepared and characterized by transmission electron microscopy (TEM), Fourier transform Raman, and ultraviolet–visible (UV–vis) spectroscopy. The color changes of nanoparticles **1** in the absence and the presence of metal ion were observed upon addition of various amino acids and proteins in aqueous solution. Among the various amino acids, the sensor **1** in the absence of metal ion shows a novel colorimetric sensor with capability to probe histidine and histidine-tagged proteins. On the other hand, the color changes of **1** in the presence of metal ions such as KCl or NiCl₂ did not occur

with any amino acids. Therefore, the sensor **1** in the absence of metal ion responds selectively to histidine, a response which can be attributed to its aggregation induced by histidine with high numbers of electrostatic interactions. This highly selective sensor **1** allows a rapid quantitative assay of histidine to concentrations as low as 5.0 μM , providing a new tool for the direct measurement of histidine and histidine-tagged proteins in vitro system. Furthermore, we examined the effect of pH on absorbance (A_{520}) of **1** in the presence of histidine (pH 4–12). The absorbance under basic conditions was higher than that under acidic or neutral conditions, in accord with the stronger aggregation of **1** with histidine by electrostatic interaction between the carboxylate anion of **1** and ammonium protons of histidine under basic conditions.

- Polymer Glass Transitions Switch Electron Transfer in Individual Molecules
Siekierzycka, J. R.; Hippus, C.; Würthner, F.; Williams, R. M.; Brouwer, A. M. *J. Am. Chem. Soc.* **2010**, *132*, 1240–1242.

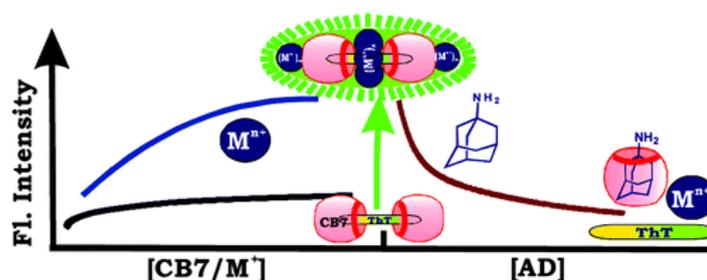
Abstract:



Essentially complete photoinduced electron transfer quenching of the fluorescence of a perylene-calixarene compound occurs in poly(methyl acrylate) and poly(vinyl acetate) above their glass transition temperatures (T_g), but the fluorescence is completely recovered upon cooling the polymer matrix to a few degrees below the T_g . The switching can be observed in an on/off fashion at the level of individual molecules.

- Cooperative Metal Ion Binding to a Cucurbit[7]uril–Thioflavin T Complex: Demonstration of a Stimulus-Responsive Fluorescent Supramolecular Capsule
Choudhury, S. D.; Mohanty, J.; Pal, H.; Bhasikuttan, A. C. *J. Am. Chem. Soc.* **2010**, *132*, 1395–1401.

Abstract:

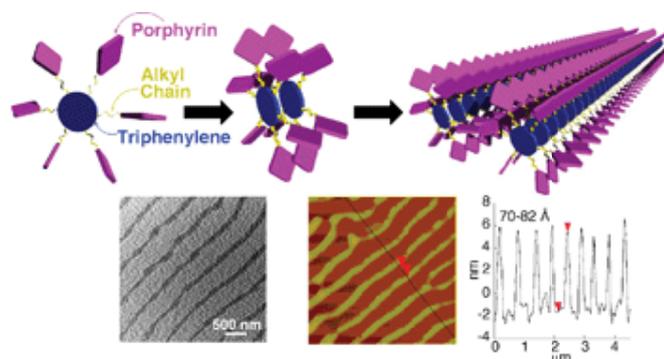


We report an intriguing noncovalent interaction of thioflavin T (ThT), a fibril diagnostic dye, with the versatile macrocyclic host molecule cucurbit[7]uril (CB7) in the presence of metal cations. ThT forms both 1:1 (CB7·ThT) and 2:1 [(CB7)₂·ThT] complexes with CB7 host, leading to specific structural arrangements. Addition of competitive guests like metal cations to the 1:1 stoichiometric complex

displays expected competitive binding interactions with CB7, leading to decreased fluorescence intensity from ThT. However, addition of metal ions to the 2:1 complex leads to unusual enhancement in the fluorescence emission (~ 270 -fold in the presence of Ca^{2+} and ~ 160 -fold in the presence of Na^+). These contrasting observations on the fluorescence enhancement with change in the stoichiometric equilibrium have been investigated explicitly for a feasible binding model. Detailed photophysical characterization with supporting data from NMR and anisotropy measurements has led to the revelation of a novel stimulus-responsive cooperative metal ion binding to the stoichiometrically selected $(\text{CB7})_2\text{-ThT}$ complex, demonstrating a highly fluorescent supramolecular nanocapsule. The first example of a noncovalently packed fluorescent complex became feasible due to the structural arrangement of the host-guest complex in the 2:1 stoichiometry with two CB7 portals providing strong negative charge density for the metal ions to group and seal the complex, thus protecting the incorporated dye. To further strengthen the usefulness of the supramolecular capsule established here, rupture of the capsular complex has been demonstrated with a strong competitive guest, 1-amantadine hydrochloride, which helped in disrupting the capsule to release the dye. It is proposed here that by judicious design of the chromophore (guest) structure, such capsular assemblies can be explored for the binding and release of drug molecules, for fluorescence on-off systems, and as building blocks for molecular architectures displaying unique properties.

- Synthesis and aggregate formation of triphenylene core-centered porphyrin hexamers
Hasobe, A.; Gulam, M.; Atula, R.; Sandanayaka, S. D.; Sakai, H.; Murakami, T. *Chem. Commun.* **2010**, 46, 889 – 891.

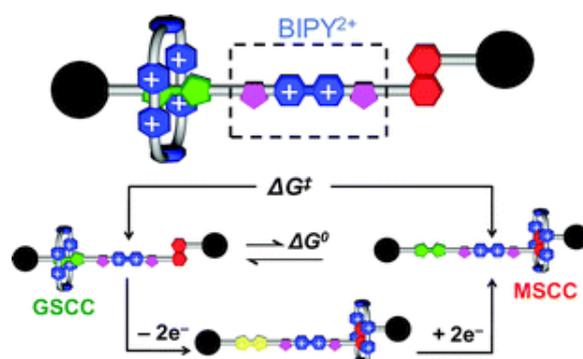
Abstract :



We demonstrate the synthesis, aggregate formation and spectroscopic property of new triphenylene core-centered porphyrin hexamers with different alkyl chain lengths.

- A tristable [2]pseudo[2]rotaxane
Trabolsi, A.; Fahrenbach, A. C.; Dey, S. K.; Share, A. I.; Friedman, D. C.; Basu, S.; Gasa, Niveen, T. B.; Khashab, M.; Saha, S.; Aprahamian, I.; Khatib, H. A.; Flood, A. H.; Stoddart, J. F. *Chem. Commun.* **2010**, 46, 871 – 873.

Abstract:

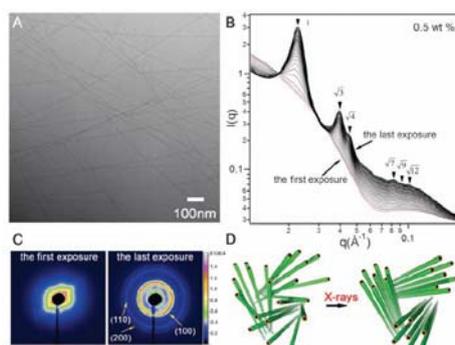


A strategy towards increasing the lifetime of the metastable state of a [2]rotaxane incorporating tetrathiafulvalene, 1,5-dioxynaphthalene and bipyridinium (BIPY^{2+}) is presented. Incorporation of BIPY^{2+} served multiple roles as an electrostatic barrier to relaxation, a supramolecular recognition site for bis-1,5-dioxynaphthalene[38]crown-10 macrocycle, and upon reduction a recognition site for the mechanically bonded cyclobis(paraquat-p-phenylene) ring.

- Spontaneous and X-ray–Triggered Crystallization at Long Range in Self-Assembling Filament Networks

Cui, H.; Pashuck, E. T.; Velichko, Y. S.; Weigand, S. J.; Cheetham, A. G.; Newcomb, C. J.; Stupp, S. I. *Science* **2010**, *327*, 555-559.

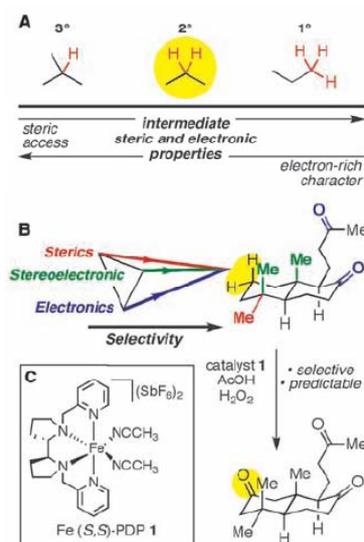
Abstract:



We report here crystallization at long range in networks of like-charge supramolecular peptide filaments mediated by repulsive forces. The crystallization is spontaneous beyond a given concentration of the molecules that form the filaments but can be triggered by x-rays at lower concentrations. The crystalline domains formed by x-ray irradiation, with interfilament separations of up to 320 angstroms, can be stable for hours after the beam is turned off, and ions that screen charges on the filaments suppress ordering. We hypothesize that the stability of crystalline domains emerges from a balance of repulsive tensions linked to native or x-ray–induced charges and the mechanical compressive entrapment of filaments within a network. Similar phenomena may occur naturally in the cytoskeleton of cells and, if induced externally in biological or artificial systems, lead to possible biomedical and lithographic functions.

- Combined Effects on Selectivity in Fe-Catalyzed Methylene Oxidation
Chen, M. S.; White, M. C. *Science* **2010**, *327*, 566-571.

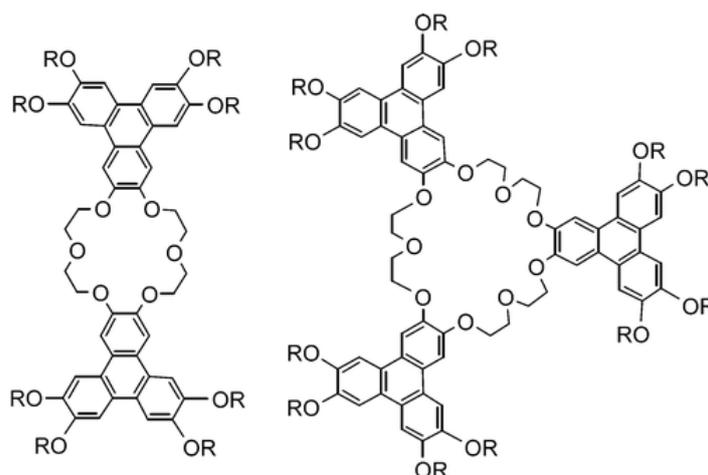
Abstract:



Methylene C–H bonds are among the most difficult chemical bonds to selectively functionalize because of their abundance in organic structures and inertness to most chemical reagents. Their selective oxidations in biosynthetic pathways underscore the power of such reactions for streamlining the synthesis of molecules with complex oxygenation patterns. We report that an iron catalyst can achieve methylene C–H bond oxidations in diverse natural-product settings with predictable and high chemo-, site-, and even diastereoselectivities. Electronic, steric, and stereoelectronic factors, which individually promote selectivity with this catalyst, are demonstrated to be powerful control elements when operating in combination in complex molecules. This small-molecule catalyst displays site selectivities complementary to those attained through enzymatic catalysis.

- Synthesis of Crown Ether-Linked Discotic Triphenylenes
Li, J.; He, Z.; Gopee, H.; Cammidge, A. N. *Org. Lett.* **2010**, *12*, 472–475.

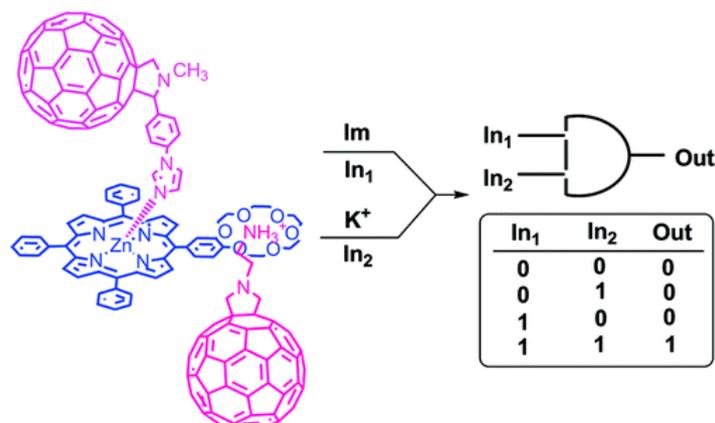
Abstract:



Novel triphenylene dimers linked by a central crown ether core have been synthesized and characterized. The crown ether is most conveniently formed as a final step to permit purification and isolation of ion-free material, and extension of the protocol permits synthesis of triad structures linked through a 27-crown-9 macrocycle. The latter compounds present a new discotic motif that supports mesophase formation.

- NOR and AND Logic Gates Based on Supramolecular Porphyrin–Fullerene Conjugates
Maligaspe, E.; D'Souza, F. *Org. Lett.* **2010**, *12*, 624–627.

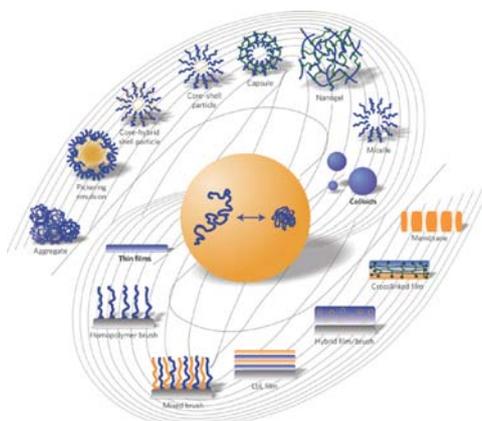
Abstract:



Supramolecular porphyrin–fullerene conjugates are employed to build NOR and AND logic gates. A crown ether appended zinc porphyrin and an imidazole or an alkyl ammonium functionalized fullerene are utilized. Quenching of zinc porphyrin fluorescence upon addition of binding-site-selective fullerene inputs forms the design basis of the NOR logic gate, while replacing the fullerene entities from the porphyrin–fullerene conjugate and restoring the original fluorescence by chemical inputs form the design basis of the AND logic gate.

- Emerging applications of stimuli-responsive polymer materials
Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Müller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. *Nature Materials* **2010**, *9*, 101 – 113.

Abstract:

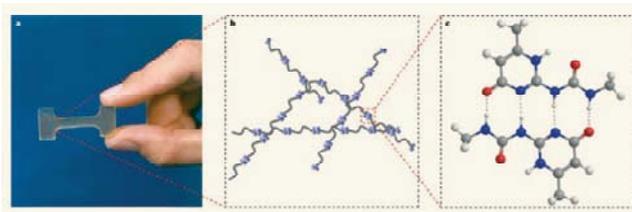


Responsive polymer materials can adapt to surrounding environments, regulate transport of ions and molecules, change wettability and adhesion of different species on external stimuli, or convert chemical and biochemical signals into optical, electrical, thermal and mechanical signals, and vice versa. These materials are playing an increasingly important part in a diverse range of applications, such as drug delivery, diagnostics, tissue engineering and 'smart' optical systems, as well as biosensors, microelectromechanical systems, coatings and textiles. We review recent advances and challenges in the developments towards applications of stimuli-responsive polymeric materials that are self-assembled from nanostructured building blocks. We also provide a critical outline of emerging developments.

- Supramolecular Polymerization

De Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687–5754.

Abstract:



In his historic review titled “Polymerization” in *Chemical Reviews* of 1931, Wallace H. Carothers described his brilliant ideas about the rapidly developing field of synthetic polymers (Figure 1). Only a few years after the general acceptance of the proposal of Hermann Staudinger that polymeric substances are long chains of short repeating molecular units linked by covalent bonds, Carothers classified macromolecules by types of compounds that are capable of polymerizing and by the types of polymerization. Even today, this classification is a commonly used strategy and is extremely useful to clarify the difference between macromolecules made by step, chain, or ring-opening polymerizations. Many different polymers are made following these three mechanisms, whereas a large variety of modern polymerization techniques, such as metathesis, living ionic, and radical polymerizations, were added, but they all follow Carothers’ classification. With the increasing number of different polymers prepared, the interactions between macromolecules became equally important to explain the materials properties at the molecular level. The importance of supramolecular interactions within polymer science actually dates back to the first synthesis of synthetic polymers; the materials properties of, for example, nylons are mainly the result of cooperative hydrogen bonding. More recently, many exciting examples of programmed structure formation of polymeric architectures based on the combination of a variety of secondary supramolecular interactions have been disclosed.

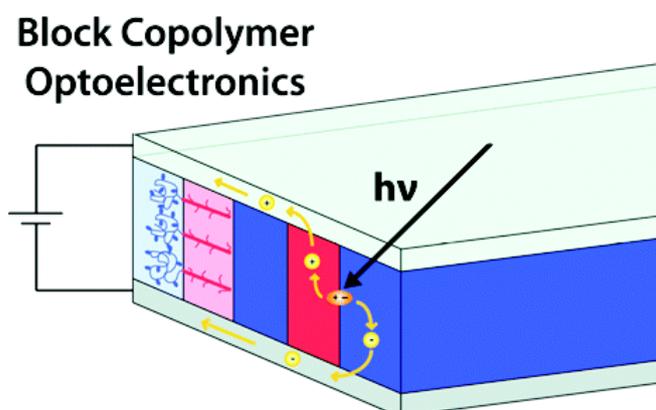
It is then not surprising that at a certain point it was questioned whether it is a requirement to use macromolecules to obtain polymer materials. With the introduction of supramolecular polymers—polymers based on monomeric units held together by directional and reversible secondary interactions—the playground for polymer scientists broadened and is no longer limited to macromolecular species only. In addition, the self-assembly of molecules to form large clusters under equilibrium conditions is a general phenomenon widely found in chemistry, physics, and biology. Examples in each field are ubiquitous and include living ionic polymerizations, the formation of molecular Bose–Einstein condensates, and the self-assembly of clathrin proteins during endocytosis. When the interaction between the monomers is generated by moderately strong, reversible noncovalent, but highly directional, forces that result in high molecular weight linear polymers under dilute conditions, the self-assembly is classified as a supramolecular polymerization.

Through the years, many excellent reviews and books have been published describing progress in the area of supramolecular polymers. In 2001, our research group published a *Chemical Reviews* paper titled “Supramolecular Polymers”; at that time it was already almost impossible to describe all details known to the field. In 2009, it is even more problematic to survey all compounds that form supramolecular polymers and discuss their functional properties. In this review, we will therefore restrict coverage to the most fundamental of supramolecular polymerizations, that of ditopic monomers in solution leading to linear polymers with high aspect ratio, the formation of which is

driven by the reversible association of two end groups, A and B. Although the two end groups can be connected via a (polymeric) spacer, this is not necessarily the case. In self-assembling disc-like monomers such spacers are absent. With any ditopic monomer, the reversible interaction can occur either between two self-complementary end groups ($A = B$) or between two complementary end groups ($A \neq B$). As a tribute to the seminal work of Carothers, we apply the same classification for supramolecular polymers as he used for macromolecules. Doing so proves to be extremely helpful to understand many aspects of supramolecular polymerizations.

- Block Copolymers for Organic Optoelectronics
Segalman, R. A.; McCulloch, B.; Kirmayer, S.; Urban, J. J. *Macromolecules* **2009**, *42*, 9205–9216.

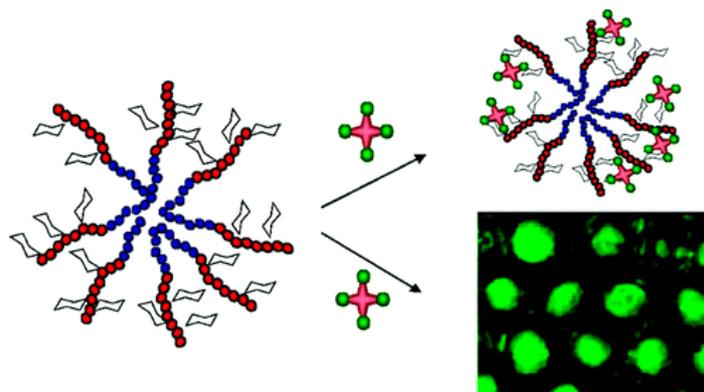
Abstract:



While polymers hold significant potential as low cost, mechanically flexible, lightweight large area photovoltaics and light emitting devices (OLEDs), their performance relies crucially on understanding and controlling the morphology on the nanometer scale. The ca. 10 nm length scale of exciton diffusion sets the patterning length scale necessary to affect charge separation and overall efficiency in photovoltaics. Moreover, the imbalance of electron and hole mobilities in most organic materials necessitates the use of multiple components in many device architectures. These requirements for 10 nm length scale patterning in large area, solution processed devices suggest that block copolymer strategies previously employed for more classical, insulating polymer systems may be very useful in organic electronics. This Perspective seeks to describe both the synthesis and self-assembly of block copolymers for organic optoelectronics. Device characterization of these inherently complex active layers remains a significant challenge and is also discussed.

- Lectin Recognizable Biomaterials Synthesized via Nitroxide-Mediated Polymerization of a Methacryloyl Galactose Monomer
Ting, S. R. S.; Min, E. H.; Escalé, P.; Save, M.; Billon, L.; Stenzel, M. H. *Macromolecules* **2009**, *42*, 9422–9434.

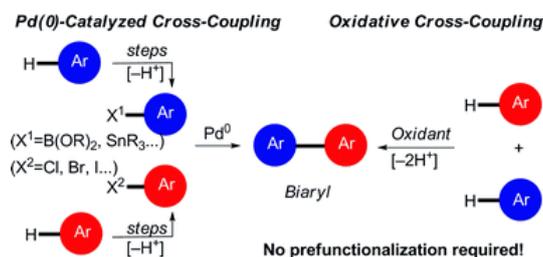
Abstract:



The preparation of poly(2-(2',3',4',6'-tetra-*O*-acetyl- β -D-galactosyloxy)ethyl methacrylate-*co*-styrene) (P(AcGalEMA-*co*-S)) glycopolymer was performed via nitroxide-mediated polymerization using a methacrylic acid-based alkoxyamine with *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) (SG1) nitroxide as mediating agent. In the presence of a low proportion of styrene, the polymerization of the glycomonomer was conducted in a controlled fashion at 85 °C. The synthesis of the diblock copolymers was investigated via two routes by using either P(AcGalEMA-*co*-S) or polystyrene macroinitiators capped with SG1 nitroxide to yield P(AcGalEMA-*co*-S)-*b*-PS and PS-*b*-P(AcGalEMA-*co*-S), respectively. The AcGalEMA moieties on the diblock copolymer were deacetylated to afford carbohydrate-based amphiphilic diblock copolymer, polystyrene-*block*-poly(2-(β -D-galactosyloxy)ethyl methacrylate-*co*-styrene) (PS-*b*-P(GalEMA-*co*-S)). The self-assembling properties of PS-*b*-P(GalEMA-*co*-S) amphiphilic diblock copolymers were thoroughly exploited to obtain micellar structures and porous films. Lectin binding assays were conducted using the UV-vis spectroscopy and dynamic light scattering to test the biofunctionality of the β -galactose moieties with peanut agglutinin (PNA) on the micelles. The polymer was used to prepare honeycomb structured porous films with bioactivity. Fluorescent PNA was eventually conjugated with the sugar moieties on the porous films. Most protein was conjugated to glycopolymer inside the pore, demonstrating that this procedure can be a simple route to pattern proteins onto surfaces.

- Intermolecular oxidative cross-coupling of arenes
Ashenhurst, J. A. *Chem. Soc. Rev.* **2010**, 39, 540 – 548.

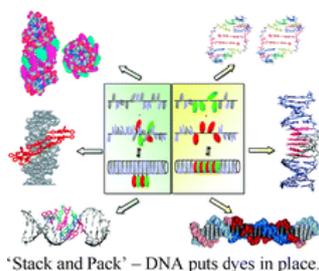
Abstract:



Biaryls constitute an important subunit found in medicinal agents, functional materials, and natural products. While the Suzuki reaction and related processes currently represent the method of choice for the construction of arene-arene bonds, the direct-coupling of two *unfunctionalized* arenes mediated by the addition of an oxidant represents a powerful alternative strategy for biaryl synthesis. This *tutorial review* describes recent progress in this rapidly developing field, focusing on intermolecular examples of selective arene oxidation strategies and metal-catalyzed oxidative cross-coupling *via* C-H activation.

- Nucleic acid-guided assembly of aromatic chromophores
Malinovskii, V. L.; Wenger, D.; Häner, R. *Chem. Soc. Rev.* **2010**, *39*, 410 – 422.

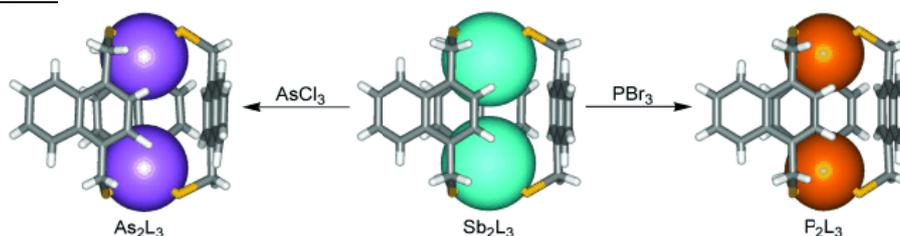
Abstract:



The rational formation of aromatic chromophore arrays is an intriguing challenge since ordered collectives of chromophores possess properties that are largely different from those of the individual molecules. Therefore, nucleic acids are increasingly used as scaffolds for the construction of multi-chromophore arrays. This *tutorial review* provides an introduction to the field of nucleic acid-guided chromophore assemblies for non-specialists and a reference point for those familiar with the area by highlighting the recent developments and describing some of the spectroscopic methods used for the study of oligonucleotide–chromophore conjugates.

- Supramolecular “Transmetalation” Leads to an Unusual Self-Assembled P₂L₃ Cryptand
Cangelosi, V. M.; Zakharov, L. N.; Johnson, D. W. *Angew. Chem. Int. Ed.* **2010**, *49*, 1248 –1251.

Abstract:



Out with the old, in with the new: Can the transmetalation of metal-organic supramolecular assemblies lead to new structure types? A series of Bi, Sb, and As-containing cryptands is reported that can be transmetalated to give a novel P₂L₃ cryptand (see scheme). The P—S bonds behave reversibly, like traditional metal-ligand bonds, suggesting a possible new motif for dynamic covalent chemistry.

- A Diatomic Molecule Receptor That Removes CO in a Living Organism
Kitagishi, H.; Negi, S.; Kiriya, A.; Honbo, A.; Sugiura, Y.; Kawaguchi, A. T.; Kano, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 1312 –1315.

Abstract:



A CO stripper: The O₂-bound form of an iron(II) porphyrin cyclodextrin supramolecular complex (hemoCD) infused into a rat vein reacted with internal CO through ligand exchange, and the CO-bound hemoCD was immediately excreted in the urine (see picture). The hemoCD acting as a CO receptor made it possible to quantify endogenous CO in a living organism.