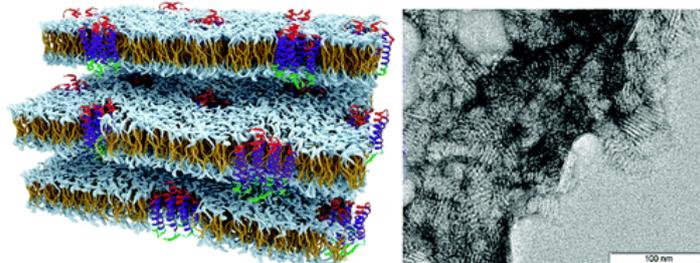


- Self-Directed Reconstitution of Proteorhodopsin with Amphiphilic Block Copolymers Induces the Formation of Hierarchically Ordered Proteopolymer Membrane Arrays
Hua, D.; Kuang, L.; Liang, H. *J. Am. Chem. Soc.* **2011**, *133*, 2354–2357.

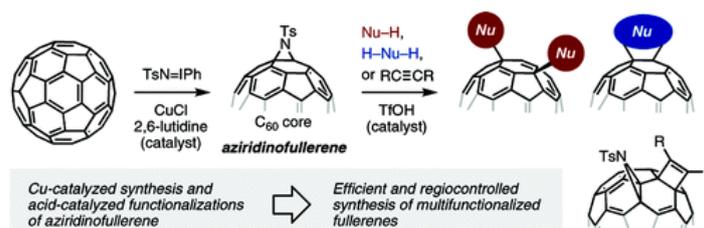
Abstract:



Manipulating recognition and transport at the nanoscale holds great promise for technological breakthroughs in energy conversion, catalysis, and information processing. Living systems evolve specialized membrane proteins (MPs) embedded in lipid bilayers to exquisitely control communications across the insulating membrane boundaries. Harnessing MP functions directly in synthetic systems opens up enormous opportunities for nanotechnology, but there exist fundamental challenges of how to address the labile nature of lipid bilayers that renders them of inadequate value under a broad range of harsh non-biological conditions, and how to reconstitute MPs coherently in two or three dimensions into non-lipid-based artificial membranes. Here we show that amphiphilic block copolymers can be designed to direct proteorhodopsin reconstitution and formation of hierarchically ordered proteopolymer membrane arrays spontaneously, even when the membrane-forming polymer blocks are in entangled states. These findings unfold a viable approach for the development of robust and chemically versatile nanomembranes with MP-regulated recognition and transport performance.

- Aziridinofullerene: A Versatile Platform for Functionalized Fullerenes
Nambo, M.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 2402–2405.

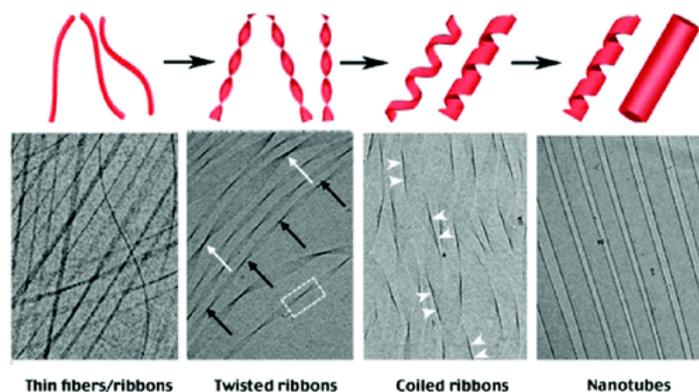
Abstract:



An aziridine moiety on the fullerene core can serve as an acid-triggered reacting template for the controlled synthesis of a range of functionalized fullerenes that are otherwise difficult to synthesize in an efficient and selective manner. A copper-catalyzed aziridination of C_{60} for the practical synthesis of aziridinofullerene **1** and acid-catalyzed reactions of **1** with mono- and bifunctional nucleophiles as well as alkynes are described. The rapid generation of structural diversity in a single chemical operation using the common platform **1** is notable.

- Unraveling the Mechanism of Nanotube Formation by Chiral Self-Assembly of Amphiphiles
Zisman, L.; Lee, H. Y.; Raghavan, S. R.; Mor, A.; Danino, D. *J. Am. Chem. Soc.* **2011**, *133*, 2511–2517.

Abstract:

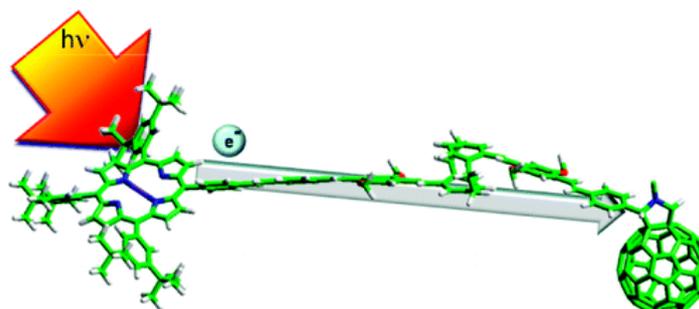


The self-assembly of nanotubes from chiral amphiphiles and peptide mimics is still poorly understood. Here, we present the first complete path to nanotubes by chiral self-assembly studied with C12- β 12 (N- α -lauryl-lysyl-aminolauryl-lysyl-amide), a molecule designed to have unique hybrid architecture. Using the technique of direct-imaging cryo-transmission electron microscopy (cryo-TEM), we show the time-evolution from micelles of C12- β 12 to closed nanotubes, passing through several types of one-dimensional (1-D) intermediates such as elongated fibrils, twisted ribbons, and coiled helical ribbons. Scattering and diffraction techniques confirm that the fundamental unit is a monolayer lamella of C12- β 12, with the hydrophobic tails in the gel state and β -sheet arrangement. The lamellae are held together by a combination of hydrophobic interactions, and two sets of hydrogen-bonding networks, supporting C12- β 12 monomers assembly into fibrils and associating fibrils into ribbons. We further show that neither the “growing width” model nor the “closing pitch” model accurately describe the process of nanotube formation, and both ribbon width and pitch grow with maturation. Additionally, our data exclusively indicate that twisted ribbons are the precursors for coiled ribbons, and the latter structures give rise to nanotubes, and we show chirality is a key requirement for nanotube formation.

- [2,2']Paracyclophane-Based π -Conjugated Molecular Wires Reveal Molecular-Junction Behavior

Ontoria, A. M.; Wielopolski, M.; Gebhardt, J.; Gouloumis, A.; Clark, T.; Guldi, D. M.; Martin, N. *J. Am. Chem. Soc.* **2011**, *133*, 2370–2373.

Abstract:



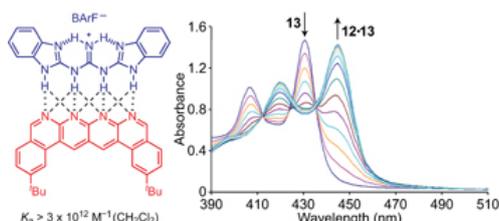
The electronic coupling as well as the attenuation factor (β), which depends primarily on the nature of the molecular bridge and is used as a benchmark to test the molecular wire behavior, have been determined in a systematic study carried out on a series of ZnP/C60 conjugates connected through a [2,2']paracyclophane-oligophenylenevinylene (pCp-oPPV). The convergent synthesis involves a series of Horner–Emmons olefination reactions or double palladium-catalyzed Heck-type reactions. ZnP–pCp–C60 conjugates were finally obtained by the 1,3-dipolar cycloaddition reaction of the in situ-generated azomethyne ylide containing the ZnP–pCp moiety to the [60]fullerene using Prato

conditions. Experimental (UV-vis, fluorescence, transient absorption spectroscopy, and solution electrochemistry) and theoretical studies revealed that the pCps act as molecular junctions. If hole transfer is assumed to be the dominant charge transfer (CT) mechanism, CT is facilitated in one direction (from C60 to ZnP via pCp) but disfavored in the other direction (from ZnP to C60 via pCp).

- An AAAA–DDDD quadruple hydrogen-bond array

Blight, B. A.; Hunter, C. A.; Leigh, D. A.; McNab, H.; Thomson, P. I. T. *Nature Chemistry* **2011**, 3, 246–250.

Abstract:

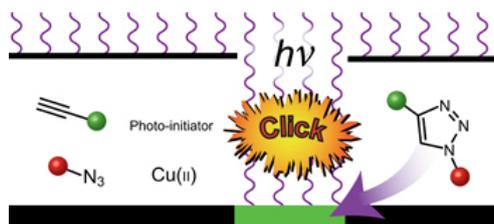


Secondary electrostatic interactions between adjacent hydrogen bonds can have a significant effect on the stability of a supramolecular complex. In theory, the binding strength should be maximized if all the hydrogen-bond donors (D) are on one component and all the hydrogen-bond acceptors (A) are on the other. Here, we describe a readily accessible AAAA–DDDD quadruple hydrogen-bonding array that exhibits exceptionally strong binding for a small-molecule hydrogen-bonded complex in a range of different solvents ($K_a > 3 \times 10^{12} \text{ M}^{-1}$ in CH_2Cl_2 , $1.5 \times 10^6 \text{ M}^{-1}$ in CH_3CN and $3.4 \times 10^5 \text{ M}^{-1}$ in 10% v/v DMSO/ CHCl_3). The association constant in CH_2Cl_2 corresponds to a binding free energy (ΔG) in excess of -71 kJ mol^{-1} (more than 20% of the thermodynamic stability of a carbon–carbon covalent bond), which is remarkable for a supramolecular complex held together by just four intercomponent hydrogen bonds.

- Spatial and temporal control of the alkyne–azide cycloaddition by photoinitiated Cu(II) reduction

Adzima, B. J.; Tao, Y.; Kloxin, C. J.; DeForest, J. A.; Anseth, K. S.; Bowman, C. N. *Nature Chemistry* **2011**, 3, 258–261.

Abstract:



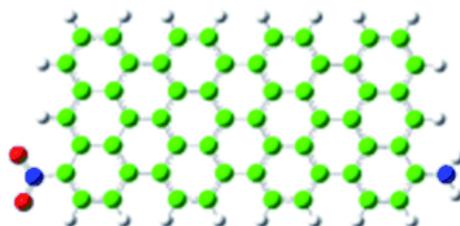
The click reaction paradigm is focused on the development and implementation of reactions that are simple to perform while being robust and providing exquisite control of the reaction and its products. Arguably the most prolific and powerful of these reactions, the copper-catalysed alkyne–azide reaction (CuAAC) is highly efficient and ubiquitous in an ever increasing number of synthetic methodologies and applications, including bioconjugation, labelling, surface functionalization, dendrimer synthesis, polymer synthesis and polymer modification. Unfortunately, as the Cu(I) catalyst is typically generated by the chemical reduction of Cu(II) to Cu(I), or added as a Cu(I) salt, temporal and spatial control of the CuAAC reaction is not readily achieved. Here, we demonstrate catalysis of the CuAAC reaction via the photochemical reduction of Cu(II) to Cu(I), affording

comprehensive spatial and temporal control of the CuAAC reaction using standard photolithographic techniques. Results reveal the diverse capability of this technique in small molecule synthesis, patterned material fabrication and patterned chemical modification.

- Exceptionally Large Second-Order Nonlinear Optical Response in Donor–Graphene Nanoribbon–Acceptor Systems

Zhou, Z.-J.; Li, X.-P.; Ma, F.; Liu, Z.-B.; Li, Z.-R.; Huang, X.-R.; Sun, C.-C. *Chem.-Eur. J.* **2011**, *17*, 2414-2419.

Abstract:

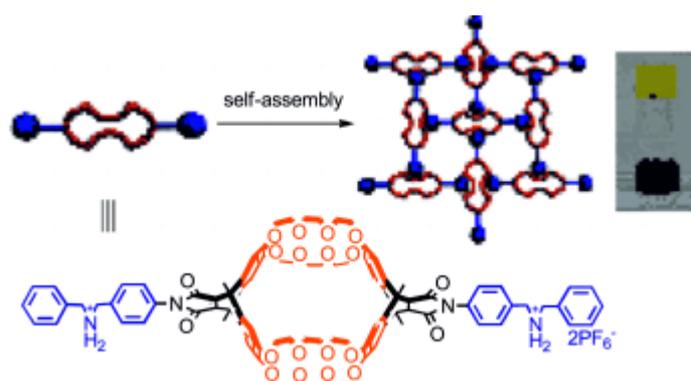


Graphene nanoribbon (GNR) has been used, for the first time, as an excellent conjugated bridge in a donor–conjugated bridge–acceptor (D–B–A) framework to design high-performance second-order nonlinear optical materials. Owing to the unique diradical planar conjugated bridge of GNR, D(NH₂)–GNR–A(NO₂) exhibits exceptionally large static first hyperpolarizability (β_0) up to 2.5×10^6 a.u. (22000×10^{-30} esu) for H₂N–(7,3)ZGNR–NO₂ (ZGNR=zigzag-edged GNR), which is about 15 times larger than the recorded value of β_0 (1470×10^{-30} esu) for the D–A polyene reported by Blanchard-Desce et al. [*Chem. Eur. J.* **1997**, *3*, 1091]. Interestingly, we have found that the size effect of GNR plays a key role in increasing β_0 for the H₂N–GNR–NO₂ system, in which the width effect of GNR perpendicular to the D–A direction is superior to the length effect along the D–A direction.

- Assembly of a Self-Complementary Monomer: Formation of Supramolecular Polymer Networks and Responsive Gels

Su, Y.-S.; Liu, J.-W.; Jiang, Y.; Chen, C.-F. *Chem.-Eur. J.* **2011**, *17*, 2435-2441.

Abstract:



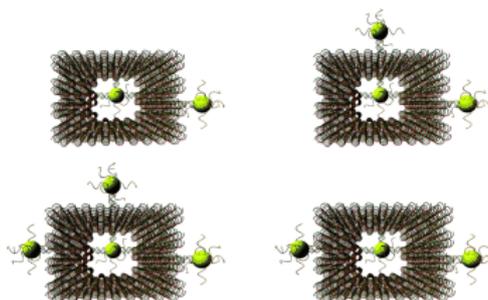
Self-complementary monomer **1**, which combines a macrotricyclic polyether and two dibenzylammonium ions together, was synthesized, and its self-assembly into supramolecular polymer networks by host–guest interactions was studied. For the purpose of comparative study, two model molecules **2** and **3** were also prepared. It was found that model molecule **2** and dibenzylammonium ion **4** form a 1:2 complex in solution and in the solid state, which afforded a model system for the investigation of the assembly behavior of monomer **1**. Consequently, the ¹H NMR spectrum of **1** in CD₃CN showed characteristic proton signals similar to the model system, which

suggested that **1** self-assembles into a supramolecular polymer network. Formation of the supramolecular polymer was further evidenced by the MALDI-TOF MS spectrum, viscometry, and dynamic light-scattering (DLS) experiments. Moreover, it was found that the decomposition and re-formation of the supramolecular polymer could be chemically controlled by the use of triethylamine and trifluoroacetic acid. Interestingly, the supramolecular polymer forms an organogel both in CD₃CN and in 1:1 (v/v) CDCl₃/CD₃CN, and reversible thermo- and pH-induced gel-sol transitions were also found. The presented work will provide a new strategy for the construction of supramolecular polymers with specific structures and properties.

- Encapsulation of Gold Nanoparticles in a DNA Origami Cage

Zhao, Z.; Jacovetty, E.; Liu, Y.; Yan, H. *Angew. Chem. Int. Ed.* **2011**, *50*, 2041-2044.

Abstract:

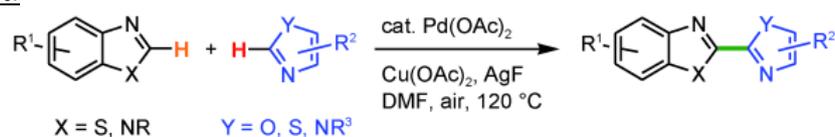


Fold and label: A critical challenge in nanoparticle (NP) surface functionalization is to label the NP surface with a single copy of a functional group or to display multiple, unique molecules on the NP surface with control of the orientation and intermolecular distance. This challenge was addressed with the construction of a spatially addressable, self-assembling DNA origami nanocage that encapsulates gold nanoparticles and interrupts its surface symmetry (see scheme).

- Palladium-Catalyzed Dehydrogenative Cross-Couplings of Benzazoles with Azoles

Han, W.; Mayer, P.; Ofial, A. R. *Angew. Chem. Int. Ed.* **2011**, *50*, 2178-2182.

Abstract:



Different enough: Palladium-catalyzed cross-couplings of benzazoles with imidazoles, oxazoles, and thiazoles furnish unsymmetrical 2,2'-bisheteroaryls in high yield (see scheme). These oxidative CC bond formations use the selective cleavage of the CH bond at C2 in the two coupling partners and are robust enough to be conducted under normal air atmosphere.

- Functionalisation of recombinant spider silk with conjugated polyelectrolytes

Müller, C.; Jansson, R.; Elfving, A.; Askarieh, G.; Karlsson, R.; Hamed, M.; Rising, A.; Johansson, J.; Inganäs, O.; Hedhammar, M. *J. Mater. Chem.* **2011**, *21*, 2909-2915.

Abstract:

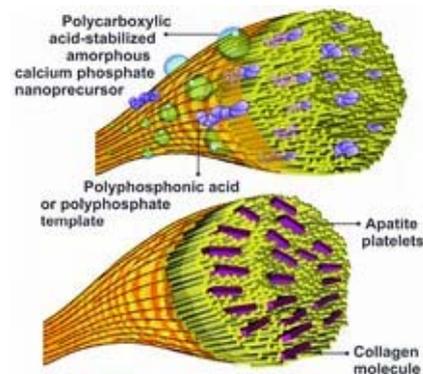


Conjugated polyelectrolytes are demonstrated to permit facile staining of recombinant spider silk fibres. We find that the polyelectrolyte concentration and pH of the staining solution as well as the incubation temperature strongly influence the efficiency of this self-assembly process, which appears to be principally mediated through favourable electrostatic interactions. Thus, depending on the choice of staining conditions as well as the polyelectrolyte, electrically conductive or photoluminescent recombinant silk fibres could be produced. In addition, staining of natural *Bombyx mori* silk is established, which emphasises the versatility of the here advanced approach to functionalise silk-based materials.

- Intrafibrillar Collagen Mineralization Produced by Biomimetic Hierarchical Nanoapatite Assembly

Liu, Y.; Li, N.; Qi, Y.; Dai, L.; Bryan, T. E.; Mao, J.; Pashley, D. H.; Tay, F. R. *Adv. Mater.* **2011**, *23*, 975-980.

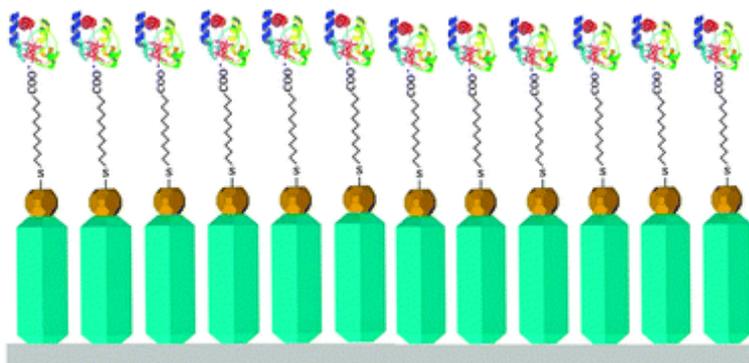
Abstract:



Phosphorous-based templating analogs of extracellular matrix proteins are used as templates in conjunction with polycarboxylic acid-stabilized amorphous calcium phosphate nanoprecursors to create a highly ordered intrafibrillar apatite crystallite assembly within a collagen fibril. The assembly recapitulates the gap and overlap arrangement of collagen molecules.

- Protein immobilisation on perpendicularly aligned gold tipped nanorod assemblies
O'Sullivan, C.; Crilly, S.; Laffir, F. R.; Singh, A.; Magner, E.; Ryan, K. M. *Chem. Commun.* **2011**, *47*, 2655-2657.

Abstract:

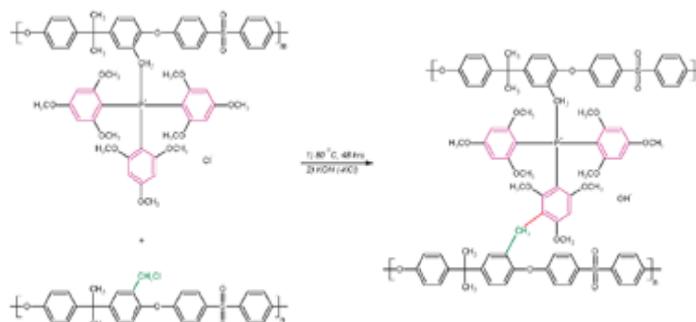


A multi component assembly consisting of the redox protein cytochrome c (cyt c) immobilised onto vertically aligned gold tipped semiconductor nanorods is described. Cyt c was successfully immobilised using a thiol linker. A faradaic response demonstrated that the protein is electroactive in this ultra high density array.

- Self-crosslinking for dimensionally stable and solvent-resistant quaternary phosphonium based hydroxide exchange membranes

Gu, S.; Cai, R.; Yan, Y. *Chem. Commun.* **2011**, 47, 2856-2858.

Abstract:



A simple self-crosslinking strategy, without the needs of a separate crosslinker or a catalyst, is reported here. The crosslinking drastically lowers the water swelling ratio (*e.g.*, 5–10 folds reduction) and provides excellent solvent-resistance. The self-crosslinked membrane (DCL: 5.3%) shows the highest IEC-normalized hydroxide conductivity among all crosslinked HEMs reported.

- Highly Fluorescent Dithieno[3,2-*b*:2',3'-*d*]pyrrole-Based Materials: Synthesis, Characterization, and OLED Device Applications

Evenson, S. J.; Mumm, M. J.; Pokhodnya, K. I.; Rasmussen, S. C. *Macromolecules* **2011**, 44, 835–841.

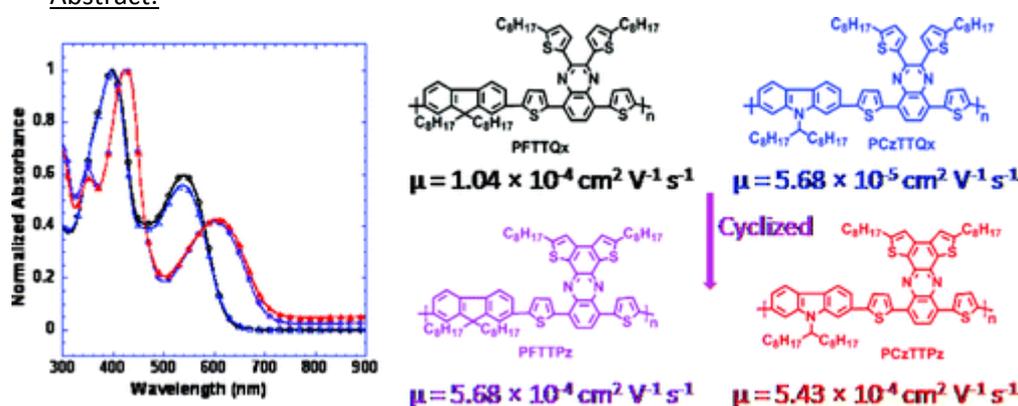
Abstract:



Dithieno[3,2-*b*:2',3'-*d*]pyrrole-arylene copolymers have been prepared via Stille coupling to produce soluble, processable materials with good molecular weights. Solution and solid-state characterization of the copolymers is described, including photophysical and electrochemical studies, and these properties are compared to those of the parent poly(dithieno[3,2-*b*:2',3'-*d*]pyrrole)s as well as analogous bithiophene-arylene copolymers. Poly(*N*-decyldithieno[3,2-*b*:2',3'-*d*]pyrrole) and the newly generated copolymers were then used as emissive layers to fabricate initial LEDs, and the initial evaluation of their device performance is presented.

- Synthesis of Quinoxaline-Based Donor–Acceptor Narrow-Band-Gap Polymers and Their Cyclized Derivatives for Bulk-Heterojunction Polymer Solar Cell Applications
Zhang, J.; Cai, W.; Huang, F.; Wang, E.; Zhong, C.; Liu, S.; Wang, M.; Duan, C.; Yang, T.; Cao, Y. *Macromolecules* **2011**, *44*, 894–901.

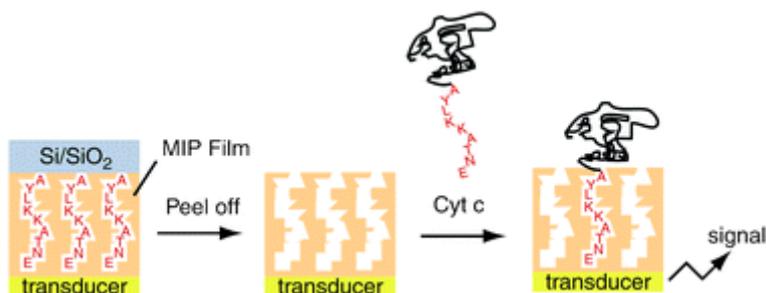
Abstract:



A series of narrow-band-gap donor–acceptor (D–A) conjugated polymers, with thiophene-substituted quinoxaline monomer 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(5-octylthiophen-2-yl)quinoxaline (TTQx) or its cyclized phenazine derivative monomer 8,11-bis(5-bromothiophen-2-yl)-2,5-dioctyldithieno[2,3-*a*:3',2'-*c*]phenazine (TTPz) as acceptors, were synthesized via Suzuki coupling reaction. It was found that the copolymers based on thiophene-substituted quinoxaline TTQx exhibit obviously red-shifted absorbance compared to previously reported D–A copolymers based on phenyl-substituted quinoxaline. Their analogous copolymers based on the cyclized TTPz acceptor show more pronounced red-shifted absorption spectra with a significantly decreased band gap due to the enlarged planar polycyclic aromatic ring of TTPz. Moreover, compared to the copolymers based on TTQx, the TTPz-based copolymers' mobilities are also significantly increased due to the reduced steric hindrance and improved structural planarity among the copolymers. Bulk-heterojunction polymer solar cells based on the blends of the copolymers with a fullerene derivative as an acceptor exhibit promising performance, and the best device performance with power conversion efficiency up to 4.4% was achieved.

- The rational development of molecularly imprinted polymer-based sensors for protein detection
Whitcombe, M. J.; Chianella, I.; Larcombe, L.; Piletsky, S. A.; Noble, J.; Porter, R.; Horgan, A. *Chem. Soc. Rev.* **2011**, *40*, 1547-1571.

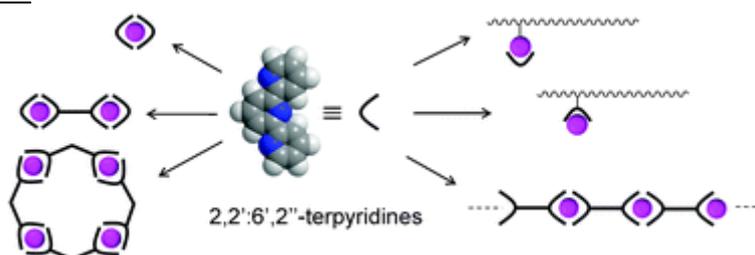
Abstract:



The detection of specific proteins as biomarkers of disease, health status, environmental monitoring, food quality, control of fermenters and civil defence purposes means that biosensors for these targets will become increasingly more important. Among the technologies used for building specific recognition properties, molecularly imprinted polymers (MIPs) are attracting much attention. In this *critical review* we describe many methods used for imprinting recognition for protein targets in polymers and their incorporation with a number of transducer platforms with the aim of identifying the most promising approaches for the preparation of MIP-based protein sensors (277 references).

- Advances in the field of π -conjugated 2,2':6',2''-terpyridines
Wild, A.; Winter, A.; Schlütter, F.; Schubert, U. *Chem. Soc. Rev.* **2011**, *40*, 1459-1511.

Abstract:



This *critical review* summarizes the research progress made in the field of π -conjugated terpyridines within the last decade. Supramolecular materials based on metal ion complexes of 2,2':6',2''-terpyridine derivatives have found manifold potential applications—from opto-electronic devices to life science. In this contribution, synthetic strategies towards π -conjugated terpyridines and their incorporation into advanced supramolecular architectures are evaluated. Applications as photoactive species in, *e.g.*, photovoltaic devices, polymer light-emitting diodes (PLEDSs) and nanotechnology are discussed comprehensively (523 references).