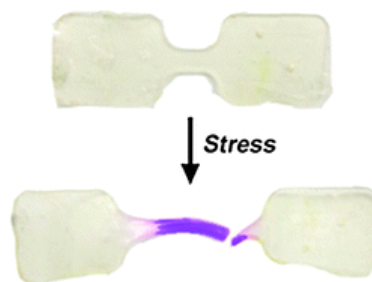


- Dye-containing polymers: methods for preparation of mechanochromic materials
Ciardelli, F.; Ruggeri, G.; Pucci, A. *Chem. Soc. Rev.* **2013**, 42, 857-870.

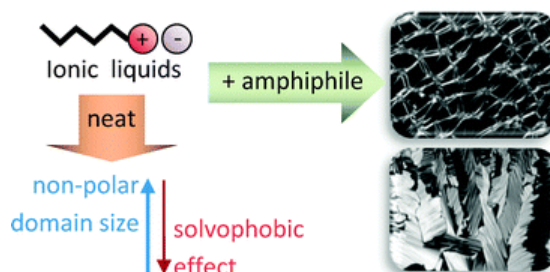
Abstract:



The detection of mechanical stress in polymeric materials through optical variations has attracted considerable interest over the past ten years. In this tutorial review, the current state of knowledge concerning the preparation of polymers with mechanochromic features is summarized. Two types of procedures are illustrated and thoroughly discussed along with their respective structure–property relationships: the first resides in the physical dispersion of the dye in the form of supramolecular aggregates in a preformed polymer matrix; the second involves the covalent insertion of chromophoric units into the macromolecule backbone or side chains. Herein we review the simplicity of the preparative routes available, and their influence over the properties of the resulting dye–polymer systems, by focussing on the most illustrative examples described in the literature. Special reference is made to stimuli-responsiveness as a mechanical means towards innovative smart and intelligent materials.

- Solvent nanostructure, the solvophobic effect and amphiphile self-assembly in ionic liquids
Greaves, T. L.; Drummond, C. J. *Chem. Soc. Rev.* **2013**, 42, 1096-1120.

Abstract:



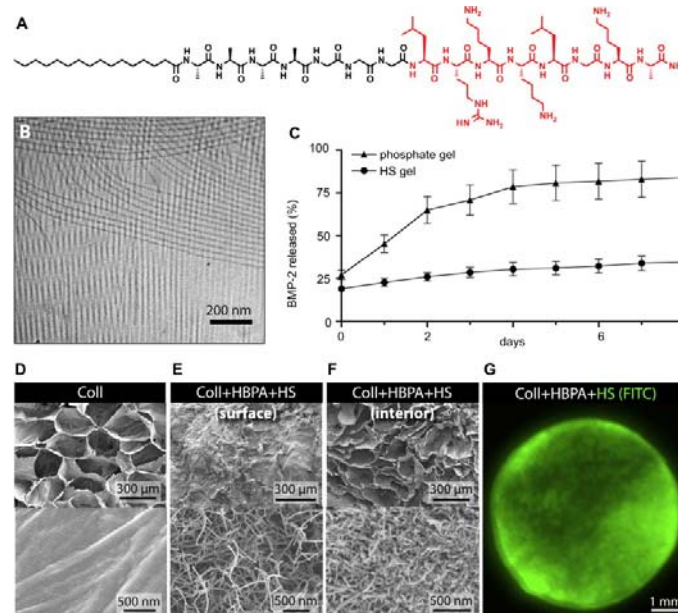
The ability of ionic liquids (ILs) to support amphiphile self-assembly into a range of mesophase structures has been established as a widespread phenomenon. From the ILs evaluated as self-assembly media, the vast majority have supported some lyotropic liquid crystal phase formation. Many neat ionic liquids have been shown to segregate into polar and non-polar domains to form a nanostructured liquid. A very strong correlation between the nanostructure of the ionic liquid and its characteristics as an amphiphile self-assembly solvent has been found. In this review we discuss ionic liquids as amphiphile self-assembly media, and identify trends that can be used to distinguish which ionic liquids are likely to have good promotion properties as self-assembly media. In particular these trends focus on the nanostructure of neat ionic liquids, their solvent cohesive energy density, and the related solvophobic effect. We forecast that many more ILs will be identified as amphiphile self-assembly solvents in the future.

- Bone regeneration with low dose BMP-2 amplified by biomimetic supramolecular nanofibers within collagen scaffolds

2

Lee, S. S.; Huang, B. J.; Kaltz, S. R.; Sur, S.; Newcomb, C. J.; Stock, S. R.; Shah, R. N.; Stupp, S. I. *Biomaterials* **2013**, 34, 452-459.

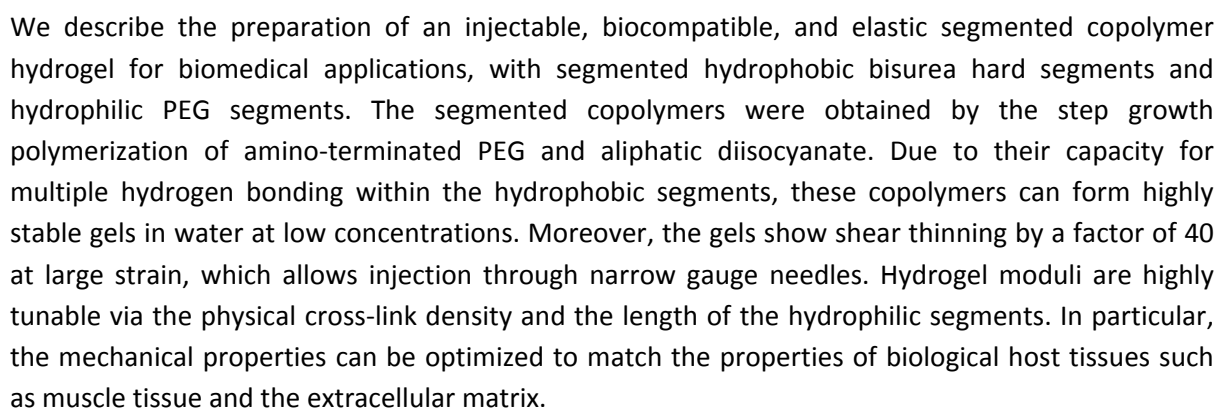
Abstract:



Bone morphogenetic protein-2 (BMP-2) is a potent osteoinductive cytokine that plays a critical role during bone regeneration and repair. In the extracellular environment, sulfated polysaccharides anchored covalently to glycoproteins such as syndecan and also non-covalently to fibronectin fibers have been shown to bind BMP-2 through a heparin-binding domain and regulate its bioactivity. We report here on a synthetic biomimetic strategy that emulates biological BMP-2 signaling through the use of peptide amphiphile nanofibers designed to bind heparin. The supramolecular nanofibers, which integrate the biological role of syndecan and fibronectin, were allowed to form gel networks within the pores of an absorbable collagen scaffold by simply infiltrating dilute solutions of the peptide amphiphile, heparan sulfate, and BMP-2. The hybrid biomaterial enhanced significantly bone regeneration in a rat critical-size femoral defect model using BMP-2 amounts that are one order of magnitude lower than required for healing in this animal model. Using micro-computed tomography, we also showed that the hybrid scaffold was more effective at bridging within the gap relative to a conventional scaffold of the type used clinically based on collagen and BMP-2. Histological evaluation also revealed the presence of more mature bone in the new ossified tissue when the low dose of BMP-2 was delivered using the biomimetic supramolecular system. These results demonstrate how molecularly designed materials that mimic features of the extracellular environment can amplify the regenerative capacity of growth factors.

- Injectable Hydrogels from Segmented PEG-Bisurea Copolymers
Pawar, G. M.; Koenigs, M.; Fahimi, Z.; Cox, M.; Voets, I. K.; Wyss, H. M.; Sijbesma, R. P. *Biomacromolecules* **2012**, 13, 3966-3976.

Abstract:



- Gobbo, C.; Li, M.; Mali, K. S.; van Esch, J. H.; De Feyter, S. *ACS Nano* **2012**, *6*, 10684-10698.

'Random Coil'

Folding and adsorption

2D Lattice

Engineered spacer

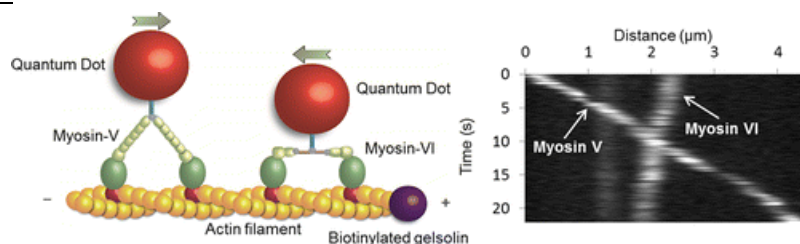
Turn element

- **Orienting Actin Filaments for Directional Motility of Processive Myosin Motors**

Wu, Y.; Wu, Z.; Yuan, J.; Pillarisetti, A.; Goldman, Y. E.; Bau, H. H. *Nano Lett.* **2013**, *13*, 79-84.

Abstract:

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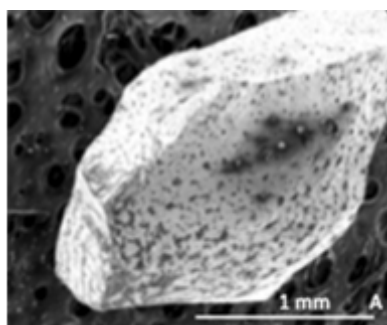


To utilize molecular motors in manmade systems, it is necessary to control the motors' motion. We describe a technique to orient actin filaments so that their barbed ends point in the same direction, enabling same-type motors to travel unidirectionally. Myosin-V and myosin-VI were observed to travel, respectively, toward and away from the filaments' barbed ends. When both motors were present, they occasionally passed each other while "walking" in opposite directions along single actin filaments.

- On the Way to Artificial Photosynthesis: Simple Materials and System Designs for Photoelectrodes

Antonietti, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 1086–1087.

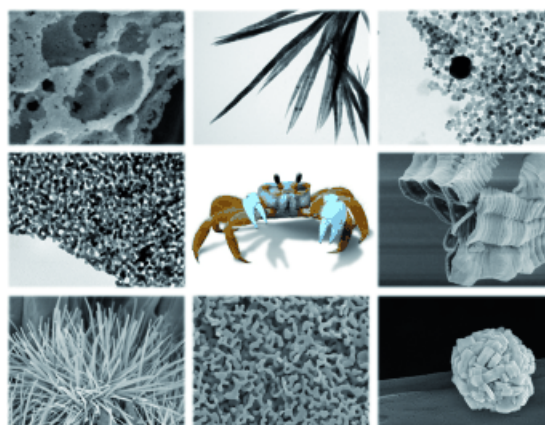
Abstract:



For commercial viability new technologies for the sustainable generation of energy should be simple and efficient. Photoelectrodes made of boron arsenide are the latest advance: they can be synthesized easily directly from the elements and convert sunlight into electric current.

- Biopolymers as a Flexible Resource for Nanochemistry
Schnepp, Z. *Angew. Chem. Int. Ed.* **2013**, *52*, 1096–1108.

Abstract:

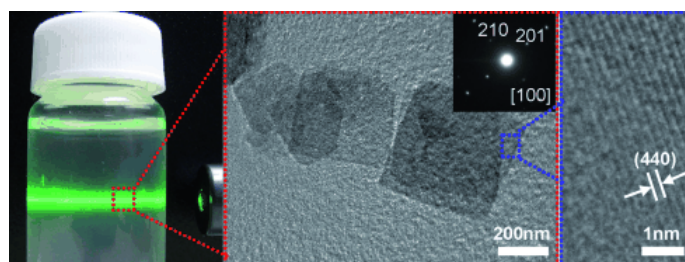


Biomass is an abundant source of chemically diverse macromolecules, including polysaccharides, polypeptides, and polyaromatics. Many of these biological polymers (biopolymers) are highly evolved for specific functions through optimized chain length, functionalization, and monomer sequence. As biopolymers are a chemical resource, much current effort is focused on the breakdown of these molecules into fuels or platform chemicals. However there is growing interest in using biopolymers directly to create functional materials. This Minireview uses recent examples to show how biopolymers are providing new directions in the synthesis of nanostructured materials.

- Bottom-Up Synthesis of Monodispersed Single-Crystalline Cyano-Bridged Coordination Polymer Nanoflakes

Hu, M.; Ishihara, S.; Yamauchi, Y. *Angew. Chem. Int. Ed.* **2013**, 52, 1235-1239.

Abstract:

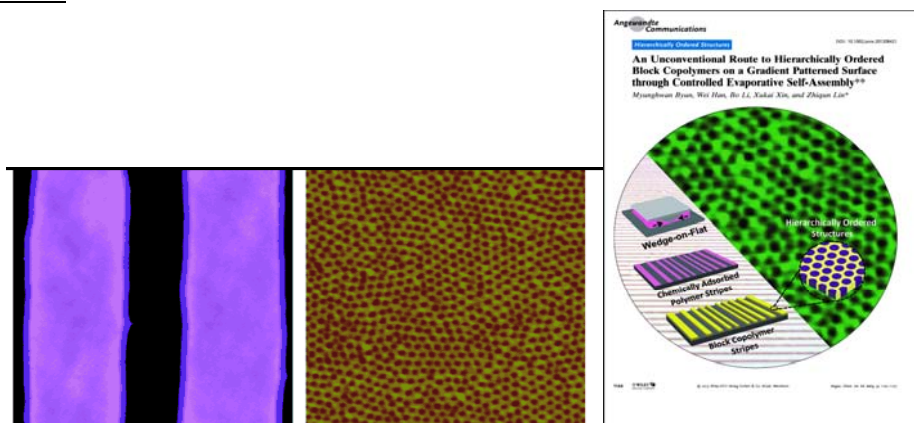


A two-dimensional morphology characterizes the nanoflakes that are obtained in the bottom-up synthesis of a single-crystalline coordination polymer, $\text{Ni}(\text{H}_2\text{O})_2[\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$. The 10 nm-thick nanoflakes are well-dispersed in solution and have a very high accessible surface area ($240 \text{ m}^2 \text{ g}^{-1}$). Thermal treatment leads to nanoporous NiO with retention of the original flake morphology.

- An Unconventional Route to Hierarchically Ordered Block Copolymers on a Gradient Patterned Surface through Controlled Evaporative Self-Assembly

Byun, M.; Han, W.; Li, B.; Xin, X.; Lin, Z. *Angew. Chem. Int. Ed.* **2013**, 52, 1122-1127.

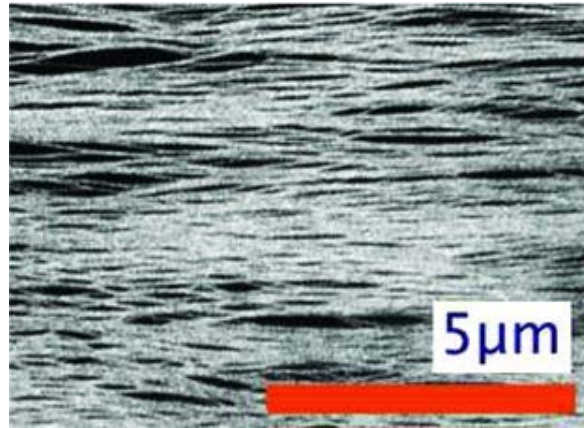
Abstract:



A chemically patterned surface was formed by controlled evaporative self-assembly of concentric polymer stripes, followed by the removal of weakly deposited polymer, giving ultrathin polymer stripes with a width gradient on the Si substrate (see picture). A thin film of diblock copolymer hierarchically self-assembled on the ultrathin polymer stripes, giving arrays of nanocylinders perpendicular to the surface of the film.

- Large-Area, Electronically Monodisperse, Aligned Single-Walled Carbon Nanotube Thin Films Fabricated by Evaporation-Driven Self-Assembly
Shastry, T. A.; Seo, J-W. T.; Lopez, J. J.; Arnold, H. N.; Kelter, J. Z.; Sangwan, V. K.; Lauhon, L. J.; Marks, J. T.; Hersam, M. C. *Small* **2013**, 9, 45–51.

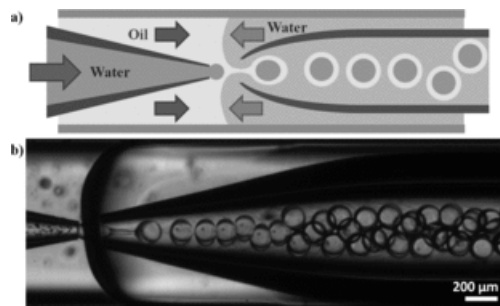
Abstract:



By varying the evaporation conditions and the nanotube and surfactant concentrations, large-area, aligned single-walled carbon nanotube (SWCNT) thin films are fabricated from electronically monodisperse SWCNT solutions by evaporation-driven self-assembly with precise control over the thin film growth geometry. Tunability is possible from 0.5 μm stripes to continuous thin films. The resulting SWCNT thin films possess highly anisotropic electrical and optical properties that are well suited for transparent conductor applications.

- Polymersomes Containing a Hydrogel Network for High Stability and Controlled Release
Kim, S. H.; Kim, J. W.; Kim, D-H; Han, S-H.; Weitz, D. A. *Small* **2013**, 9, 124–131.

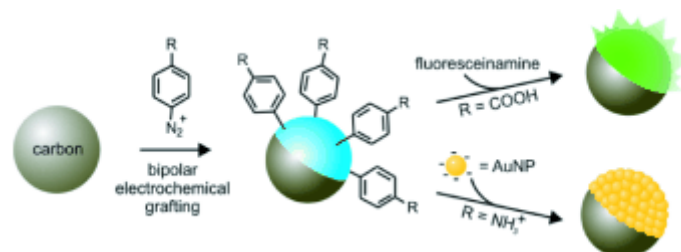
Abstract:



Capillary microfluidic devices are used to prepare monodisperse polymersomes consisting of a hydrogel core and a bilayer membrane of amphiphilic diblock-copolymers. To make polymersomes, water-in-oil-in-water double-emulsion drops are prepared as templates through single-step emulsification in a capillary microfluidic device. The amphiphile-laden middle oil phase of the double-emulsion drop dewets from the surface of the innermost water drop, which contains hydrogel prepolymers; this dewetting leads to the formation of a bilayer membrane. Subsequently, the oil phase completely separates from the innermost water drop, leaving a polymersome. Upon UV illumination of the polymersome, the prepolymers encapsulated within the interior are crosslinked, forming a hydrogel core. The hydrogel network within the polymersomes facilitates sustained release of the encapsulated materials and increases the stability of the polymersomes through the formation of a scaffold to support the bilayer. In addition, this approach provides a facile method to make monodisperse hydrogel particles directly dispersed in water.

- Wireless Electrografting of Molecular Layers for Janus Particle Synthesis
Kumsapaya, C.; Bakai, M.-F.; Loget, G.; Goudeau, B.; Warakulwit, C.; Limtrakul, J.; Kuhn, A.; Zigah, D. *Chem. Eur. J.* **2013**, *19*, 1577–1580.

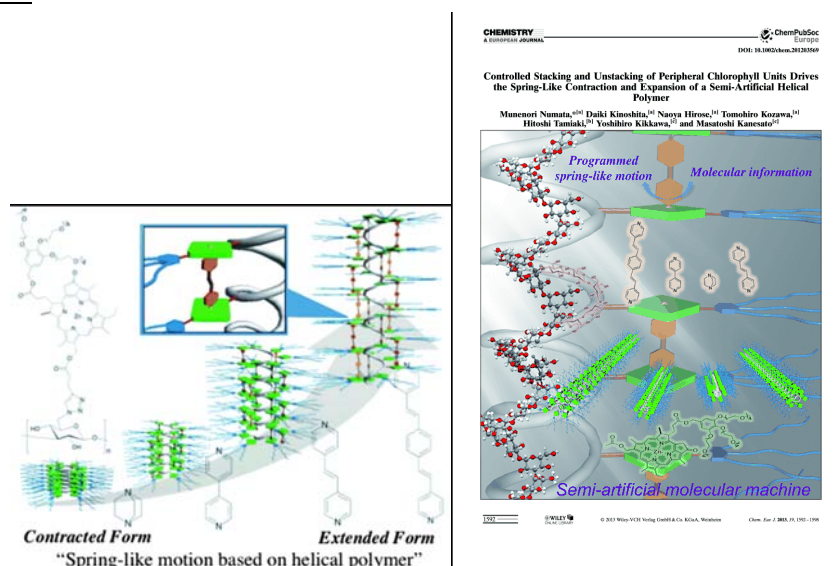
Abstract:



Glassy carbon beads are selectively functionalized on one side with an ultrathin organic layer by bipolar electrochemical reduction of diazonium salts to give Janus-type beads with a hybrid organic–inorganic composition (see scheme). The presence of the grafted organic layers is revealed either by co-adsorption of gold nanoparticles or by coupling with a fluorescent molecule.

- Controlled Stacking and Unstacking of Peripheral Chlorophyll Units Drives the Spring-Like Contraction and Expansion of a Semi-Artificial Helical Polymer
Numata, M.; Kinoshita, D.; Hirose, N.; Kozawa, T.; Tamiaki, H.; Kikkawa, Y.; Kanetsato, M. *Chem. Eur. J.* **2013**, *19*, 1592–1598.

Abstract:

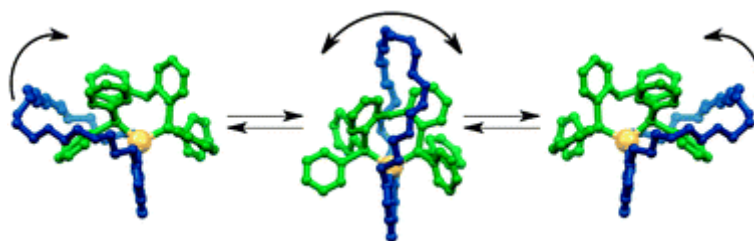


Developing new strategies for controlling polymer conformations through precise molecular recognition can potentially generate a machine-like motion that is dependent on molecular information—an important process for the preparation of new intelligent nanomaterials (e.g., polymer-based nanomachines) in the field bordering between polymer chemistry and conventional supramolecular sciences. Herein, we propose a strategy to endow a helical polymer chain with dynamic spring-like (contraction/expansion) motion through the one-dimensional self-assembly (aggregation/disaggregation) of peripheral amphiphilic molecules. In this developing system, we employed a semi-artificial helical polysaccharide presenting peripheral amphiphilic chlorophyll units as a power device that undergoes contractive motion in aqueous media, driven by strong π – π interactions of its chlorophyll units or by cooperative molecular recognition of bipyridyl-type ligands

through pairs of chlorophyll units, thereby converting molecular information into the regulated motion of a spring. In addition, this system also undergoes expansive motion through coordination of pyridine. We anticipate that this strategy will be applicable (when combined with the established wrapping chemistry of the helical polysaccharide) to the development of, for example, drug carriers (e.g., nano-syringes), actuators (stimuli-responsive films), and directional transporters (nano-railways), thereby extending the frontiers of supramolecular science.

- Dynamic topomerization of Cu(I)-complexed pseudorotaxanes
Mohankumar, M.; Holler, M.; Schmitt, M.; Sauvage, J.-P.; Nierengarten, J.-F. *Chem. Commun.* **2013**, 49, 1261-1263.

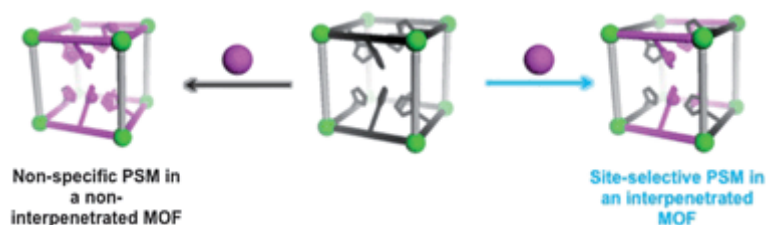
Abstract:



Dynamic molecular motions resulting from the folding of a flexible macrocyclic component in a Cu(I)-complexed pseudorotaxane have been evidenced by variable temperature NMR experiments. The proposed conformational changes are also supported by the X-ray crystal structures of the compounds and computational studies.

- Site-selective cyclometalation of a metal–organic framework
Dau, P. V.; Kim, M.; Cohen, S. M. *Chem. Sci.*, **2013**, 4, 601-605.

Abstract:

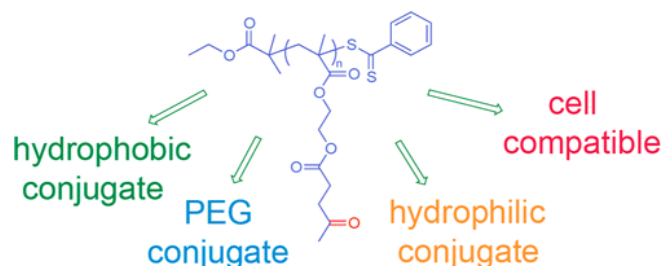


Although porous materials, including metal–organic frameworks (MOFs), can be functionalized using heterogeneous reactions (solution–solid, gas–solid), there are no reports that modify chemically identical sites in a spatially selective, periodic fashion. Herein, the cyclometalation of two non-interpenetrated MOFs and an interpenetrated MOF in the solid state is reported using $[\text{Ir}(\text{COD})(\text{OCH}_3)]_2$ and $[\text{Rh}(\text{COD})(\text{Cl})]_2$ (COD = 1,5-cyclooctadiene). Incredibly, the cyclometalation of the interpenetrated MOF occurs only on ligands that lie along, one crystallographic axis, providing an unprecedented example of site-selective postsynthetic modification (PSM). This represents a degree of control on the functionalization of a porous, material that has not been otherwise realized, and is achieved in part because of the crystalline, periodic nature of MOFs. Furthermore, it was found that the degree of cyclometalation, increases the sorption capacity of the interpenetrated MOF.

- Keto-Functionalized Polymer Scaffolds as Versatile Precursors to Polymer Side-Chain Conjugates

Liu, J.; Li, R. C.; Sand, G. J.; Bulmus, V.; Davis, T. P.; Maynard, H. D. *Macromolecules*, **2013**, *46*, 8-14.

Abstract:

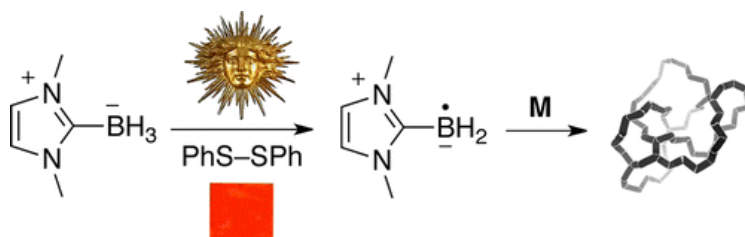


A new methacrylate monomer with a reactive ketone side chain, 2-(4-oxopentanoate)ethyl methacrylate (PAEMA), was synthesized and subsequently polymerized by reversible addition-fragmentation chain transfer (RAFT) polymerization to give a polymer with a narrow molecular weight distribution (PDI = 1.25). The polymer was chain extended with poly(ethylene glycol methyl ether methacrylate) (PEGMA) to yield a block copolymer. Aminoxy-containing small molecules and oligoethylene glycol were conjugated to the ketone functionality of the side chains in high yields. Cytotoxicity of the oxime-linked tetra(ethylene glycol) polymer to mouse fibroblast cells was investigated; the polymer was found to be noncytotoxic up to 1 mg/mL. The ease with which this polymer is functionalized suggests that it may be useful in forming tailored polymeric medicines.

- Soft Photopolymerizations Initiated by Dye-Sensitized Formation of NHC-Boryl Radicals under Visible Light

Telitel, S.; Schweizer, S.; Morlet-Savary, F.; Graff, B.; Tschamber, T.; Blanchard, N.; Fouassier, J.-P.; Lelli, M.; Lacôte, E.; Lalevée, J. *Macromolecules* **2013**, *46*, 43-48.

Abstract:

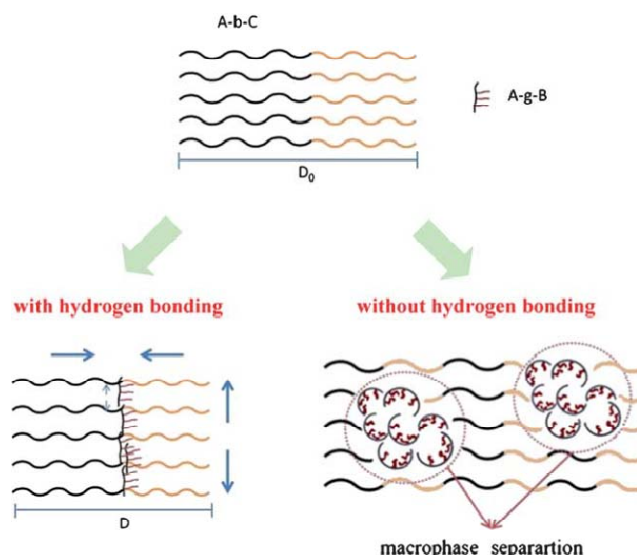


A procedure for the production of N-heterocyclic carbene-boryl radicals (NHC-BH_2^\bullet) upon visible light irradiation under soft conditions is presented. New acridine orange (dye)/diphenyl disulfide/NHC-BH₃ and dye/sulfonium salt/NHC-BH₃ three-component initiating systems are introduced for the efficient visible light photopolymerization of trimethylolpropane triacrylate. The new systems could be extended to polymerization reactions in water (hydroxyethyl acrylate and hydroxyethyl methyl acrylate), which proceeded with strongly improved polydispersity. The chemical mechanisms are investigated through EPR and photolysis experiments.

- Self-assembled structures in block copolymer/graft copolymer blends with hydrogen bonding interaction

Chen, Y.-T.; Lo, C.-T. *Soft Matter* **2013**, *9*, 1756-1760.

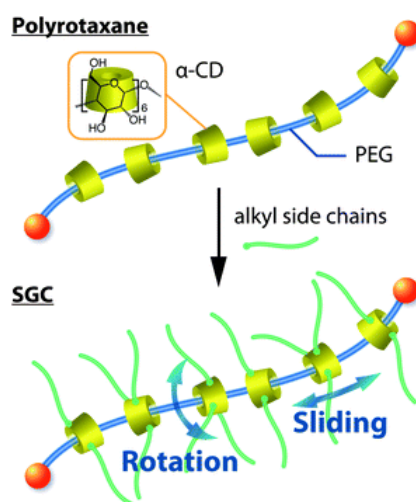
Abstract:



The effect of hydrogen bonding on the phase behavior of PS-based block copolymer and poly(styrene-*graft*-acrylic acid) (PS-*g*-PAA) blends was investigated. The presence of hydrogen bonding enhanced the compatibility of two copolymers. This caused PS-*g*-PAA to intervene in the interface between microdomains of the block copolymer. Consequently, an order–disorder transition occurred at a high concentration of PS-*g*-PAA. On the other hand, poor miscibility and the lack of hydrogen bonding in the blends prevented PS-*g*-PAA from being incorporated into microdomains of the block copolymer, causing the macrophase separation of two copolymers.

- Structure and dynamics of polyrotaxane-based sliding graft copolymers with alkyl side chains Sakai, Y.; Gomi, R.; Kato, K.; Yokoyama, H.; Ito, K. *Soft Matter* **2013**, 9, 1895-1901.

Abstract:



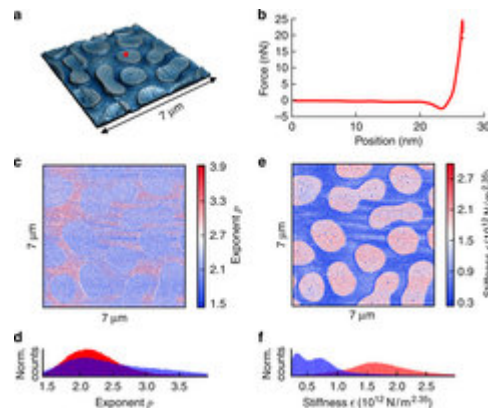
Polyrotaxanes (PRs) with side chains grafted onto cyclic molecules (sliding graft copolymers, SGCs) can be categorized as a new type of graft copolymer, in the sense that the grafting point of the side chains can move along the main chain. In this work, alkyl oligomers were employed as side chains for the precise control of side chain length. Several SGCs with different side chain lengths were prepared from the PR of polyethylene glycol and α -cyclodextrin (α -CD). The solid-state structures of the SGCs were investigated by X-ray scattering. The SGCs formed periodic structures whose sizes increased linearly with the side chain length. SGCs with crystalline side chains exhibited crystalline structures of side chain and packing structures of the α -CDs; these were synchronously driven by the

sliding and rearrangement of the α -CDs with the side chains on the main backbone chain. Viscoelastic measurements of solid-state SGCs revealed that SGCs with non-crystalline side chains commonly had a broad relaxation process corresponding to the cooperative fluctuation of the CDs and PEG backbone, and some of them also exhibited an anomalous shoulder. This new viscoelastic mode was presumably due to the sliding motion of CD molecules with the side chains along the backbone.

- Interaction imaging with amplitude-dependence force spectroscopy

Platz, D.; Forchheimer, D.; Tholén, E. A.; Haviland, D. B. *Nature Commun.* **2013**, 4, 1360.

Abstract:

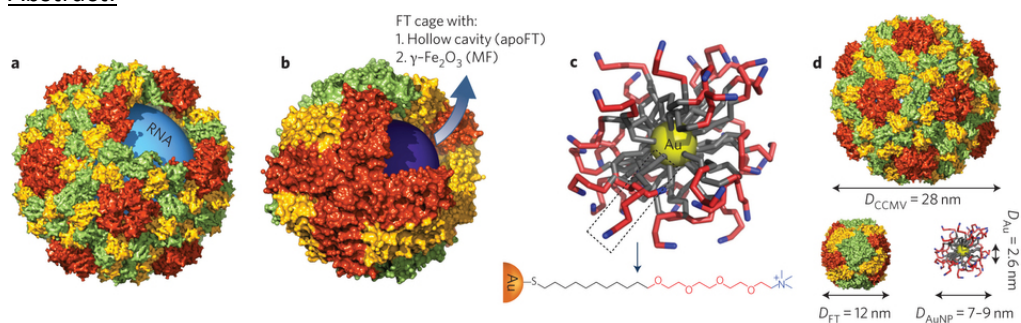


Knowledge of surface forces is the key to understanding a large number of processes in fields ranging from physics to material science and biology. The most common method to study surfaces is dynamic atomic force microscopy (AFM). Dynamic AFM has been enormously successful in imaging surface topography, even to atomic resolution, but the force between the AFM tip and the surface remains unknown during imaging. Here we present a new approach that combines high-accuracy force measurements and high-resolution scanning. The method, called amplitude-dependence force spectroscopy (ADFS), is based on the amplitude dependence of the cantilever's response near resonance and allows for separate determination of both conservative and dissipative tip-surface interactions. We use ADFS to quantitatively study and map the nano-mechanical interaction between the AFM tip and heterogeneous polymer surfaces. ADFS is compatible with commercial atomic force microscopes and we anticipate its widespread use in taking AFM toward quantitative microscopy.

- Electrostatic assembly of binary nanoparticle superlattices using protein cages

Kostiainen, M. A.; Hiekkataipale, P.; Laiho, A.; Lemieux, V.; Seitsonen, J.; Ruokolainen, J.; Ceci, P. *Nature Nanotech.* **2013**, 8, 52–56.

Abstract:

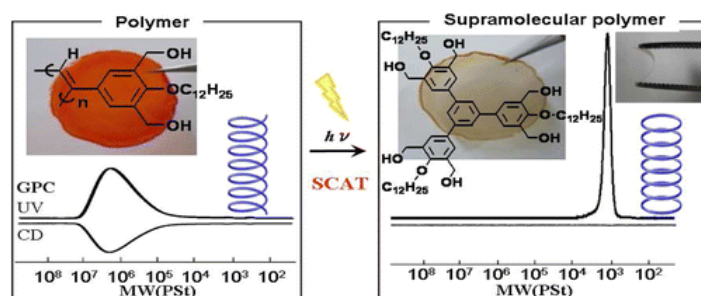


Binary nanoparticle superlattices are periodic nanostructures with lattice constants much shorter than the wavelength of light and could be used to prepare multifunctional metamaterials. Such superlattices are typically made from synthetic nanoparticles, and although biohybrid structures have been developed, incorporating biological building blocks into binary nanoparticle superlattices remains challenging. Protein-based nanocages provide a complex yet monodisperse and geometrically well-defined hollow cage that can be used to encapsulate different materials. Such protein cages have been used to program the self-assembly of encapsulated materials to form free-standing crystals and superlattices at interfaces or in solution. Here, we show that electrostatically patchy protein cages—cowpea chlorotic mottle virus and ferritin cages—can be used to direct the self-assembly of three-dimensional binary superlattices. The negatively charged cages can encapsulate RNA or superparamagnetic iron oxide nanoparticles, and the superlattices are formed through tunable electrostatic interactions with positively charged gold nanoparticles. Gold nanoparticles and viruses form an AB_8^{fcc} crystal structure that is not isostructural with any known atomic or molecular crystal structure and has previously been observed only with large colloidal polymer particles. Gold nanoparticles and empty or nanoparticle-loaded ferritin cages form an interpenetrating simple cubic AB structure (isostructural with CsCl). We also show that these magnetic assemblies provide contrast enhancement in magnetic resonance imaging.

- Top-Down Preparation of Self-Supporting Supramolecular Polymeric Membranes Using Highly Selective Photocyclic Aromatization of Cis–Cisoid Helical Poly(phenylacetylene)s in the Membrane State

Liu, L.; Namikoshi, T.; Zang, Y.; Aoki, T.; Hadano, S.; Abe, Y.; Wasuzu, I.; Tsutsuba, T.; Teraguchi, M.; Kaneko, T. *J. Am. Chem. Soc.* **2013**, *135*, 272–279.

Abstract:



A novel, highly selective photocyclic aromatization (SCAT) of π -conjugated polymers from phenylacetylene having two hydroxyl groups to exclusively yield a 1,3,5-trisubstituted benzene derivative was developed, and its success was confirmed by ^1H NMR, GPC, and TOF-MS. The SCAT reaction has many unique characteristics. (1) It is a quantitative reaction: it gave only the corresponding cyclic trimer, i.e., a 1,3,5-trisubstituted benzene derivative, quantitatively (100%). No byproducts were produced under the best conditions. (2) It is an intramolecular reaction: it occurred between three adjacent monomer units in one macromolecule. (3) It is a stereospecific and topochemical or template reaction: the reactivity strongly depended on the configuration and conformation of the starting polymer substrates. (4) It is a photoreaction: high selectivity (100%) was observed only by the use of visible light irradiation, not by heating. (5) It is a solid-state reaction: high selectivity (100%) was observed only in the solid state, not in solution. In addition, (6) the resulting cyclic trimers could form a self-supporting membrane, despite their low molecular weights. This new approach resulted in a new class of supramolecular polymers consisting of a 1,3,5-trisubstituted benzene derivative, numbers of which were linearly linked by hydrogen bonds and

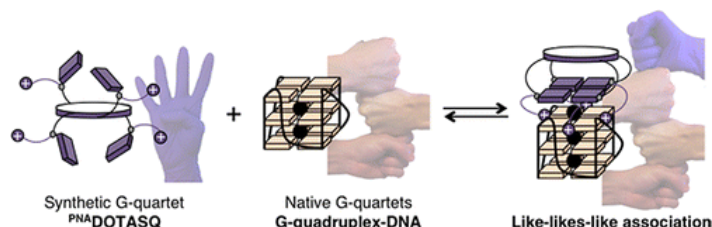
stacked benzene derivatives. Since SCAT has such high selectivities and is useful for the preparation of a self-supporting supramolecular polymer membrane, many applications can be expected.

13

- A Model of Smart G-Quadruplex Ligand

Haudecoeur, R.; Stefan, L.; Denat, F.; Monchaud, D. *J. Am. Chem. Soc.* **2013**, *135*, 550–553.

Abstract:

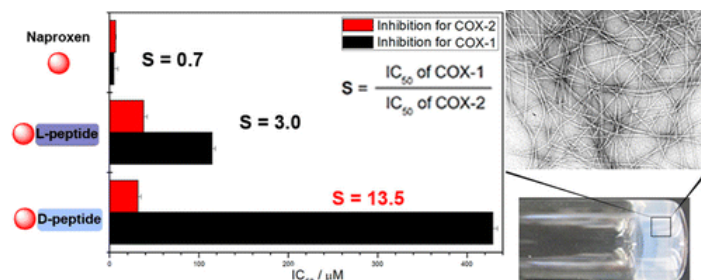


An unprecedented strategy to control the quadruplex- vs duplex-DNA selectivity of a ligand is reported. We designed a compound whose structure can rearrange when it interacts with a G-quadruplex, thereby controlling its affinity. Thus, the first “smart G-quadruplex ligand” is reported, since this ligand experiences a structural change in the presence of quadruplexes but not in the presence of duplexes, ensuring a high level of quadruplex selectivity.

- D-Amino Acids Boost the Selectivity and Confer Supramolecular Hydrogels of a Nonsteroidal Anti-Inflammatory Drug (NSAID)

Li, J.; Kuang, Y.; Gao, Y.; Du, X.; Shi, J.; Xu, B. *J. Am. Chem. Soc.* **2013**, *135*, 542–545.

Abstract:

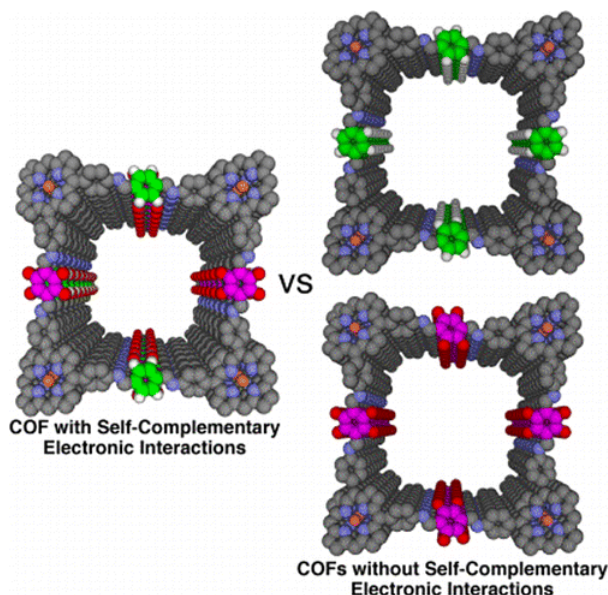


As systemically used therapeutics for treating acute or chronic pains or inflammations, nonsteroidal anti-inflammatory drugs (NSAIDs) also associate with the adverse gastrointestinal and renal effects and cardiovascular risks. Thus, it is beneficial to develop topical gels that selectively inhibit cyclooxygenase-2 (COX-2) for the management of local inflammation. In this work, we demonstrate that the covalent conjugation of D-amino acids to naproxen (i.e., a NSAID) not only affords supramolecular hydrogelators for the topical gels but also unexpectedly and significantly elevates the selectivity toward COX-2 about 20× at little expense of the activity of naproxen. This work illustrates a previously unexplored approach that employs D-amino acids for the development of functional molecules that have dual or multiple roles and exceptional biostability, which offers a new class of molecular hydrogels of therapeutic agents.

- Control of Crystallinity and Porosity of Covalent Organic Frameworks by Managing Interlayer Interactions Based on Self-Complementary π -Electronic Force

Chen, X.; Addicoat, M.; Irle, S.; Nagai, A.; Jiang, D. *J. Am. Chem. Soc.* **2013**, *135*, 546–549.

Abstract:

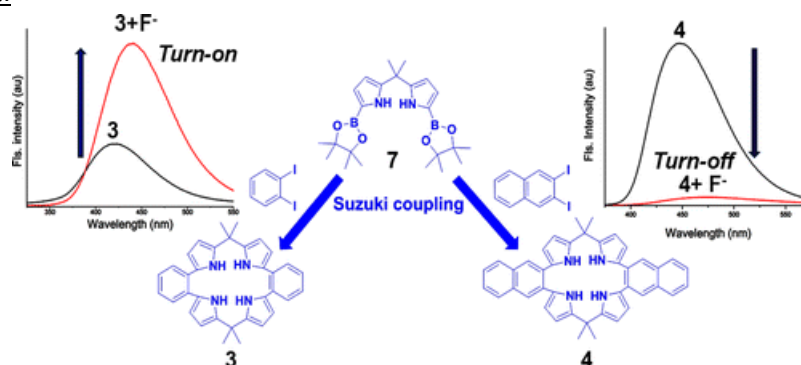


Crystallinity and porosity are crucial for crystalline porous covalent organic frameworks (COFs). Here we report synthetic control over the crystallinity and porosity of COFs by managing interlayer interactions based on self-complementary π -electronic forces. Fluoro-substituted and nonsubstituted aromatic units at different molar ratios were integrated into the edge units that stack to trigger self-complementary π -electronic interactions in the COFs. The interactions improve the crystallinity and enhance the porosity by maximizing the total crystal stacking energy and minimizing the unit cell size. Consequently, the COF consisting of equimolar amounts of fluoro-substituted and nonsubstituted units showed the largest effect. These results suggest a new approach to the design of COFs by managing the interlayer interactions.

- Calix[2]bispyrrolylarenes: New Expanded Calix[4]pyrroles for Fluorometric Sensing of Anions via Extended π -Conjugation

Chandra, B.; Mahanta, S. P.; Pati, N. N.; Baskaran, S.; Kanaparthi, R. K.; Sivasankar, C.; Panda, P. K. *Org. Lett.* **2013**, *15*, 306–309.

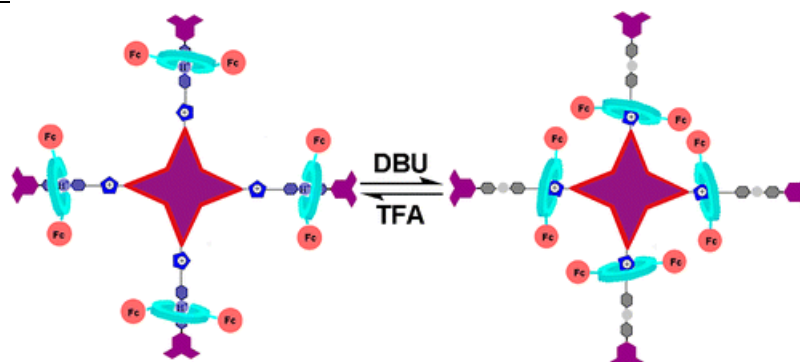
Abstract:



Two new expanded calix[4]pyrroles 3 and 4 were synthesized by '2 + 2' cyclocoupling of easily prepared diboryldipyrromethane 7 (by Ir-catalyzed CH-bond activation) with appropriate diiodoarenes using the Suzuki protocol. Owing to the unique design, both macrocycles exhibited extended π -conjugation and enhanced fluorescence. Upon complexation with anions (fluoride and acetate), receptor 3 displayed *turn-on* sensing of fluorescence, whereas 4 showed *turn-off* sensing.

- A Novel Star-Shaped Zinc Porphyrin Cored [5]Rotaxane
Zhang, H.; Liu, Q.; Li, J.; Qu, D.-H. *J. Org. Lett.* **2013**, *15*, 338–341.

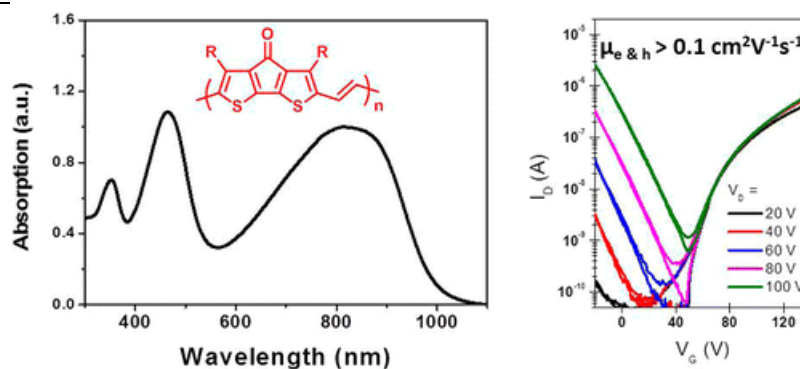
Abstract:



A novel star-shaped zinc porphyrin cored [5]rotaxane with four rotaxane arms was synthesized and well characterized by ^1H , ^{13}C NMR spectroscopy and HR-ESI mass spectrometry. The introduction of the zinc porphyrin core enabled the [5]rotaxane to have a fixed shape and symmetrical structure, and the simultaneous shuttling motion of four macrocycles can be driven by external acid–base stimuli. This kind of topological structure exhibits important potential in the design and construction of large sophisticated assemblies.

- Near Infrared Absorbing Soluble Poly(cyclopenta[2,1-b:3,4-b']dithiophen-4-one)vinylene Polymers Exhibiting High Hole and Electron Mobilities in Ambient Air
Fei, Z.; Gao, X.; Smith, J.; Pattanasattayavong, P.; Buchaca Domingo, E.; Stingelin, N.; Watkins, S. E.; Anthopoulos, T. D.; Kline, R. J.; Heeney, M. *Chem. Mater.* **2013**, *25*, 59–68.

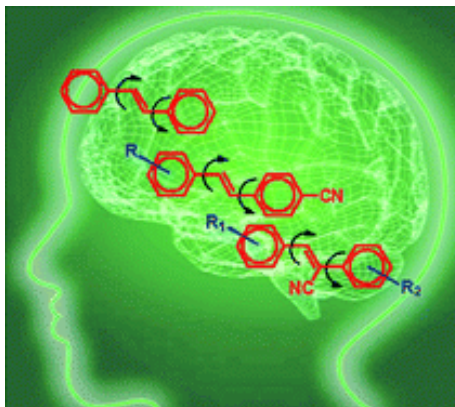
Abstract:



We report the synthesis of two novel cyclopenta[2,1-b:3,4-b']dithiophen-4-one monomers containing solubilizing alkyl groups in the peripheral 3,5 positions. Polymerization with (E)-1,2-bis(tributylstannyl)-ethylene under Stille coupling conditions afforded the first reported examples of soluble poly(cyclopentadithiophen-4-one)vinylene. The resulting polymers absorb in the near-infrared, with a maximum thin film absorbance around 815 nm and have optical band gaps of 1.25 eV. The polymers exhibit promising ambipolar field effect transistor performance, with average saturated mobilities of $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons. The ambipolar transistors operate in both the hole and electron transport regimes in ambient air. Prolonged exposure to ambient atmosphere leads to a gradual loss of the electron transport behavior, with little change observed in the p-type mobility.

- Cyanostilbene-based intelligent organic optoelectronic materials
Zhu, L.; Zhao, Y. *J. Mater. Chem. C* **2013**, 1, 1059-1065.

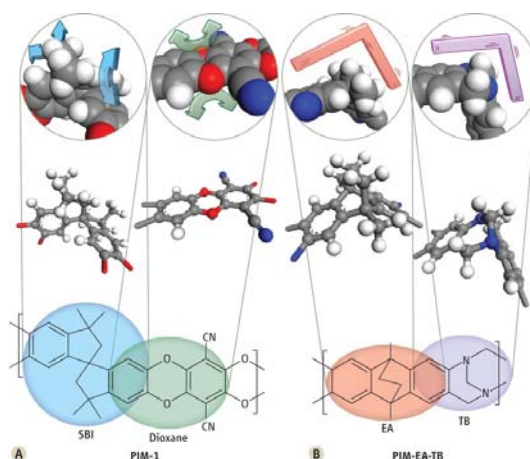
Abstract:



π -Conjugated organic luminophores are one of the essential ingredients for modern optoelectronics. This short review highlights recent research progress on a type of smart π -conjugated systems based on cyanostilbene and its derivatives, in which their photophysical properties can be tuned in response to a variety of external stimuli (*e.g.* polarity, viscosity, pH, light and thermal changes). To take advantage of the unique tunable features, cyanostilbene and its derivatives have been implanted into polymers, sol-gel systems, solid films, supramolecular architectures, functional nanoparticles, and so on. In addition to discussing the preparation and characterization of cyanostilbene-based hybrid materials, this review highlights their charming functionalities, such as AIEE (aggregation-induced enhanced emission) effect, solid-state emission, photochromism, photovoltaics, and biological imaging. Future studies on the applications of cyanostilbene-based intelligent materials are also predicted. The blossoming of cyanostilbene-based intelligent hybrids promises a new generation of integrated multifunctional materials, an outcome which is essential for the development of responsive materials that interface with physics, materials chemistry, biology, and medical science.

- An Efficient Polymer Molecular Sieve for Membrane Gas Separations
Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. *Science* **2013**, 339, 303-307.

Abstract:



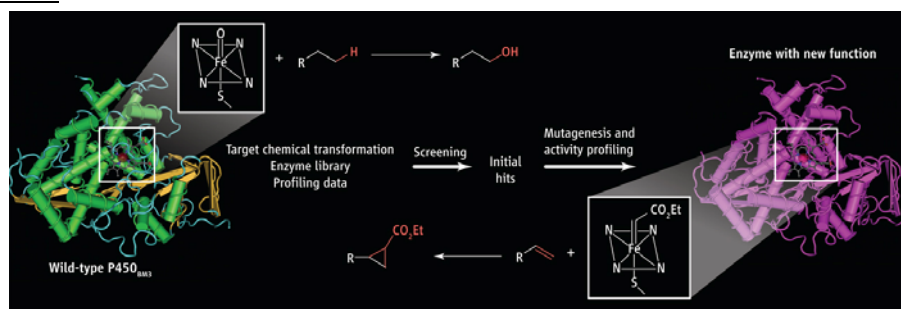
Microporous polymers of extreme rigidity are required for gas-separation membranes that combine high permeability with selectivity. We report a shape-persistent ladder polymer consisting of

benzene rings fused together by inflexible bridged bicyclic units. The polymer's contorted shape ensures both microporosity—with an internal surface area greater than 1000 square meters per gram—and solubility so that it is readily cast from solution into robust films. These films demonstrate exceptional performance as molecular sieves with high gas permeabilities and good selectivities for smaller gas molecules, such as hydrogen and oxygen, over larger molecules, such as nitrogen and methane. Hence, this polymer has excellent potential for making membranes suitable for large-scale gas separations of commercial and environmental relevance.

- Olefin Cyclopropanation via Carbene Transfer Catalyzed by Engineered Cytochrome P450 Enzymes

Coelho, P. S.; Brustad, E. M.; Kannan, A.; Arnold, F. H. *Science* **2013**, 339, 307-310.

Abstract:

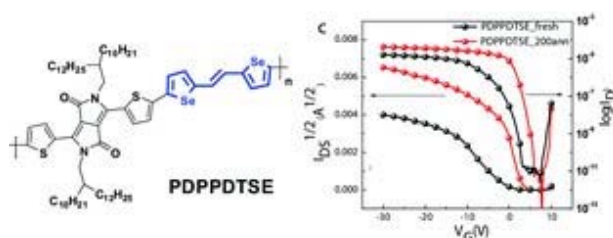


Transition metal-catalyzed transfers of carbenes, nitrenes, and oxenes are powerful methods for functionalizing C=C and C-H bonds. Nature has evolved a diverse toolbox for oxene transfers, as exemplified by the myriad monooxygenation reactions catalyzed by cytochrome P450 enzymes. The isoelectronic carbene transfer to olefins, a widely used C-C bond-forming reaction in organic synthesis, has no biological counterpart. Here we report engineered variants of cytochrome P450_{BM3} that catalyze highly diastereo- and enantioselective cyclopropanation of styrenes from diazoester reagents via putative carbene transfer. This work highlights the capacity to adapt existing enzymes for the catalysis of synthetically important reactions not previously observed in nature.

- Effect of Selenophene in a DPP Copolymer Incorporating a Vinyl Group for High-Performance Organic Field-Effect Transistors

Kang, I.; An, T. K.; Hong, J.; Yun, H.-J.; Kim, R.; Chung, D. S.; Park, C. E.; Kim, Y.-H.; Kwon, S.-K. *Adv. Mater.* **2013**, 25, 524–528.

Abstract:

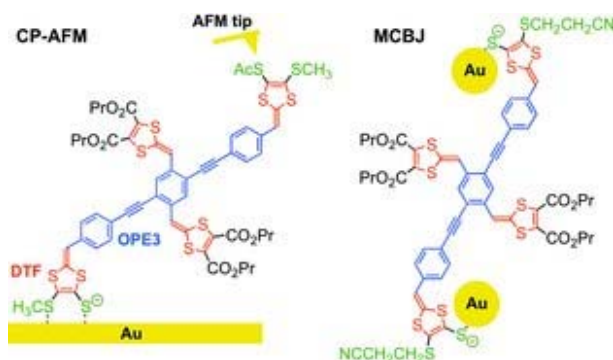


A new polymeric semiconductor, PDPPDTSE, is reported which is composed of a diketopyrrolopyrrole moiety and selenophenylene vinylene selenophene, with a high field-effect mobility achieved through intermolecular donor-acceptor interactions. The field-effect mobility of OFET devices based on PDPPDTSE by spin-casting is $4.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is higher than predecessor polymeric semiconductors.

- A New Class of Extended Tetrathiafulvalene Cruciform Molecules for Molecular Electronics with Dithiafulvene-4,5-Dithiolate Anchoring Groups

Parker, C. R.; Wei, Z.; Arroyo, C. R.; Jennum, K.; Li, T.; Santella, M.; Bovet, N.; Zhao, G.; Hu, W.; van der Zant, H. S. J.; Vanin, M.; Solomon, G. C.; Laursen, B. W.; Nørgaard, K.; Nielsen, M. B. *Adv. Mater.* **2013**, 25, 405–409.

Abstract:



Cruciform motifs with two orthogonally oriented π -extended tetrathiafulvalenes and with differently protected thiolate end-groups are synthesized by stepwise coupling reactions. The molecules are subjected to single-molecule conductivity studies in a break-junction and to conducting probe atomic force microscopy studies in a self-assembled monolayer on gold.