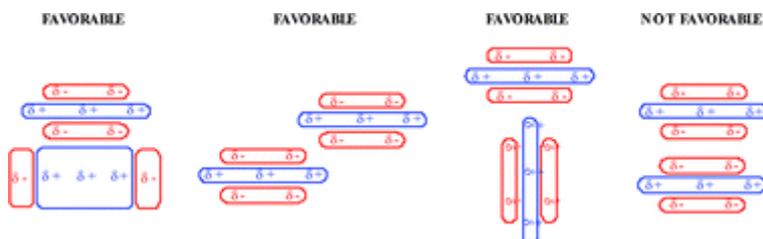


- Rethinking the term “pi-stacking”
Martinez, C. R.; Iverson, B. L. *Chem. Sci.* **2012**, *3*, 2191-2201.

Abstract:

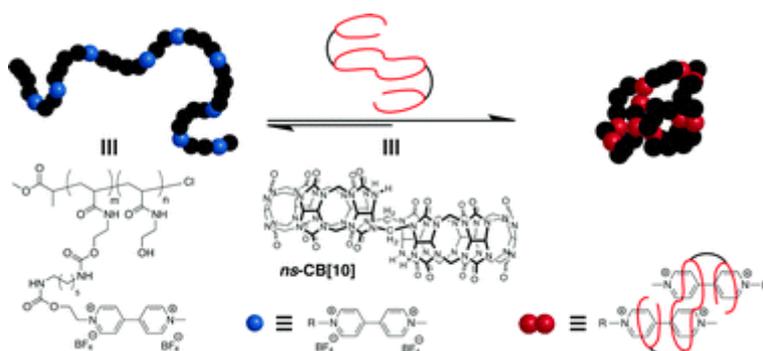


A review of experimental and theoretical literature across several fields reinforces the conclusion that the terms “pi-stacking” and “pi-pi interactions” do not accurately describe the forces that drive association between aromatic molecules of the types most commonly studied in chemistry or biology laboratories.

- Metastable single-chain polymer nanoparticles prepared by dynamic cross-linking with nor-seco-cucurbit[10]uril

Appel, E. A.; Barrio, J.; Dyson, J.; Isaacs, L.; Scherman, O. A. *Chem. Sci.* **2012**, *3*, 2278-2281.

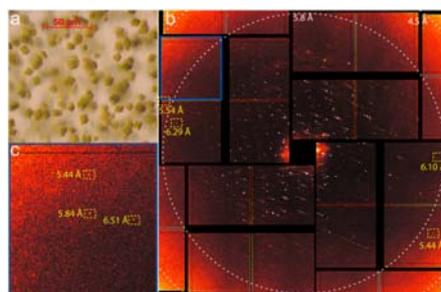
Abstract:



Dynamic and reversible collapse of a single polymer chain in water through 2 : 1 encapsulation of pendant viologen moieties with nor-seco-cucurbit[10]uril to produce single chain nanoparticles.

- Room temperature femtosecond X-ray diffraction of photosystem II microcrystals
Kern, J.; Alonso-Mori, R.; Hellmich, J.; Tran, R.; Hattne, J.; Laksmono, H.; Glöckner, C.; Echols, N.; Sierra, R. G.; Sellberg, J.; Lassalle-Kaiser, B.; Gildea, R. J.; Glatzel, P.; Grosse-Kunstleve, R. W.; Latimer, M. J.; McQueen, T. A.; DiFiore, D.; Fry, A. R.; Messerschmidt, M.; Miahnahri, A.; Schafer, D. W.; Seibert, M. M.; Sokaras, D.; Weng, T.-C.; Zwart, P. H.; White, W. E.; Adams, P. D.; Bogan, M. J.; Boutet, S.; Williams, G. J.; Messinger, J.; Sauter, N. K.; Zouni, A.; Bergmann, U.; Yano, J.; Yachandra, V. K. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 9721-9726.

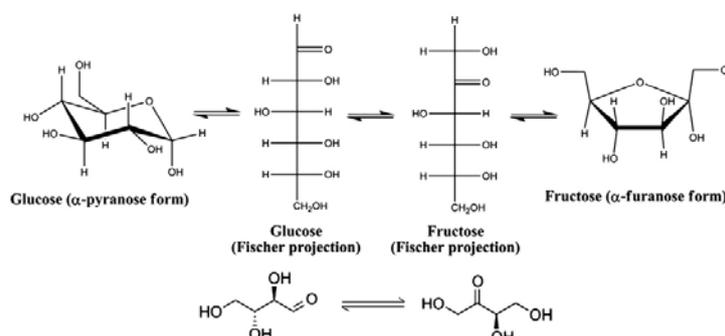
Abstract:



Most of the dioxygen on earth is generated by the oxidation of water by photosystem II (PS II) using light from the sun. This lightdriven, four-photon reaction is catalyzed by the Mn_4CaO_5 cluster located at the luminal side of PS II. Various X-ray studies have been carried out at cryogenic temperatures to understand the intermediate steps involved in the water oxidation mechanism. However, the necessity for collecting data at room temperature, especially for studying the transient steps during the O-O bond formation, requires the development of new methodologies. In this paper we report room temperature X-ray diffraction data of PS II microcrystals obtained using ultrashort (<50 fs) 9 keV X-ray pulses from a hard X-ray free electron laser, namely the Linac Coherent Light Source. The results presented here demonstrate that the “probe before destroy” approach using an X-ray free electron laser works even for the highly-sensitive Mn_4CaO_5 cluster in PS II at room temperature. We show that these data are comparable to those obtained in synchrotron radiation studies as seen by the similarities in the overall structure of the helices, the protein subunits and the location of the various cofactors. This work is, therefore, an important step toward future studies for resolving the structure of the Mn_4CaO_5 cluster without any damage at room temperature, and of the reaction intermediates of PS II during O-O bond formation.

- Metalloenzyme-like catalyzed isomerizations of sugars by Lewis acid zeolites. Bermejo-Deval, R.; Assary, R. S.; Nikolla, E.; Moliner, M.; Román-Leshkov, Y.; Hwang, S.-J.; Palsdottir, A.; Silverman, D.; Lobo, R. F.; Curtiss, L. A.; Davis, M. E. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 9727-9732.

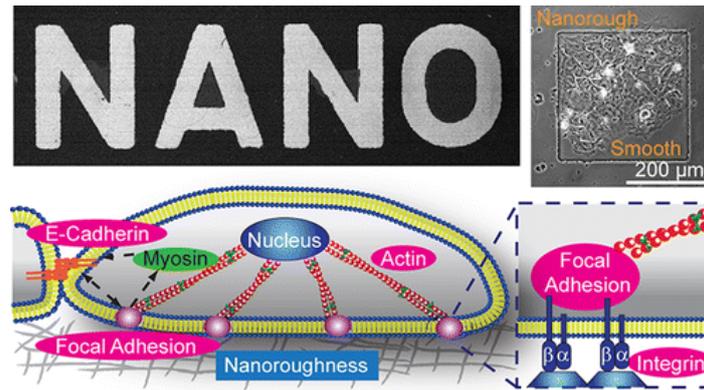
Abstract:



Isomerization of sugars is used in a variety of industrially relevant processes and in glycolysis. Here, we show that hydrophobic zeolite beta with framework tin or titanium Lewis acid centers isomerizes sugars, e.g., glucose, via reaction pathways that are analogous to those of metalloenzymes. Specifically, experimental and theoretical investigations reveal that glucose partitions into the zeolite in the pyranose form, ring opens to the acyclic form in the presence of the Lewis acid center, isomerizes into the acyclic form of fructose, and finally ring closes to yield the furanose product. The zeolite catalysts provide processing advantages over metalloenzymes such as an ability to work at higher temperatures and in acidic conditions that allow for the isomerization reaction to be coupled with other important conversions.

- Nanotopography Influences Adhesion, Spreading, and Self-Renewal of Human Embryonic Stem Cells
Chen, W.; Villa-Diaz, L. G.; Sun, Y.; Weng, S.; Kim, J. K.; Lam, R. H. W.; Han, L.; Fan, R.; Krebsbach, P. H.; Fu, J. *ACS Nano* **2012**, *6*, 4094-4103.

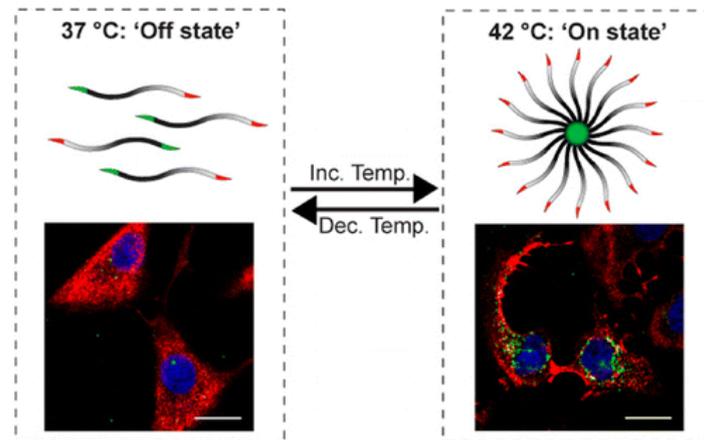
Abstract:



Human embryonic stem cells (hESCs) have great potentials for future cell-based therapeutics. However, their mechanosensitivity to biophysical signals from the cellular microenvironment is not well characterized. Here we introduced an effective microfabrication strategy for accurate control and patterning of nanoroughness on glass surfaces. Our results demonstrated that nanotopography could provide a potent regulatory signal over different hESC behaviors, including cell morphology, adhesion, proliferation, clonal expansion, and self-renewal. Our results indicated that topological sensing of hESCs might include feedback regulation involving mechanosensory integrin-mediated cell–matrix adhesion, myosin II, and E-cadherin. Our results also demonstrated that cellular responses to nanotopography were cell-type specific, and as such, we could generate a spatially segregated coculture system for hESCs and NIH/3T3 fibroblasts using patterned nanorough glass surfaces.

- Digital Switching of Local Arginine Density in a Genetically Encoded Self-Assembled Polypeptide Nanoparticle Controls Cellular Uptake
MacEwan, S. R.; Chilkoti, A. *Nano Letters* **2012**, *12*, 3322-3328.

Abstract:

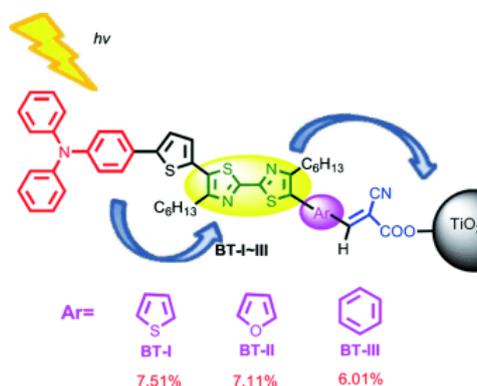


Cell-penetrating peptides (CPPs) are a class of molecules that enable efficient internalization of a wide variety of cargo in diverse cell types, making them desirable for delivery of anticancer drugs to solid tumors. For CPPs to be useful, it is important to be able to turn their function on in response to an external trigger that can be spatially localized *in vivo*. Here we describe an approach to turning on CPP function by modulation of the local density of arginine (Arg) residues by temperature-triggered micelle assembly of diblock copolymer elastin-like polypeptides (ELP_{BC}). A greater than 8-fold increase in cellular uptake occurs when Arg residues are presented on the corona of ELP_{BC} micelles, as compared to the same ELP_{BC} at a temperature in which it is a soluble unimer. This approach is the

first to demonstrate digital 'off-on' control of CPP activity by an extrinsic thermal trigger in a clinically relevant temperature range by modulation of the interfacial density of Arg residues on the exterior of a nanoparticle.

- New Bithiazole-Based Sensitizers for Efficient and Stable Dye-Sensitized Solar Cells
He, J.; Guo, F.; Li, X.; Wu, W.; Yang, J.; Hua, J. *Chem. Eur. J.* **2012**, *18*, 7903–7915.

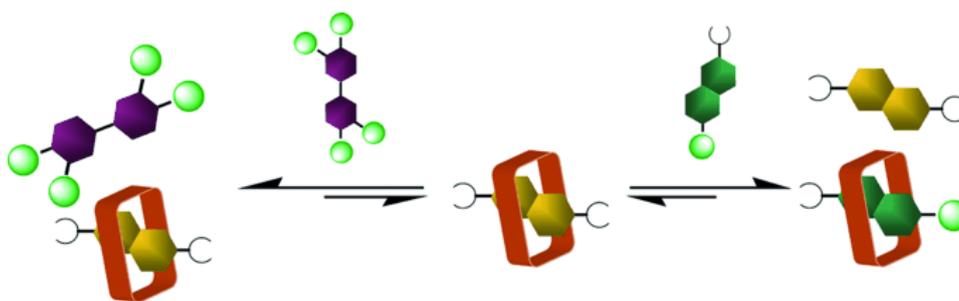
Abstract:



A series of new push–pull organic dyes (BT-I–VI), incorporating electron-withdrawing bithiazole with a thiophene, furan, benzene, or cyano moiety, as π spacer have been synthesized, characterized, and used as the sensitizers for dye-sensitized solar cells (DSSCs). In comparison with the model compound T1, these dyes containing a thiophene moiety between triphenylamine and bithiazole display enhanced spectral responses in the red portion of the solar spectrum. Electrochemical measurement data indicate that the HOMO and LUMO energy levels can be tuned by introducing different π spacers between the bithiazole moiety and cyanoacrylic acid acceptor. The incorporation of bithiazole substituted with two hexyl groups is highly beneficial to prevent close π – π aggregation, thus favorably suppressing charge recombination and intermolecular interaction. The overall conversion efficiencies of DSSCs based on bithiazole dyes are in the range of 3.58 to 7.51%, in which BT-I-based DSSCs showed the best photovoltaic performance: a maximum monochromatic incident photon-to-current conversion efficiency (IPCE) of 81.1%, a short-circuit photocurrent density (J_{sc}) of 15.69 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 778 mV, and a fill factor (ff) of 0.61, which correspond to an overall conversion efficiency of 7.51% under standard global AM 1.5 solar light conditions. Most importantly, long-term stability of the BT-I–III-based DSSCs with ionic-liquid electrolytes under 1000 h of light soaking was demonstrated and BT-II with a furan moiety exhibited better photovoltaic performance of up to 5.75% power conversion efficiency.

- Neutral and Anionic Guests and Their Effect on the Formation of Pseudorotaxanes by Using a Flexible Tetracationic Imidazolium Macrocycle
Gong, H.-Y.; Rambo, B. M.; Lynch, V. M.; Keller, K. M.; Sessler, J. L. *Chem. Eur. J.* **2012**, *18*, 7803–7809.

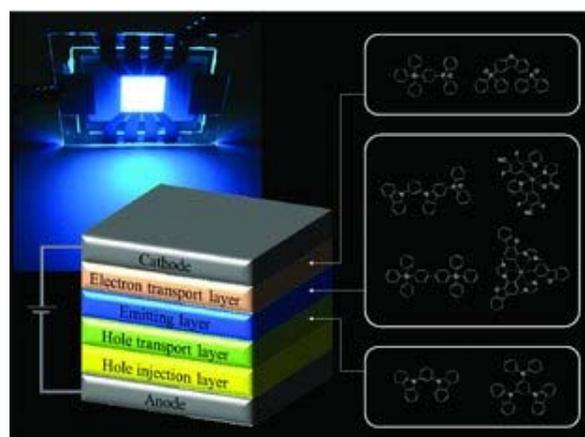
Abstract:



The ability to control and direct molecular assembly has important implications in the design of environmentally responsive materials. Reported here is the use of competitive neutral- and anionic-guest recognition to control the formation, disruption, replacement-based construction and higher-order assembly properties of pseudorotaxane structures involving a large, cationic tetraimidazolium receptor. In particular, we showed that the chloride anion (as the tetrabutylammonium (TBA⁺) salt) serves to replace directly the 2,6-naphthalene dicarboxylate dianion from the preformed complex, involving this dianion. In contrast, the addition of the nitrate anion (as the TBA⁺ salt) serves to effect displacement of a pre-bound 2,6-naphthalene dicarboxylate dianion in a stepwise manner allowing for stabilization of a so-called “outside”-binding mode under appropriate conditions. We have also found that by using biphenyl-3,4,3',4'-tetraamine as the guest, a 1D-donor–acceptor–donor coordination polymer can be stabilized, whereas the addition of 6-amino-naphthalene-2-sulfonate anion to the pre-formed complex between the tetraimidazolium receptor and the 2,6-naphthalene dicarboxylate dianion produces a new pseudorotaxane complex. This guest-based competition and subsequent molecular translocation is supported by solution-state NMR spectroscopic studies as well as solid-state single-crystal X-ray structural analyses. The results described herein provide initial evidence that guest competition can be used to control molecular “switching” and substrate binding within an appropriately designed anion receptor.

- Organic Materials for Deep Blue Phosphorescent Organic Light-Emitting Diodes
Yook, K. S.; Lee, J. Y. *Adv. Mater.* **2012**, *24*, 3169–3190.

Abstract:

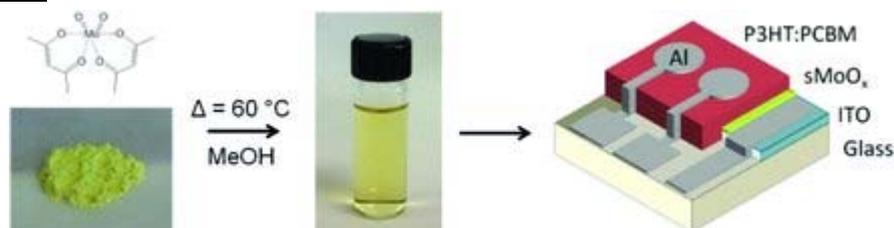


Recently, great progress has been made in the device performance of deep blue phosphorescent organic light-emitting diodes (PHOLEDs) by developing high triplet energy charge-transport materials, high triplet energy host and deep blue emitting phosphorescent dopant materials. A high quantum efficiency of over 25% and a high power efficiency of over 15 lm/W have already been achieved at 1000 cd m⁻² in the deep blue PHOLEDs with a γ color coordinate less than 0.20. In this work, recent

developments in organic materials for high efficiency deep blue PHOLEDs are reviewed and a future strategy for the development of high efficiency deep blue PHOLEDs is proposed.

- A Solution-Processed MoO_x Anode Interlayer for Use within Organic Photovoltaic Devices
Jasieniak, J. J.; Seifter, J.; Jo, J.; Mates, T.; Heeger, A. J. *Adv. Funct. Mater.* **2012**, *22*, 2594–2605.

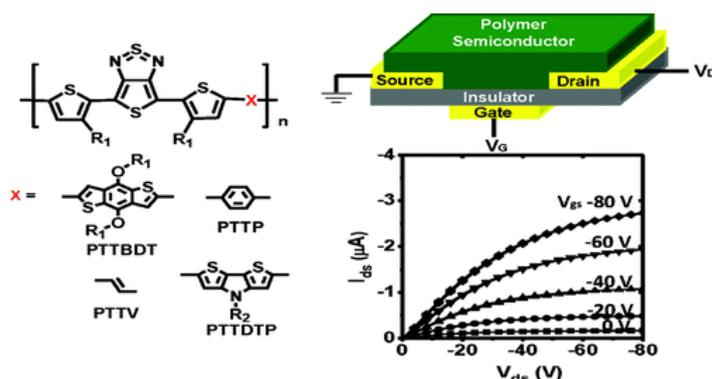
Abstract:



A simple, solution-processed route to the development of MoO_x thin-films using oxomolybdate precursors is presented. The chemical, structural, and electronic properties of these species are characterized in detail, within solution and thin-films, using electrospray ionization mass spectrometry, grazing angle Fourier transform infrared spectroscopy, thermogravimetric analysis, atomic force microscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy. These analyses show that under suitable deposition conditions the resulting solution processed MoO_x thin-films possess the appropriate morphological and electronic properties to be suitable for use in organic electronics. This is exemplified through the fabrication of poly(3-hexylthiophene):[6,6]-phenyl C₆₁ butyric acid methyl ester (P3HT:PC₆₁BM) bulk heterojunction (BHJ) solar cells and comparisons to the traditionally used poly(3,4-ethyldioxythiophene)/poly(styrenesulfonate) anode modifying layer.

- New Thienothiadiazole-Based Conjugated Copolymers for Electronics and Optoelectronics
Hwang, Y.-J.; Kim, F. S.; Xin, H.; Jenekhe, S. A. *Macromolecules* **2012**, *45*, 3732–3739.

Abstract:

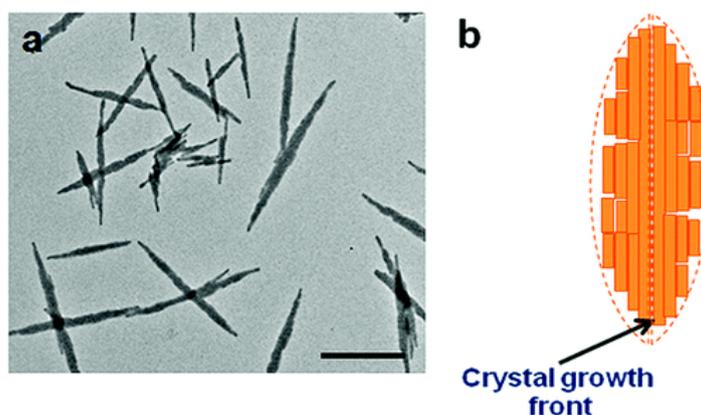


Four new donor–acceptor conjugated copolymers incorporating thieno[3,4-*c*][1,2,5]thiadiazole as the acceptor moiety and various electron donor moieties were synthesized and their electronic structures and properties were investigated. The new thienothiadiazole copolymers obtained by Stille coupling polymerizations had weight-average molecular weights of 10–46 kDa. Their broad absorption bands and optical band gaps of 0.9–1.2 eV demonstrate strong intramolecular charge transfer and potential for extending light harvesting deep into the near-infrared. The HOMO/LUMO energy levels were 4.9–5.1/3.4–3.6 eV (below vacuum). As p-channel semiconductors in field-effect transistors, the thienothiadiazole copolymers had a carrier mobility of up to $4.6 \times 10^{-3} \text{ cm}^2/(\text{Vs})$. Bulk

heterojunction solar cells made from blends of the thienothiadiazole copolymers with fullerenes gave a photovoltaic efficiency of 0.4%.

- Formation of Lenticular Platelet Micelles via the Interplay of Crystallization and Chain Stretching: Solution Self-Assembly of Poly(ferrocenyldimethylsilane)-*block*-poly(2-vinylpyridine) with a Crystallizable Core-Forming Metalloblock
Yusoff, S. F. M.; Hsiao, M.-S.; Schacher, F. H.; Winnik, M. A.; Manners, I. *Macromolecules* **2012**, *45*, 3883–3891.

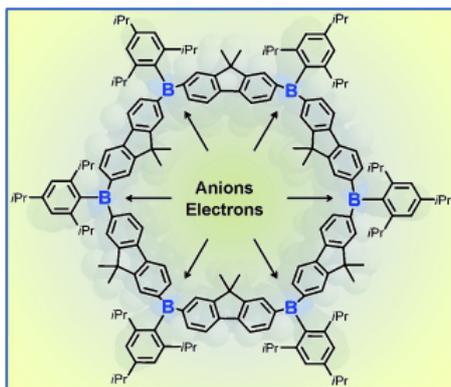
Abstract:



The influence of solvent composition on micelle morphology has been investigated for two crystalline-coil poly(ferrocenyldimethylsilane-*block*-2-vinylpyridine) (PFS-*b*-P2VP) diblock copolymers with different block ratios (5:1 and 1:1). The solution self-assembly of these materials was explored in solvent mixtures containing different ratios of a good solvent for both blocks (THF) and a selective solvent for the P2VP block (isopropanol). Various micellar morphologies such as spheres and platelets were characterized using transmission electron microscopy (TEM), selected area electron diffraction (SAED), dynamic light scattering (DLS), wide-angle X-ray scattering (WAXS), and atomic force microscopy (AFM). The results showed that the solution self-assembly of PFS-*b*-P2VP block copolymers (5:1, 1:1) gave spherical micelles with an amorphous PFS core at low THF content (10 vol %). Subsequently, the amorphous spheres were slowly transformed into platelet micelles with a lenticular shape that consisted of a crystalline PFS core sandwiched by two coronal P2VP layers. This indicated that the amorphous spherical micelles were in a metastable state. The transformation of spheres into platelets was significantly slower for the 5:1 block copolymer with the longer PFS core-forming segment presumably due to a lower rate of crystallization of the metalloblock. Platelets were found to be dominant for both block copolymers at higher THF content (THF \geq 30 vol %). The formation of lenticular rather than regular platelets was attributed to a poisoning effect whereby interference of the P2VP corona-forming blocks in the growth of the crystalline PFS core leads to the creation of defects in the crystal growth fronts.

- Incorporation of Boron in the Walls of an “All-Carbon” Cyclophane: A Novel Approach to Lewis Acidic Macrocycles
Gabbai, F. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 6316-6318.

Abstract:

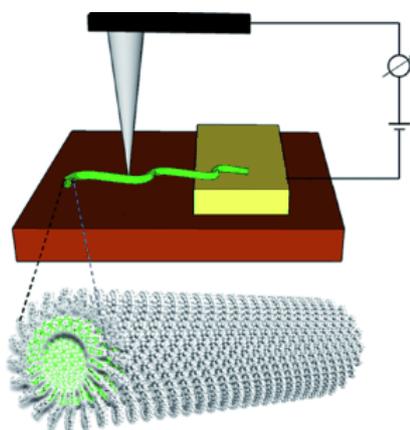


A p-doped conjugated cyclophane! The six boron atoms of the bora-cyclophane (see picture) recently reported by Chen and Jäkle team up to impart a set of unique properties to this novel macrocycle. In particular, this macrocycle undergoes six consecutive reversible reductions to afford the hexaanion. It also binds up to six small nucleophilic anions, a process that quenches the fluorescence of the ring and changes its character to electron-rich.

- Biosupramolecular Nanowires from Chlorophyll Dyes with Exceptional Charge-Transport Properties

Sengupta, S.; Ebeling, D.; Patwardhan, S.; Zhang, X.; vonBerlepsch, H.; Böttcher, C.; Stepanenko, V.; Uemura, S.; Hentschel, C.; Fuchs, H.; Grozema, F. C.; Siebbeles, L. D. A.; Holzwarth, A. R.; Chi, L.; Würthner, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 6378-6382.

Abstract:

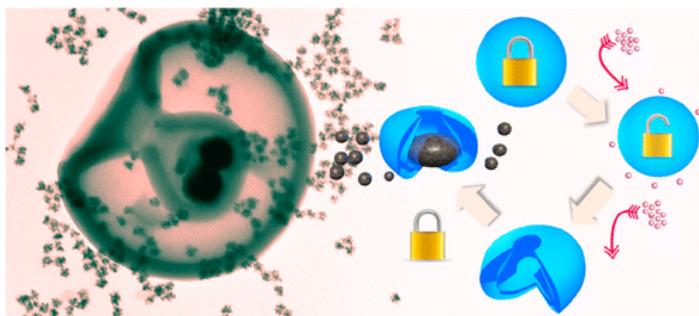


Conductive tubes: Self-assembled nanotubes of a bacteriochlorophyll derivative are reminiscent of natural chlorosomal light-harvesting assemblies. After deposition on a substrate that consists of a non-conductive silicon oxide surface (see picture, brown) and contacting the chlorin nanowires to a conductive polymer (yellow), they show exceptional charge-transport properties.

- Entrapment of Metal Nanoparticles in Polymer Stomatocytes

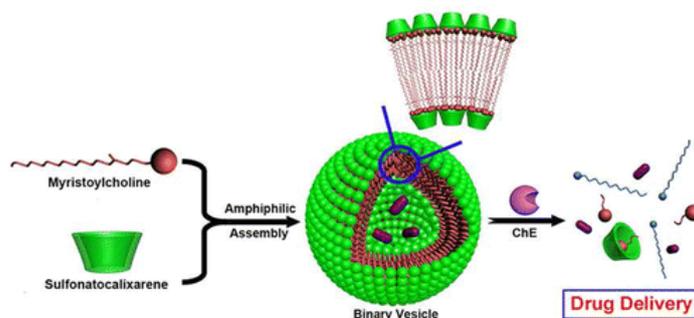
Wilson, D. A.; Nolte, R. J. M.; van Hest, J. C. M. *J. Am. Chem. Soc.* **2012**, *134*, 9894–9897.

Abstract:



Polymersomes assembled from amphiphilic block copolymers containing a glassy hydrophobic segment can be further re-engineered to perform a controlled shape transformation from a thermodynamically stable spherical morphology to a kinetically trapped stomatocyte structure. The stable bowl-shape stomatocyte morphology is ideal for the specific physical entrapment of nanoparticles for potential use in heterogeneous catalysis and drug delivery. Herein we report two approaches to obtain a selective and controlled entrapment of platinum nanoparticles (PtNP) of different sizes and shapes inside the stomatocyte structure. In the first approach, the stomach of the stomatocytes is used to template the growth of the PtNP by controlling and confining the nucleation points inside the cavity. In the second method, preformed nanoparticles are engulfed during the stomatocyte formation process. Synergistically, the reverse effect is observed, that is, differently shaped nanoparticles were shown to exhibit a templating effect on the stomach formation of the stomatocytes.

- Cholinesterase-Responsive Supramolecular Vesicle
Guo, D.-S.; Wang, K.; Wang, Y.-X.; Liu, Y. *J. Am. Chem. Soc.* **2012**, *134*, 10244–10250.
Abstract:



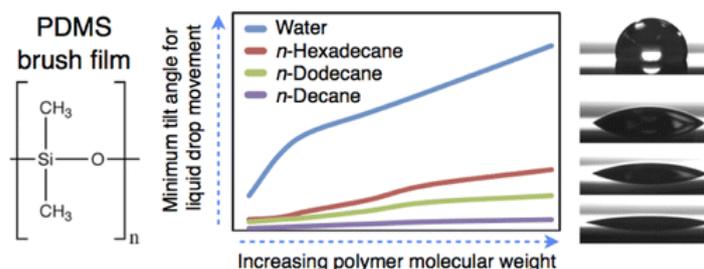
Enzyme-responsive, amphiphilic self-assembly represents one of the increasingly significant topics in biomaterials research and finds feasible applications to the controlled release of therapeutic agents at specific sites where the target enzyme is located. The supramolecular approach, using “superamphiphiles”, provides a smart way to fabricate drug delivery systems responsive to enzymatic catalysis. In this work based on the concept of supramolecular chemistry, we report an enzyme-responsive vesicle using *p*-sulfonatocalix[4]arene as the macrocyclic host and natural enzyme-cleavable myristoylcholine as the guest molecule. The complexation of *p*-sulfonatocalix[4]arene with myristoylcholine directs the formation of a supramolecular binary vesicle, which is dissipated by cholinesterase with high specificity and efficiency. Cholinesterase is a key protein overexpressed in Alzheimer’s disease, and therefore, the present system may have potential for the delivery of Alzheimer’s disease drugs.

- A Physical Approach To Specifically Improve the Mobility of Alkane Liquid Drops

Cheng, D. F.; Urata, C.; Mashed, B.; Hozumi, A. *J. Am. Chem. Soc.* **2012**, *134*, 10191–10199.

Abstract:

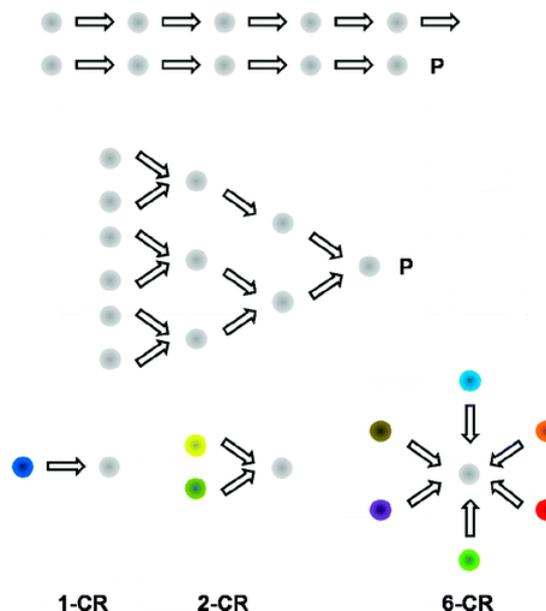
10



Seamless control of resistance to liquid drop movement for polar (water) and nonpolar alkane (*n*-hexadecane, *n*-dodecane, and *n*-decane) probe liquids on substrate surfaces was successfully demonstrated using molten linear poly(dimethylsiloxane) (PDMS) brush films with a range of different molecular weights (MWs). The ease of movement of liquid drops critically depended on polymer chain mobility as it relates to both polymer MW and solvent swelling on these chemically- and topographically identical surfaces. Our brush films therefore displayed lower resistances to liquid drop movement with decreasing polymer MW and surface tension of probe liquid as measured by contact angle (CA) hysteresis and tilt angle measurements. Subsequently, while mobility of water drops was inferior and became worse at higher MWs, *n*-decane drops were found to experience little resistance to movement on these polymer brush films. Calculating CA hysteresis as $\Delta\theta_{\cos} = \cos \theta_R - \cos \theta_A$ (θ_A and θ_R are the advancing and receding CAs, respectively) rather than the standard $\Delta\theta = \theta_A - \theta_R$ was found to be advantageous for estimation of the actual dynamic dewetting behavior of various probe liquids on an inclined substrate.

- Chemistry and Biology Of Multicomponent Reactions
Dömling, A.; Wang, W.; Wang, K. *Chem. Rev.* **2012**, *112*, 3083–3135.

Abstract:

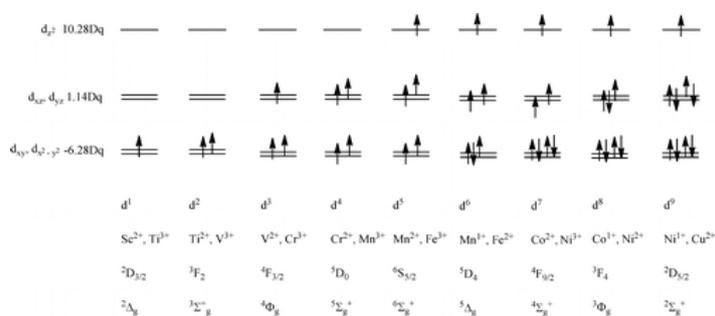


Multicomponent reactions (MCRs) are one-pot reactions employing more than two starting materials, where most of the atoms of the starting materials are incorporated in the final product. Several descriptive tags are regularly attached to MCRs they are atom economic, for example, the majority if not all of the atoms of the starting materials are incorporated in the product; they are efficient, for example, they efficiently yield the product since the product is formed in one-step

instead of multiple sequential steps; they are convergent, for example, several starting materials combine in one reaction to form the product; they exhibit a very high bond-forming-index (BFI), for example, several non-hydrogen atom bonds are formed in one synthetic transformation. Therefore MCRs are often a useful alternative to sequential multistep synthesis. Additionally, since MCRs are often highly compatible with a range of unprotected orthogonal functional groups, on a second level, the scaffold diversity of MCR can be greatly enhanced by the introduction of orthogonal functional groups into the primary MCR product and reacting them in subsequent transformations, e.g. ring forming reaction. This two layered strategy has been extremely fruitful in the past leading to a great manifold of scaffolds now routinely used in combinatorial and medicinal chemistry for drug discovery purposes.

- Stable Two-Coordinate, Open-Shell (d^1 – d^9) Transition Metal Complexes
Power, P. P. *Chem. Rev.* **2012**, *112*, 3482–3507.

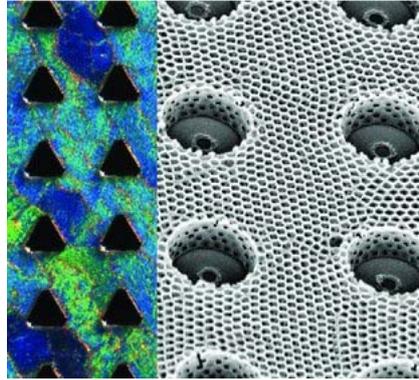
Abstract:



Stable, open-shell (d^1 – d^9) transition metal complexes in which the metal is two-coordinate or quasi-two-coordinate are among the rarest and least investigated species in coordination chemistry. Their scarcity is due to several factors. Foremost among these is the difficulty in preventing association of monomeric coordinatively unsaturated two-coordinate species to give aggregates or extended ionic lattices in which the metal coordination number is increased to four or six. Despite these difficulties, the two-coordinate complexes are attracting attention for several reasons. A major one is that the transition metal, which is complexed through just two atoms, has a very high degree of coordinative unsaturation with several open or singly occupied valence orbitals. This facilitates a rich coordination chemistry spanning a wide variety of substitution, addition, or oxidation reactions. In addition, the two-coordinate complexes, particularly those of iron, have been shown to be useful synthetic precursors for the synthesis of nanomaterials and well-defined catalytic sites. Two-coordinate complexes are also of interest because of their magnetic properties.

- Patterning Hierarchy in Direct and Inverse Opal Crystals
Mishchenko, L.; Hatton, B.; Kolle, M.; Aizenberg, J. *Small* **2012**, *8*, 1904–1911.

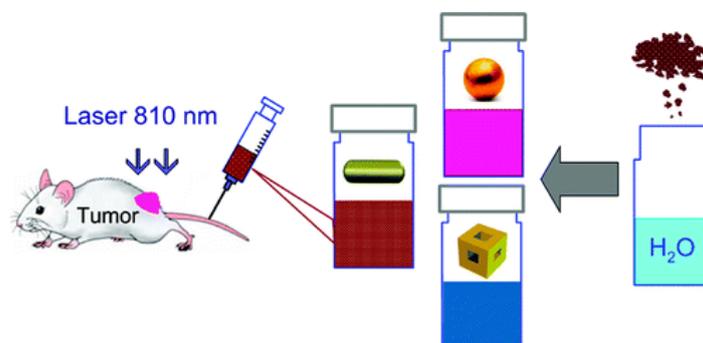
Abstract:



Biological strategies for bottom-up synthesis of inorganic crystalline and amorphous materials within topographic templates have recently become an attractive approach for fabricating complex synthetic structures. Inspired by these strategies, herein the synthesis of multi-layered, hierarchical inverse colloidal crystal films formed directly on topographically patterned substrates via evaporative deposition, or “co-assembly”, of polymeric spheres with a silicate sol–gel precursor solution and subsequent removal of the colloidal template, is described. The response of this growing composite colloid–silica system to artificially imposed 3D spatial constraints of various geometries is systematically studied, and compared with that of direct colloidal crystal assembly on the same template. Substrates designed with arrays of rectangular, triangular, and hexagonal prisms and cylinders are shown to control crystallographic domain nucleation and orientation of the direct and inverse opals. With this bottom-up topographical approach, it is demonstrated that the system can be manipulated to either form large patterned single crystals, or crystals with a fine-tuned extent of disorder, and to nucleate distinct colloidal domains of a defined size, location, and orientation in a wide range of length-scales. The resulting ordered, quasi-ordered, and disordered colloidal crystal films show distinct optical properties. Therefore, this method provides a means of controlling bottom-up synthesis of complex, hierarchical direct and inverse opal structures designed for altering optical properties and increased functionality.

- Plasmonic Nanopowders for Photothermal Therapy of Tumors
Khlebtsov, B. N.; Panfilova, E. V.; Terentyuk, G. S.; Maksimova, I. L.; Ivanov, A. V.; Khlebtsov, N. G. *Langmuir* **2012**, *28*, 8994-9002.

Abstract:

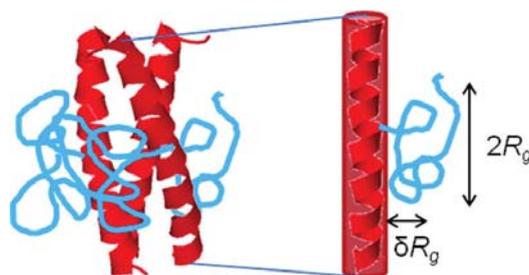


We describe a novel strategy for the fabrication of plasmonic nanopowders (dried gold nanoparticles) by using wet chemical nanoparticle synthesis, PEG-SH functionalization, and a standard freeze-drying technique. Our strategy is illustrated by successful fabrication of different plasmonic nanopowders, including gold nanorods, gold–silver nanocages, and gold nanospheres. Importantly, the dried nanoparticles can be stored for a long time under usual conditions and then

can easily be dissolved in water at a desired concentration without such hard manipulations as sonication or heating. Redispersed samples maintain the plasmonic properties of parent colloids and do not form aggregates. These properties make pegylated freeze-dried gold nanoparticles attractive candidates for plasmonic photothermal therapy in clinical settings. In this work, redispersed gold nanorods were intravenously administered to mice bearing Ehrlich carcinoma tumors at doses of 2 and 8 mg (Au)/kg (animal). Particle biodistribution was measured by atomic absorption spectroscopy, and tumor hyperthermia effects were studied under laser NIR irradiation. Significant tumor damage was observed only at the higher dose of the nanorods.

- Solution Structural Characterization of Coiled-Coil Peptide–Polymer Side-Conjugates
Shu, J. Y.; Lund, R.; Xu, T. *Biomacromolecules* **2012**, *13*, 1945–1955.

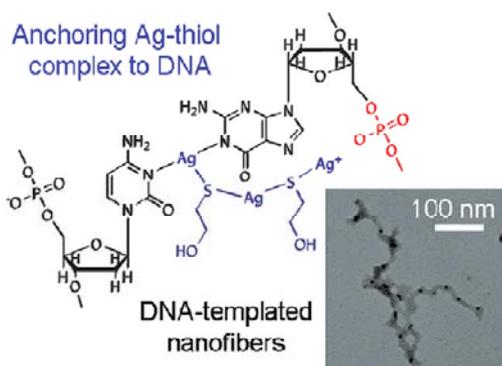
Abstract:



Detailed structural characterization of protein–polymer conjugates and understanding of the interactions between covalently attached polymers and biomolecules will build a foundation to design and synthesize hybrid biomaterials. Conjugates based on simple protein structures are ideal model system to achieve these ends. Here we present a systematic structural study of coiled-coil peptide–poly(ethylene glycol) (PEG) side-conjugates in solution, using circular dichroism, dynamic light scattering, and small-angle X-ray scattering, to determine the conformation of conjugated PEG chains. The overall size and shape of side-conjugates were determined using a cylindrical form factor model. Detailed structural information of the covalently attached PEG chains was extracted using a newly developed model where each peptide–PEG conjugate was modeled as a Gaussian chain attached to a cylinder, which was further arranged in a bundle-like configuration of three or four cylinders. The peptide–polymer side-conjugates were found to retain helix bundle structure, with the polymers slightly compressed in comparison with the conformation of free polymers in solution. Such detailed structural characterization of the peptide–polymer conjugates, which elucidates the conformation of conjugated PEG around the peptide and assesses the effect of PEG on peptide structure, will contribute to the rational design of this new family of soft materials.

- Thiol-Mediated Anchoring of Silver Cations to DNA for Construction of Nanofibers on DNA Scaffold
Zinchenk, A. A.; Chen, N.; Baigl, D.; Lopatina, L. I.; Sergeyev, V. G. *Biomacromolecules* **2012**, *13*, 1787–1793.

Abstract:

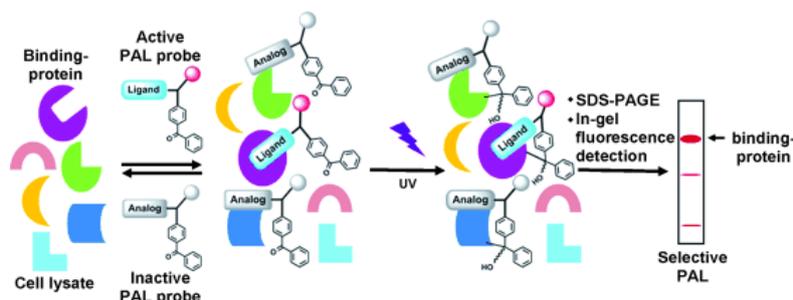


The formation of metal-containing Ag-mercaptoethanol ($-\text{Ag-S(R)}-)_n$ complexes on DNA chain scaffold was studied by UV spectroscopy, zeta potential measurement, and fluorescence and transmission electron microscopies. Experimental results made clear the mechanism of DNA mineralization and compaction, according to which intercalation of silver cations into DNA scaffold and further formation of $(-\text{Ag-S(R)}-)_n$ oligomeric complexes on DNA induce efficient DNA chain compaction by terminal Ag^+ cations. By transmission electron microscopy the formation of fiber-like DNA-templated nanostructures was observed. DNA-Ag-thiol complexes are promising for DNA-templated engineering of hybrid 1D nanostructures with adjustable chemical functionalities by choosing appropriate thiol ligand.

- Active/Inactive Dual-Probe System for Selective Photoaffinity Labeling of Small Molecule-Binding Proteins

Sakurai, K.; Tawa, M.; Okada, A.; Yamada, R.; Sato, N.; Inahara, M.; Inoue, M. *Chem. Asian J.* **2012**, *7*, 1567–1571.

Abstract:



Two are better than one: A new approach to selective photoaffinity labeling is described in which a bioactive probe is used in combination with its inactive analog as a scavenger of nonspecific proteins.

- Microwave-Enhanced Solid-Phase Synthesis of N,N' -Linked Aliphatic Oligoureas and Related Hybrids

Douat-Casassus, C.; Pulka, K.; Claudon, P.; Guichard, G. *Org. Lett.* **2012**, *14*, 3130-3133.

Abstract:

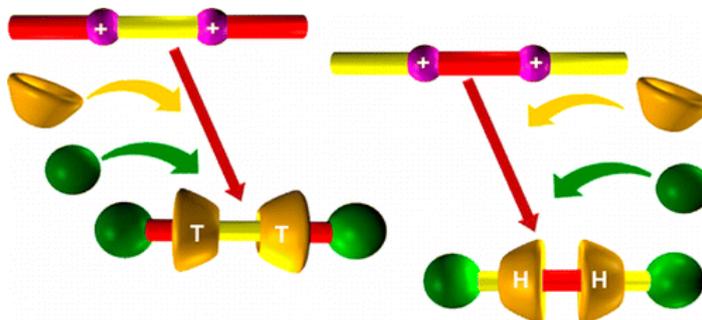


A practical and efficient microwave-assisted solid-phase method for the synthesis of N,N' -linked oligoureas and related amide/urea hybrid oligomers, featuring the use of succinimidyl (2-azido-2-substituted ethyl) carbamate monomers, is reported. The rate enhancement of urea formation under

microwave irradiation combined with the mild conditions of the phosphine-based azide reduction makes this approach very effective for routine synthesis of oligoureas and possibly for library production.

- Stereoprogrammed Direct Synthesis of Calixarene-Based [3]Rotaxanes
Talotta, C.; Gaeta, C.; Neri, P. *Org. Lett.* **2012**, *14*, 3104-3107.

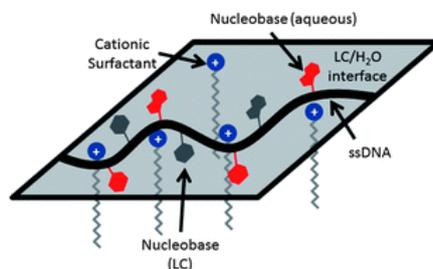
Abstract:



Directional calixarene wheels were threaded along a bis(benzylalkylammonium) axle in a stereoprogrammed way to obtain the first examples of calixarene-based [3]rotaxanes. The base/acid treatment demonstrated that these systems act as nanosized molecular shuttles. An unprecedented switching between the *tail-to-tail* and *head-to-head* relative orientation of the calix-wheels was observed.

- Surfactant–DNA interactions at the liquid crystal–aqueous interface
McUmber, A. C.; Noonan, P. S.; Schwartz, D. K. *Soft Matter* **2012**, *8*, 4335-4342.

Abstract:

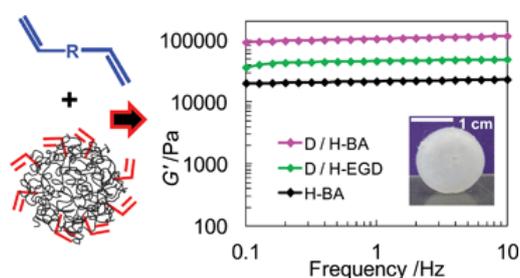


The presence of single-stranded (ssDNA) vs. double-stranded (dsDNA) DNA at a surfactant-laden aqueous–nematic liquid crystal (LC) interface results in distinctly different orientations of the LC molecular axis; this is of practical interest as a method to detect DNA hybridization. Results presented here provide new insights into the molecular-level mechanisms of these phenomena. The adsorption of ssDNA to a cationic surfactant-laden aqueous–LC interface caused LC reorientation, leading to coexistence between homeotropic and planar (birefringent) oriented regions. Fluorescence microscopy revealed that ssDNA preferentially partitioned into the birefringent regions, presumably causing a decreased surface coverage of surfactant and the resultant planar LC orientation. Both electrostatic and hydrophobic effects were found to be critical to inducing LC reorientation. In particular, insufficient ssDNA adsorption occurred in the absence of a cationic surfactant (*e.g.* with no surfactant or with a non-ionic surfactant), demonstrating the importance of electrostatic interactions with the polyanionic ssDNA. Even in the presence of a cationic surfactant, however, polyanions without hydrophobic side-group moieties (poly[acrylic acid] and dsDNA) caused no LC reorientation, while polyanions with hydrophobic side groups (polystyrene sulfonate and ssDNA) initiated the desired LC reorientation. These observations are consistent with the fact that

interfacial hybridization of adsorbed probe ssDNA to complementary target ssDNA caused a reorientation from planar back to homeotropic. We propose that ssDNA forms an electrostatic interfacial complex with cationic surfactant where the hydrophobic nucleobases associate directly with the LC phase, effectively competing with surfactant molecules for interfacial sites. Upon hybridization, the hydrophobic character of the ssDNA is lost and the nucleobases no longer associate directly with the LC phase, allowing the surfactant molecules to pack more closely at the interface.

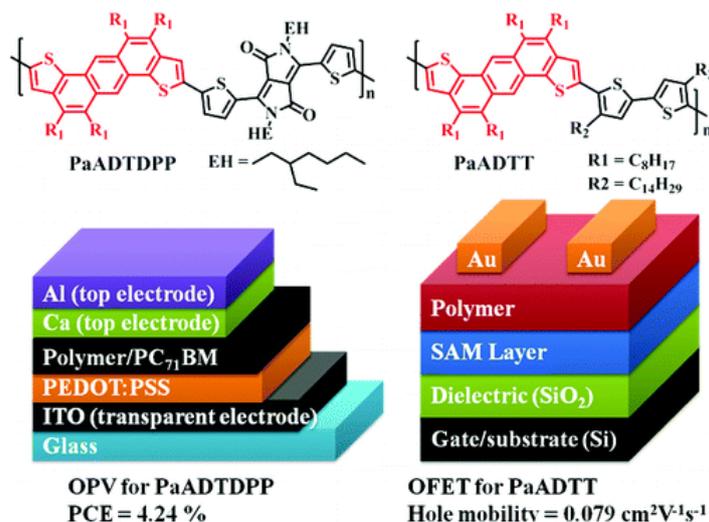
- A study of hydrogel composites containing pH-responsive doubly crosslinked microgels Supasuteekul, C.; Milani, A. H.; Saunders, J. M.; Lally, S.; Freemont, T.; Saunders, B. R. *Soft Matter* **2012**, *8*, 3234-3242.

Abstract:



Recently, our group established a new approach for preparing injectable hydrogels using vinyl-functionalised pH-responsive microgel particles [Liu *et al.*, *Soft Matter*, 2011, **7**, 4696]. pH-responsive microgels swell when the pH approaches the pK_a of the particles. Liu *et al.* used inter-particle crosslinking of vinyl-functionalised microgel particles to prepare hydrogels composed of doubly crosslinked microgels (D-microgels). Here, we combine vinyl-functionalised microgels with added, small-molecule, crosslinkers to prepare high modulus D-microgel/hydrogel (H-X) composites for the first time. The vinyl-functionalised microgel particles used were poly(EA/MAA/BDD)/GM; where, EA, MAA, BDD and GM are ethyl acrylate and methacrylic acid, 1,4-butanediol diacrylate and glycidyl methacrylate, respectively. Two added crosslinkers were used to demonstrate the versatility of our approach. They were ethyleneglycol dimethacrylate (EGD) and *N,N'*-methylenebisacrylamide (BA). We compare the data to control hydrogel composites prepared using non-vinyl-functionalised singly crosslinked microgels (S-microgels). All of the composites showed pH-dependent swelling behaviours and mechanical properties. The storage modulus value for the as-made D-microgel/H-EGD composite was 0.12 MPa and is the highest reported to date for a hydrogel containing pH-responsive microgels. The as-made control S-microgel/H-X composites had high ductilities. Dynamic rheology data were used to determine the effects of vinyl functionalisation on the composite mechanical properties. All of the composites exhibited pH-dependent swelling and a “breathing in” transition occurred. The swollen D-microgel/H-X composites retained their high modulus values upon swelling; although, their ductilities decreased. Because we used two different crosslinkers and pH-responsive microgels containing carboxylic acid groups, the method introduced here for preparing high modulus hydrogel composites should be widely applicable.

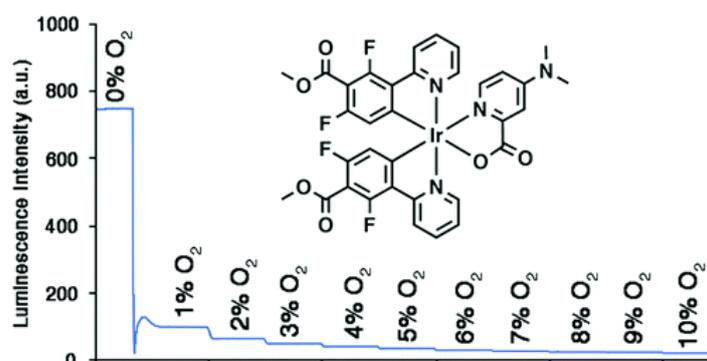
- New Angular-Shaped and Isomerically Pure Anthradithiophene with Lateral Aliphatic Side Chains for Conjugated Polymers: Synthesis, Characterization, and Implications for Solution-Processed Organic Field-Effect Transistors and Photovoltaics Wu, J.-S.; Lin, C.-T.; Wang, C.-L.; Cheng, Y.-J.; Hsu, C.-S. *Chem. Mater.* **2012**, *24*, 2391–2399.

Abstract:

An isomerically pure anti-anthradithiophene (aADT) arranged in an angular shape is developed. Formation of the framework of aADT incorporating four lateral alkyl substituents was accomplished by a one-pot benzannulation via multiple Suzuki coupling. This newly designed 2,8-stannylated aADT monomer was copolymerized with a dithenodiketopyrrolopyrrole (DPP) unit and a bithiophene unit, respectively, to furnish an alternating donor–acceptor copolymer poly(anthradithiophene-*alt*-dithienyldiketopyrrolopyrrole) (**PaADTDPP**) and a thiophene-rich poly(anthradithiophene-*alt*-bithiophene) (**PaADTT**). **PaADTT** with crystalline nature achieved a high FET mobility of $7.9 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an on–off ratio of 1.1×10^7 . The photovoltaic device based on the **PaADTDPP**:PC₇₁BM (1:2.5, w/w) blend exhibited a V_{oc} of 0.66 V, a J_{sc} of 9.49 mA/cm², and a FF of 58.4%, delivering a power conversion efficiency (PCE) of 3.66%. By adding 1.5 vol % 1-chloronaphthalene (CN) as a processing additive, the PCE can be improved to 4.24%. We demonstrated that these angular-shaped and alkylated aADT-based polymers have better organic photovoltaic (OPVs) and field-effect transistor (FETs) characteristics than the linear-shaped ADT-containing polymers.

- Nanocomposites Containing Neutral Blue Emitting Cyclometalated Iridium(III) Emitters for Oxygen Sensing

Marín-Suárez, M.; Curchod, B. F. E.; Tavernelli, I.; Rothlisberger, U.; Scopelliti, R.; Jung, I.; Di Senso, D.; Grätzel, M.; Fernández-Sánchez, J. F.; Fernández-Gutiérrez, A.; Nazeeruddin, Md. K.; Baranoff, E. *Chem. Mater.* **2012**, *24*, 2330–2338.

Abstract:

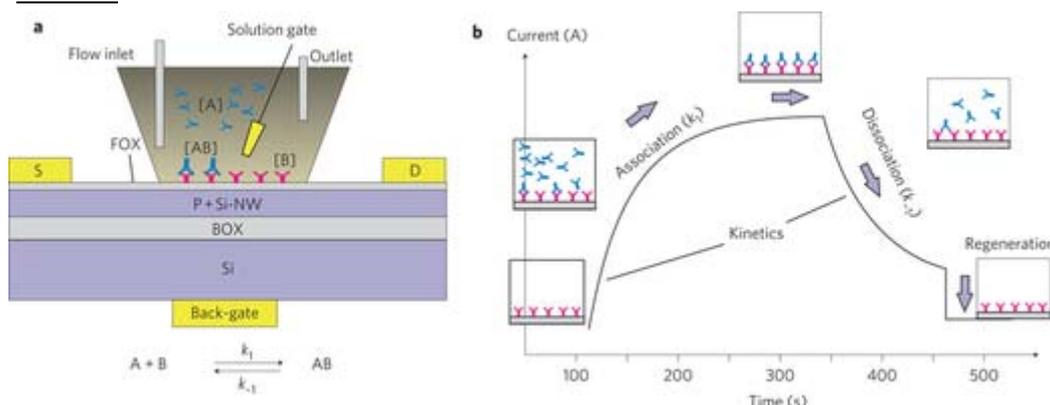
The behavior toward oxygen sensing of nanocomposites made of the aluminum oxide-hydroxide nanostructured solid support (AP200/19) and neutral blue emitting cyclometalated iridium(III) complexes was studied. The results are compared with the same dyes immobilized in polystyrene

films. Since the photoluminescence of the complexes is totally quenched for oxygen concentrations just over 10%, these systems using the blue region of the visible spectrum are promising for oxygen detection at low concentration. In particular, dyes supported into the AP200/19 provide the best sensitivity to oxygen concentration, with the possibility to detect oxygen below 1% O₂ in gas (0.01 bar).

- Quantification of the affinities and kinetics of protein interactions using silicon nanowire biosensors

Duan, X.; Li, Y.; Rajan, N. K.; Routenberg, D. A.; Modis, Y.; Reed, M. A. *Nature Nanotech.* **2012**, 7, 401–407.

Abstract:

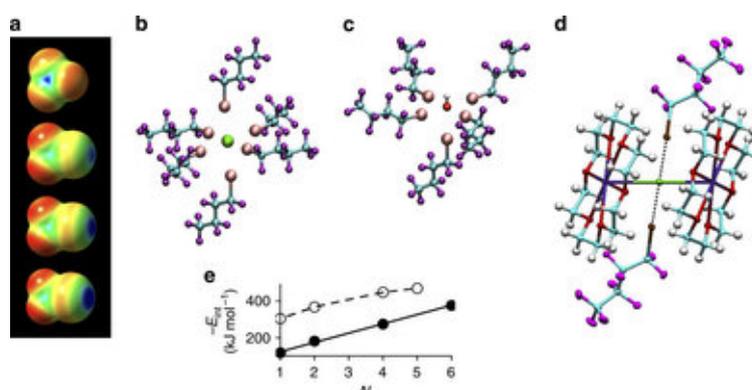


Monitoring the binding affinities and kinetics of protein interactions is important in clinical diagnostics and drug development because such information is used to identify new therapeutic candidates. Surface plasmon resonance is at present the standard method used for such analysis, but this is limited by low sensitivity and low-throughput analysis. Here, we show that silicon nanowire field-effect transistors can be used as biosensors to measure protein–ligand binding affinities and kinetics with sensitivities down to femtomolar concentrations. Based on this sensing mechanism, we develop an analytical model to calibrate the sensor response and quantify the molecular binding affinities of two representative protein–ligand binding pairs. The rate constant of the association and dissociation of the protein–ligand pair is determined by monitoring the reaction kinetics, demonstrating that silicon nanowire field-effect transistors can be readily used as high-throughput biosensors to quantify protein interactions.

- Transmembrane anion transport mediated by halogen-bond donors

Jentzsch, A. V.; Emery, D.; Mareda, J.; Nayak, S. K.; Metrangolo, P.; Resnati, G.; Sakai, N.; Matile, S. *Nature Communications* **2012**, 3, 905.

Abstract:



In biology and chemistry, the transport of anions across lipid bilayer membranes is usually achieved by sophisticated supramolecular architectures. Significant size reduction of transporters is hampered by the intrinsically hydrophilic nature of typical anion-binding functionalities, hydrogen-bond donors or cations. To maximize the atom efficiency of anion transport, the hydrophobic nature, directionality, and strength of halogen bonds seem promising. Unlike the ubiquitous, structurally similar hydrogen bonds, halogen bonds have not been explored for anion transport. Here we report that transport across lipid bilayers can be achieved with small perfluorinated molecules that are equipped with strong halogen-bond donors. Transport is observed with trifluoroiodomethane (boiling point = $-22\text{ }^{\circ}\text{C}$); that is, it acts as a 'single-carbon' transporter. Contrary to the destructive action of small-molecule detergents, transport with halogen bonds is leakage-free, cooperative, non-ohmic and highly selective, with anion/cation permeability ratios <37 .