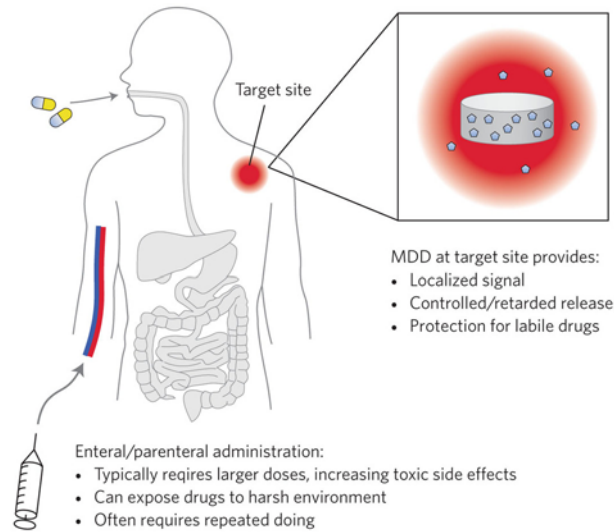


- Macroscale delivery systems for molecular and cellular payloads
Kearney, C. J.; Mooney, D. J. *Nature Mater.* **2013**, *12*, 1004–1017.

Abstract:

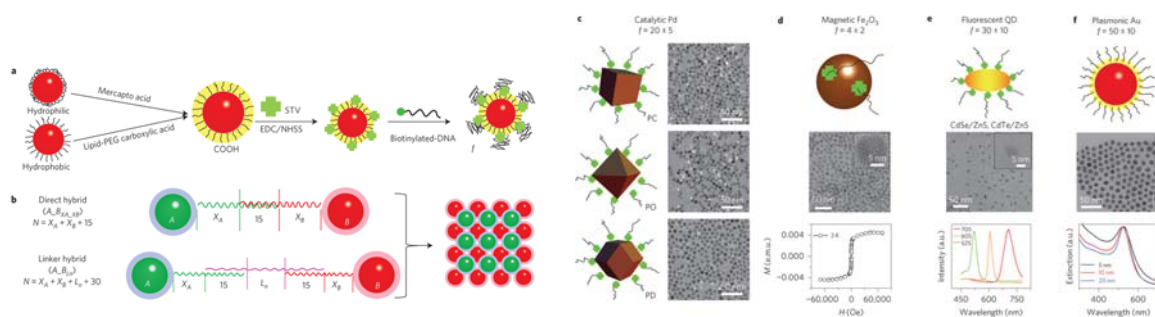


Macroscale drug delivery (MDD) devices are engineered to exert spatiotemporal control over the presentation of a wide range of bioactive agents, including small molecules, proteins and cells. In contrast to systemically delivered drugs, MDD systems act as a depot of drug localized to the treatment site, which can increase drug effectiveness while reducing side effects and confer protection to labile drugs. In this Review, we highlight the key advantages of MDD systems, describe their mechanisms of spatiotemporal control and provide guidelines for the selection of carrier materials. We also discuss the combination of MDD technologies with classic medical devices to create multifunctional MDD devices that improve integration with host tissue, and the use of MDD technology in tissue-engineering strategies to direct cell behaviour. As our ever-expanding knowledge of human biology and disease provides new therapeutic targets that require precise control over their application, the importance of MDD devices in medicine is expected to increase.

- A general strategy for the DNA-mediated self-assembly of functional nanoparticles into heterogeneous systems

Zhang, Y.; Lu, F.; Yager, K. G.; van der Lelie, D.; Gang, O. *Nature Nanotech.* **2013**, *8*, 865–872.

Abstract:



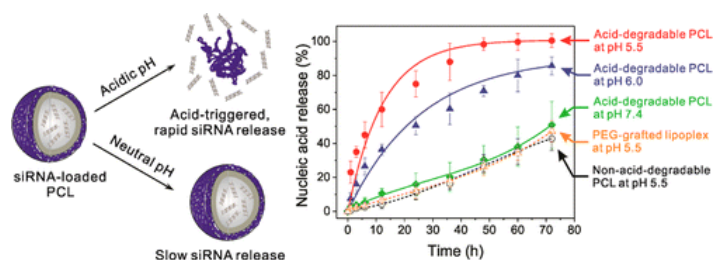
Nanoparticles coated with DNA molecules can be programmed to self-assemble into three-dimensional superlattices. Such superlattices can be made from nanoparticles with different functionalities and could potentially exploit the synergetic properties of the nanoscale components. However, the approach has so far been used primarily with single-component systems. Here, we report a general strategy for the creation of heterogeneous nanoparticle superlattices using DNA and

carboxylic-based conjugation. We show that nanoparticles with all major types of functionality— plasmonic (gold), magnetic (Fe_2O_3), catalytic (palladium) and luminescent (CdSe/Te@ZnS and CdSe@ZnS)—can be incorporated into binary systems in a rational manner. We also examine the effect of nanoparticle characteristics (including size, shape, number of DNA per particle and DNA flexibility) on the phase behaviour of the heterosystems, and demonstrate that the assembled materials can have novel optical and field-responsive properties.

- Acid-Degradable Polymer-Caged Lipoplex (PCL) Platform for siRNA Delivery: Facile Cellular Triggered Release of siRNA

Hong, B. J.; Chipre, A. J.; Nguyen, S. B. T. *J. Am. Chem. Soc.* **2013**, *135*, 17655-17658.

Abstract:

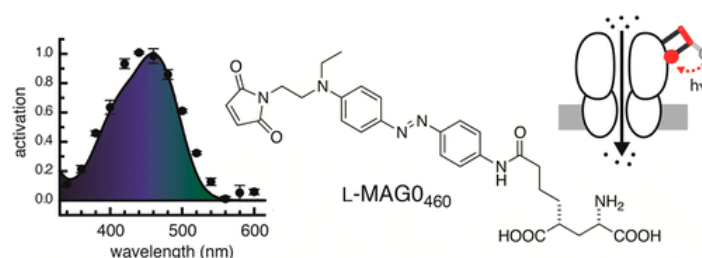


An acid-degradable polymer-caged lipoplex (PCL) platform consisting of a cationic lipoplex core and a biocompatible, pH-responsive polymer shell has been developed for the effective delivery of small interfering RNA (siRNA) through a combination of facile loading, rapid acid-triggered release, cellular internalization, and effective endosomal escape. In vitro testing of this degradable PCL delivery platform reveals ~45- and ~2.5-fold enhancement of enhanced green fluorescent protein knockdown in cancer cells in comparison to either free siRNA or siRNA-loaded non-acid-degradable lipoplex formulations, respectively.

- A Red-Shifted, Fast-Relaxing Azobenzene Photoswitch for Visible Light Control of an Ionotropic Glutamate Receptor

Kienzler, M. A.; Reiner, A.; Trautman, E.; Yoo, S.; Trauner, D.; Isacoff, E. Y. *J. Am. Chem. Soc.* **2013**, *135*, 17683-17686.

Abstract:

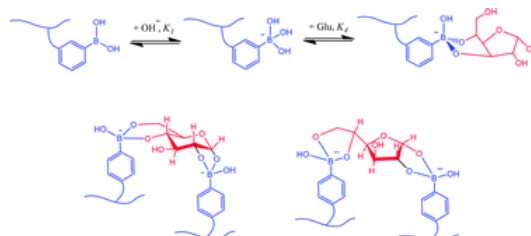


The use of azobenzene photoswitches has become a dependable method for rapid and exact modulation of biological processes and material science systems. The requirement of ultraviolet light for azobenzene isomerization is not ideal for biological systems due to poor tissue penetration and potentially damaging effects. While modified azobenzene cores with a red-shifted cis-to-trans isomerization have been previously described, they have not yet been incorporated into a powerful method to control protein function: the photoswitchable tethered ligand (PTL) approach. We report the synthesis and characterization of a red-shifted PTL, L-MAGO₄₆₀, for the light-gated ionotropic glutamate receptor LiGluR. In cultured mammalian cells, the LiGluR+L-MAGO₄₆₀ system is activated rapidly by illumination with 400-520 nm light to generate a large ionic current. The current

rapidly turns off in the dark as the PTL relaxes thermally back to the trans configuration. The visible light excitation and single-wavelength behavior considerably simplify use and should improve utilization in tissue.

- Boronic acid-containing hydrogels: synthesis and their applications
Guana, Y.; Zhang, Y. *Chem. Soc. Rev.* **2013**, *42*, 8106-8121.

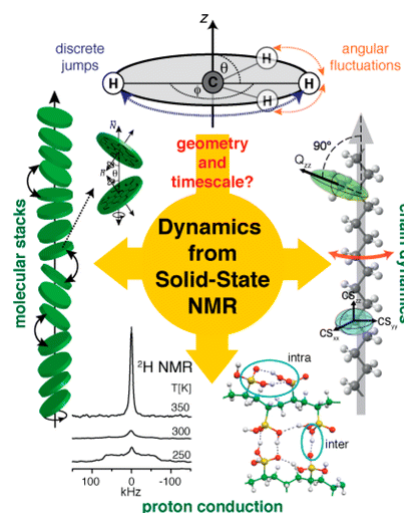
Abstract:



Boronic acid-containing hydrogels are important intelligent materials. With the introduction of boronic acid functionality, these hydrogels exhibit a lot of interesting properties, such as glucose-sensitivity, reversibility and self-healing. These materials have found important applications in many areas, especially in biomedical areas. This paper aims to provide an overview of the current state of the art of the study in this area. We review the synthesis and properties of various boronic acid-containing hydrogels, including macroscopic hydrogels, microgels and layer-by-layer self-assembled films. Their applications were described, with an emphasis on the design of various glucose sensors and self-regulated insulin delivery devices. New development in this area was highlighted. Problems and the new directions were discussed.

- Solid-State NMR in Macromolecular Systems: Insights on How Molecular Entities Move
Hansen, M. R.; Graf, R.; Spiess, H. W. *Acc. Chem. Res.* **2013**, *46*, 1996–2007.

Abstract:



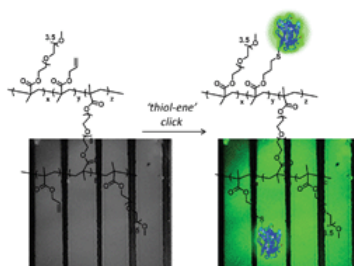
The function of synthetic and natural macromolecular systems critically depends on the packing and dynamics of the individual components of a given system. Not only can solid-state NMR provide structural information with atomic resolution, but it can also provide a way to characterize the amplitude and time scales of motions over broad ranges of length and time. These movements include molecular dynamics, rotational and translational motions of the building blocks, and also the motion of the functional species themselves, such as protons or ions. This Account examines solid-state NMR methods for correlating dynamics and function in a variety of chemical systems.

In the early days, scientists thought that the rotational motions reflected the geometry of the moving entities. They described these phenomena as jumps about well-defined axes, such as phenyl flips, even in amorphous polymers. Later, they realized that conformational transitions in macromolecules happen in a much more complex way. Because the individual entities do not rotate around well-defined axes, they require much less space. Only recently researchers have appreciated the relative importance of large angle fluctuations of polymers over rotational jumps. Researchers have long considered that cooperative motions might be at work, yet only recently they have clearly detected these motions by NMR in macromolecular and supramolecular systems.

In correlations of dynamics and function, local motions do not always provide the mechanism of long-range transport. This idea holds true in ion conduction but also applies to chain transport in polymer melts and semicrystalline polymers. Similar chain motions and ion transport likewise occur in functional biopolymers, systems where solid-state NMR studies are also performed. In polymer science, researchers have appreciated the unique information on molecular dynamics available from advanced solid-state NMR at times, where their colleagues in the biomacromolecular sciences have emphasized structure. By contrast, following X-ray crystallographers, researchers studying proteins using solution NMR introduced the combination of NMR with computer simulation before that became common practice in solid-state NMR. Today's simulation methods can handle partially ordered or even disordered systems common in synthetic polymers. Thus, the multitechnique approaches employed in NMR of synthetic and biological macromolecules have converged. Therefore, this Account will be relevant to both researchers studying synthetic macromolecular and supramolecular systems and those studying biological complexes.

- 'Clickable' hydrogels for all: facile fabrication and functionalization
Beria, L.; Gevrek, T. N.; Erdogan, A.; Sanyal, R.; Pasini, D.; Sanyal, A. *Biomater. Sci.* **2014**, *2*, 67-75.

Abstract:



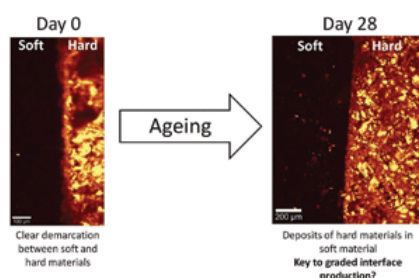
In this study, we report a facile fabrication of poly(ethylene glycol) (PEG) based bulk and micro-patterned hydrogels that are amenable to functionalization with thiol-bearing molecules using the metal-free radical 'thiol-ene' click reaction. The hydrogels were synthesized using photopolymerization of commercially available monomers, namely allyl methacrylate and PEG-methacrylate in the presence of a PEG-dimethacrylate based crosslinker. Swelling behaviour of these hydrogels could be tailored by varying the amount of the hydrophilic monomer in the feed as well as varying the length of the PEG-chain in the methacrylate monomer. Importantly, the extent of functionalization of these hydrogels could be readily tuned by varying the amount of the reactive allyl methacrylate monomer. Analysis of nitrogen content in the hydrogels after conjugation of cysteamine demonstrated that the amount of cysteamine incorporation was in correlation with the amount of allyl groups in the hydrogels. Three-dimensional hydrogel patterns were fabricated using micromolding in capillaries. Tuneable conjugation of a thiol-containing dye molecule and a ligand-

mediated immobilization of streptavidin onto these hydrogel patterns were realized. It was found that the swellability of the hydrogel patterns control the diffusion of streptavidin into the interior of the hydrogel matrix. These bio-inert hydrogels could be appended with peptides to promote cellular adhesion. Furthermore, it was demonstrated that the photochemical thiol-ene based method of conjugation enables localized attachment of thiol-containing molecules within these reactive hydrogels.

- A novel method for monitoring mineralisation in hydrogels at the engineered hard–soft tissue interface

Koburger, S.; Bannerman, A.; Grover, L. M.; Müller, F. A.; Bowen, J.; Paxton, J. Z. *Biomater. Sci.* **2014**, *2*, 41-51.

Abstract:

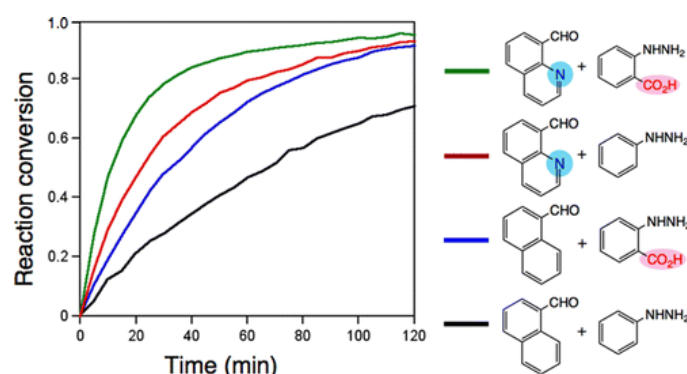


The capacity to study the deposition of mineral within a hydrogel structure is of significant interest to a range of therapies that seek to replace the hard tissues and the hard–soft tissue interface. Here, a method is presented that utilises Confocal Raman microscopy as a tool for monitoring mineralisation within hydrogels. Synthetic hard–soft material interfaces were fabricated by apposing brushite (a sparingly soluble calcium phosphate) and biopolymer gel monoliths. The resulting structures were matured over a period of 28 days in phosphate buffered saline. Confocal Raman microscopy of the interfacial region showed the appearance of calcium phosphate salt deposits away from the original interface within the biopolymeric structures. Furthermore, the appearance of octacalcium phosphate and carbonated hydroxyapatite was observed in the region of the brushite cement opposing the biopolymer gel. This study describes not only a method for analysing these composite structures, but also suggests a method for recapitulating the graduated tissue structures that are often found *in vivo*.

- Fast Hydrazone Reactants: Electronic and Acid/Base Effects Strongly Influence Rate at Biological pH

Kool, E. T.; Park, D-H.; Crisalli, P. J. *Am. Chem. Soc.* **2013**, *135*, 17663–17666.

Abstract:

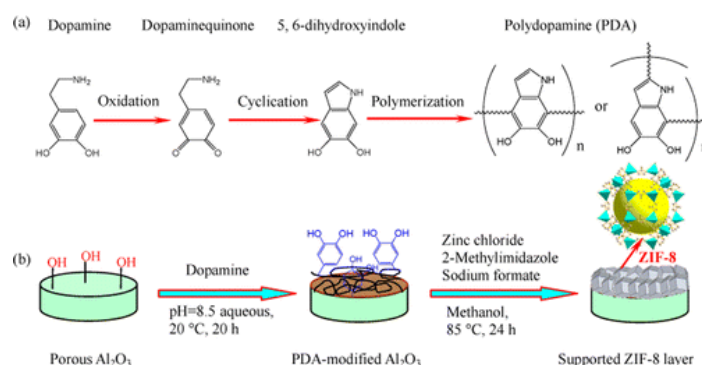


Kinetics studies with structurally varied aldehydes and ketones in aqueous buffer at pH 7.4 reveal that carbonyl compounds with neighboring acid/base groups form hydrazones at accelerated rates. Similarly, tests of a hydrazine with a neighboring carboxylic acid group show that it also reacts at an accelerated rate. Rate constants for the fastest carbonyl/hydrazine combinations are $2\text{--}20\text{ M}^{-1}\text{ s}^{-1}$, which is faster than recent strain-promoted cycloaddition reactions.

- Bio-Inspired Polydopamine: A Versatile and Powerful Platform for Covalent Synthesis of Molecular Sieve Membranes

Liu, Q.; Wang, N.; Caro, J.; Huang, A. *J. Am. Chem. Soc.* **2013**, *135*, 17679–17682.

Abstract:

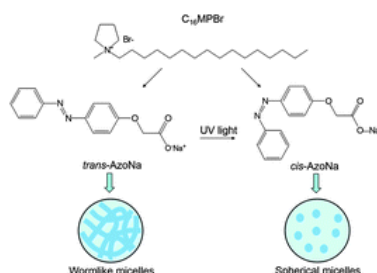


Inspired by the bioadhesive ability of the marine mussel, a simple, versatile, and powerful synthesis strategy was developed to prepare highly reproducible and permselective molecular sieve membranes by using polydopamine as a novel covalent linker. Attributing to the formation of strong covalent and noncovalent bonds, ZIF-8 nutrients are attracted and bound to the support surface, thus promoting the ZIF-8 nucleation and the growth of uniform, well intergrown, and phase-pure ZIF-8 molecular sieve membranes. The developed ZIF-8 membranes show high hydrogen selectivity and thermal stability. At 150 °C and 1 bar , the mixture separation factors of H_2/CO_2 , H_2/N_2 , H_2/CH_4 , and $\text{H}_2/\text{C}_3\text{H}_8$ are 8.9, 16.2, 31.5 and 712.6, with H_2 permeances higher than $1.8 \times 10^{-7}\text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$, which is promising for hydrogen separation and purification.

- Photo-induced transformation from wormlike to spherical micelles based on pyrrolidinium ionic liquids

Yan, H.; Long, Y.; Song, K.; Tung, C.-H.; Zheng, L. *Soft Matter* **2014**, *10*, 115-121.

Abstract:



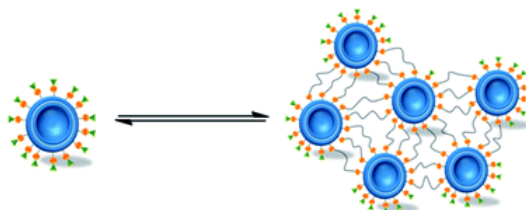
A UV-induced self-assembly based on *N*-methyl-*N*-cetylpyrrolidinium bromide (C_{16}MPBr) and sodium (4-phenylazo-phenoxy)-acetate (AzoNa) was fabricated in the present work through facile mixing of C_{16}MPBr and trans-AzoNa in water. Due to the *trans*–*cis* photoisomerization functionality of the AzoNa, this self-assembly possesses photo-responsive properties. Under ambient conditions, the morphology of the self-assembly was wormlike micelles with a high viscosity of about 10 Pa s , whereas after applying UV light, the self-assembly transformed into spherical micelles with a

dramatically lowered viscosity of about 0.01 Pa s. Different from most reported photo-responsive wormlike micelles consisting of conventional cationic surfactant CTAB, our system was constructed from a novel pyrrolidinium ionic liquid. We hope this study may provide a deeper understanding of photo-responsive wormlike micelles constructed by cationic surfactants and photo-sensitive additives in water.

- Dynamic reactions of liposomes

Berg, S. A.; Ravoo, B. J. *Soft Matter* **2014**, *10*, 69-74.

Abstract:

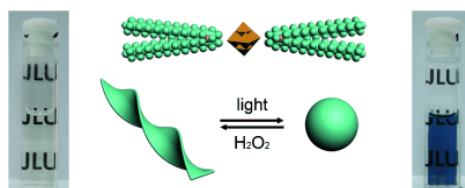


Dynamic chemical reactions at the surface of liposomes are of fundamental interest to the understanding of physiological processes at biological membranes and can be exploited to prepare responsive soft materials. In this paper we describe a covalent yet reversible reaction between liposomes. To this end we explored the reversible thioester exchange reaction of membrane embedded amphiphilic thioesters with dithiols from solution. It was found that thioester exchange leads to the formation of covalent inter-liposomal cross-links and aggregation of liposomes. Liposome aggregation has a characteristic lag phase and the rate of aggregation depends on the concentration of dithiols as well as on the concentration of liposomes in solution. The reversibility of the aggregation could be demonstrated by dissociation of the liposome clusters by the addition of a monothiol. Furthermore we developed a fluorescence anisotropy assay to monitor the thioester exchange reaction on the membrane surface. To the best of our knowledge, the formation of a dynamic covalent network of liposomes is unprecedented.

- Redox-Controlled Helical Self-Assembly of a Polyoxometalate Complex

Zhang, J.; Li, W.; Wu, C.; Li, B.; Zhang, J.; Wu, L. *Chem. Eur. J.* **2013**, *19*, 8129–8135.

Abstract:



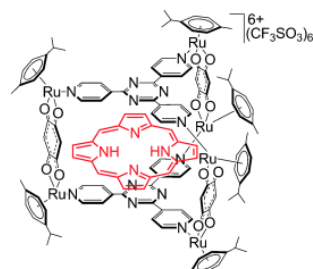
Polyoxometalate (POM) complex $(\text{DODA})_2[\text{Mo}_6\text{O}_{19}]$ with a symmetrical linear structure was prepared conveniently by replacing the tetrabutylammonium (TBA) counterions of Lindquist-type cluster $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$ with cationic surfactant dioctadecyldimethylammonium (DODA). A helical self-assembled structure of the complex was formed in dichloromethane/propanol. The dynamically reversible transformation between helical and spherical assemblies on alternate UV irradiation and H_2O_2 oxidation was characterized by SEM, TEM, and UV/Vis studies. The redox-controlled morphology change is modulated by variation of the electrostatic interactions between the inorganic polyanion and the organic cation DODA through controlling the redox properties of the POM component, as shown by the XRD, X-ray photoelectron spectroscopic, and ^1H NMR measurements.

The strategy applied herein is a unique example of targeted smart and helical assembly of POM complexes.

- Transporting and Shielding Photosensitisers by Using Water-Soluble Organometallic Cages: A New Strategy in Drug Delivery and Photodynamic Therapy

Therrien, B. *Chem. Eur. J.* **2013**, *19*, 8378–8386.

Abstract:

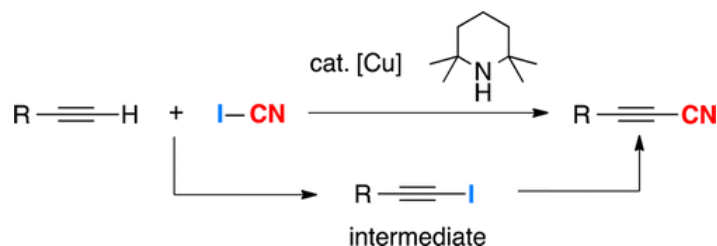


Skin photosensitivity remains one of the main limitations in photodynamic therapy. In this Concept article a strategy to overcome this limitation is described, in which the photosensitizer is hidden inside the hydrophobic cavity of a water-soluble organometallic cage. The metallacage not only protects the photosensitizer from light, it also facilitates its delivery to cancer cells.

- Copper-Catalyzed C–H Cyanation of Terminal Alkynes with Cyanogen Iodide

Okamoto, K.; Watanabe, M.; Sakata, N.; Murai, M.; Ohe, K. *Org. Lett.* **2013**, *15*, 5810-5813.

Abstract:

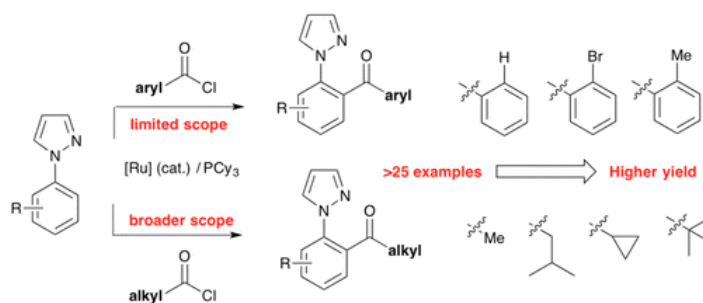


A copper-catalyzed reaction of terminal alkynes with cyanogen iodide (ICN) that produces alkynyl cyanides has been developed. The use of tetramethylpiperidine as a sterically congested base was successful in this reaction. Some control experiments revealed that the reaction involves the noncatalyzed formation of alkynyl iodides followed by copper-catalyzed cyanation of the iodides without the formation of copper(I) acetylide. This observation contrasts with what is normally observed in various copper-mediated reactions using terminal alkynes.

- Ruthenium-Catalyzed C–H Functionalization of Arylpyrazoles: Regioselective Acylation with Acid Chlorides

Liu, P. M.; Frost, C. G. *Org. Lett.* **2013**, *15*, 5862-5865.

Abstract:

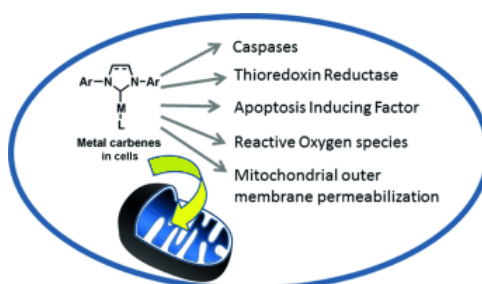


A ruthenium-catalyzed C-H acylation of arylpyrazoles with a variety of acyl chlorides is described. The acylation reaction exhibits good regioselectivity and both aromatic and aliphatic acyl chlorides can be effectively coupled to the arylpyrazoles at the ortho-position.

- Metal/N-Heterocyclic Carbene Complexes: Opportunities for the Development of Anticancer Metallodrugs

Cisnetti, F.; Gautier, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 11976–11978.

Abstract:

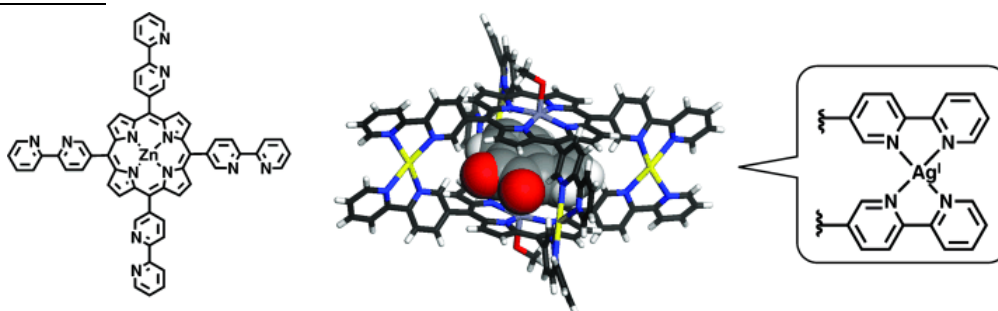


Subtle differences: Two recent crystal structures have provided the first insight into nitrate/nitrite exchangers (example shown with bound nitrite), which are crucial to bacterial metabolism. A direct comparison of the structures reveals how the proteins can distinguish between their highly similar substrates and translate this into a conformational change to translocate ions across the membrane.

- Silver-Mediated Formation of a Cofacial Porphyrin Dimer with the Ability to Intercalate Aromatic Molecules

Nakamura, T.; Ube, H.; Shionoya, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12096–12100.

Abstract:



Guests welcome: Complex formation between Ag^{I} ions and a Zn-porphyrin ligand (**L**) possessing four 2,2'-bipyridyl groups produced a dimeric complex $[\text{Ag}_4\text{L}_2]^{4+}$, wherein the interplane distance between the Zn-porphyrin groups was ideal for intercalation of aromatic molecules through π - π interactions. The cofacial dimer $[\text{Ag}_4\text{L}_2]^{4+}$ serves as an excellent receptor for π -electron-deficient guests.

- Extremely Low Operating Voltage Green Phosphorescent Organic Light-Emitting Devices

Sasabe, H.; Nakanishi, H.; Watanabe, Y.; Yano, S.; Hirasawa, M.; Pu, Y.-J.; Kido, J. *Adv. Mater.* **2013**, *23*, 5550-5555.

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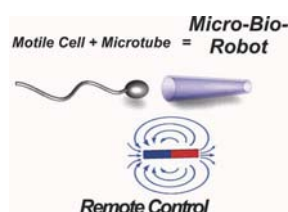
Abstract:



Organic light-emitting devices (OLEDs) are expected to be adopted as the next generation of general lighting because they are more efficient than fluorescent tubes and are mercury-free. The theoretical limit of operating voltage is generally believed to be equal to the energy gap, which corresponds to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the emitter molecule divided by the electron charge (e). Here, green OLEDs operating below a theoretical limit of the energy gap (E_g) voltage with high external quantum efficiency over 20% are demonstrated using fac-tris(2-phenylpyridine)iridium(III) with a peak emission wavelength of 523 nm, which is equivalent to a photon energy of 2.38 eV. An optimized OLED operates clearly below the theoretical limit of the E_g voltage at 2.38 V showing 100 cd m^{-2} at 2.25 V and 5000 cd m^{-2} at 2.95 V without any light outcoupling enhancement techniques.

- Development of a Sperm-Flagella Driven Micro-Bio-Robot
Magdanz, V.; Sanchez, S.; Schmidt, O. G. *Adv. Mater.* **2013**, *25*, 6581-6588.

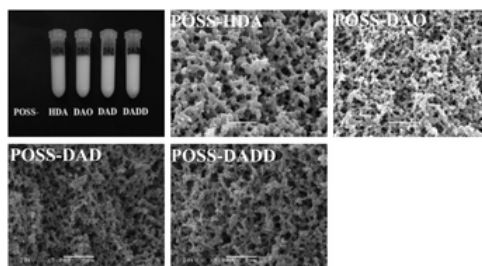
Abstract :



A new biohybrid micro-robot is developed by capturing bovine sperm cells inside magnetic microtubes that use the motile cells as driving force. These micro-bio-robots can be remotely controlled by an external magnetic field. The performance of micro-robots is described in dependence on tube radius, cell penetration, and temperature. The combination of a biological power source and a microdevice is a compelling approach to the development of new microbotic devices with fascinating future applications.

- Ring-opening polymerization reaction of polyhedral oligomeric silsesquioxanes (POSSs) for preparation of well-controlled 3D skeletal hybrid monoliths
Lin, H.; Ou, J.; Zhang, Z.; Dong, J.; Zou, H. *Chem. Commun.* **2013**, *49*, 231-233.

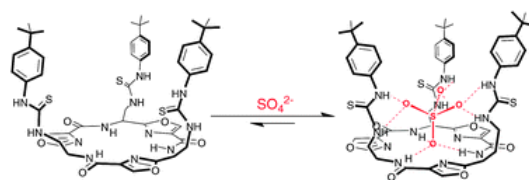
Abstract:



A novel, facile, highly flexible process was developed for the first preparation of well-controlled 3D skeletal polyhedral oligomeric silsesquioxane (POSS)-based functionalizable porous hybrid monoliths *via* ring-open polymerization. This approach represents an ideal pathway for easy access to a series of hybrid monoliths with high separation efficiency in cLC.

- High affinity sulfate binding in aqueous media by cyclic peptide with thiourea arms
Dungan, V. J.; Ngo, H. T.; Young, P. G.; Jolliffe, K. A. *Chem. Commun.* **2013**, 49, 264-266.

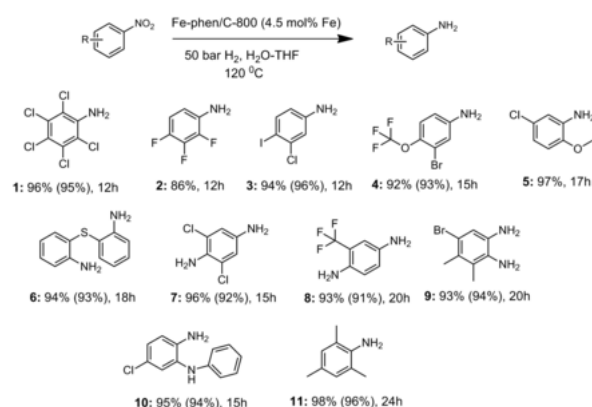
Abstract:



Tripodal thioureas based on a cyclic peptide scaffold have been synthesized and their anion binding properties evaluated. These receptors show high affinity towards sulfate ions in aqueous solution.

- Nanoscale Fe₂O₃-Based Catalysts for Selective Hydrogenation of Nitroarenes to Anilines
Jagadeesh, R. V.; Surkus, A.-E.; Junge, H.; Pohl, M.-M.; Radnik, J.; Rabeah, J.; Huan, H.; Schünemann, V.; Brückner, A.; Beller, M. *Science* **2013**, 342, 1073-1076.

Abstract:



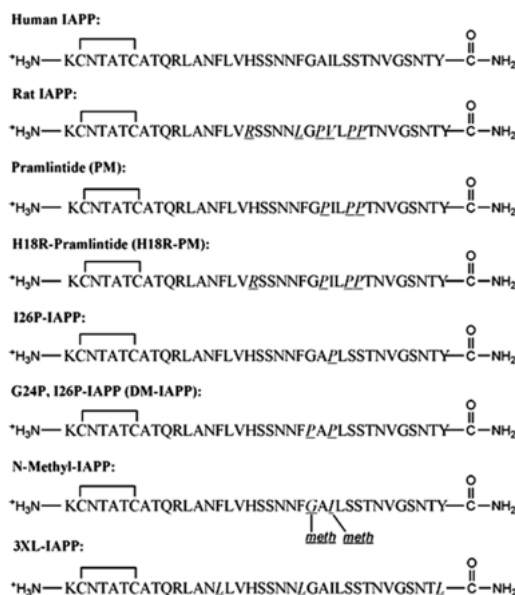
Production of anilines—key intermediates for the fine chemical, agrochemical, and pharmaceutical industries—relies on precious metal catalysts that selectively hydrogenate aryl nitro groups in the presence of other easily reducible functionalities. Herein, we report convenient and stable iron oxide (Fe₂O₃)-based catalysts as a more earth-abundant alternative for this transformation. Pyrolysis of iron-phenanthroline complexes on carbon furnishes a unique structure in which the active Fe₂O₃ particles are surrounded by a nitrogen-doped carbon layer. Highly selective hydrogenation of numerous structurally diverse nitroarenes (more than 80 examples) proceeded in good to excellent yield under industrially viable conditions.

- Islet amyloid polypeptide toxicity and membrane interactions

Cao, P.; Abedini, A.; Wang, H.; Tu, L.-H.; Zhang, X.; Schmidt, A. M.; Raleigh, D. P. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 19279-19284.

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Abstract:

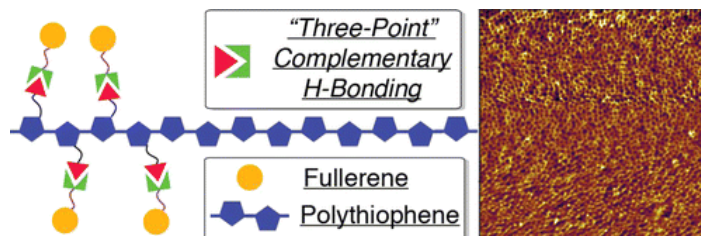


Amyloid formation is a hallmark of a range of human diseases. The polypeptide hormone amylin forms amyloid deposits in type 2 diabetes, and amyloid formation is thought to be a contributor to the decline in β -cell mass in the disease, however the basis of amylin-induced cytotoxicity is not fully understood. Amylin-induced membrane disruption has attracted considerable interest, and the interactions of amylin with model membranes have been characterized, but the relationship between studies with model membranes and toxicity is not understood. In this article the relationship between cell toxicity and the ability to disrupt model membranes is examined. There is no direct correlation between the two processes.

- Complementary Hydrogen Bonding and Block Copolymer Self-Assembly in Cooperation toward Stable Solar Cells with Tunable Morphologies

Li, F.; Yager, K. G.; Dawson, N. M.; Yang, J.; Malloy, K. J.; Qin, Y. *Macromolecules* **2013**, *46*, 9021–9031.

Abstract:



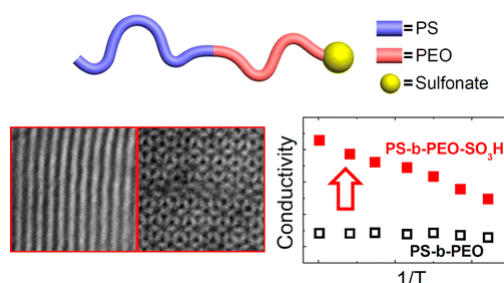
We report the synthesis and characterization of a polythiophene diblock copolymer selectively functionalized with 1-n-hexylisocytotic acid moieties (P4) and a 2,6-diaminopyridine tethered fullerene derivative (PCBP). Self-assembly between P4 and PCBP through “three-point” complementary hydrogen bonding interactions is utilized to control and stabilize blend morphologies. These interactions have been studied both in solution and in solid state by 1H NMR and UV-vis spectroscopies as well as optical and atomic force microscopies (AFM). Solar cells employing P4 blended with different weight ratios of PCBP and phenyl-C61-butyl ester

(PCBM) were fabricated and tested. The best power conversion efficiencies (PCEs) were observed in devices made from P4/PCBP blends (10/8 by wt) and ternary blends of P4/PCBP/PCBM (10/4/4 by wt) as active layers. Thermal stabilities of these solar cells were studied in detail by aging tests, and corresponding morphological changes were closely monitored by absorption spectroscopy, optical microscopy, AFM, and X-ray analyses. The “three-point” complementary hydrogen bonding interactions between P4 and PCBP, in cooperation with block polymer self-assembly, were found to not only improve the thermal stability of solar cells significantly but also lead to tunable active layer morphologies. Nanostructures with long-range order were identified in blend films employing P4, which has never been observed before in conventional polymer/fullerene bulk heterojunction (BHJ) films.

- Simple Route for Tuning the Morphology and Conductivity of Polymer Electrolytes: One End Functional Group is Enough

Jo, G.; Ahn, H.; Jeong Park, M. *ACS Macro Lett.* **2013**, *2*, 990–995.

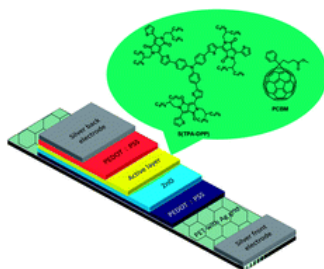
Abstract:



We have investigated a new means to control the morphology and conductivity of block copolymer electrolytes by the inclusion of ionic units at the chain ends. A set of poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) block copolymers having dissimilar PEO end groups (–OH, –SO₃H, and –SO₃Li) exhibited various self-assembled morphologies including disordered, lamellar, and hexagonal cylindrical phases. Strikingly, the addition of Li salts to PS-*b*-PEO with sulfonate terminal groups afforded enriched nanostructures with significant differences in their conductivities depending on the salt concentration. In particular, a gyroid morphology with a 2-fold-enhanced normalized ionic conductivity was found for the sulfonate-terminated PS-*b*-PEO when compared to disordered PS-*b*-PEO-OH. This is closely related to the structural advantages of gyroid having cocontinuous ionic channels, which enable efficient transport of Li⁺ ions via less tortuous ion conduction pathways. This work presents fascinating experimental insights on the enhancement of ion transport efficiencies by modulating the self-assembly nature of polymer electrolytes by substituting with a single end-functional group.

- Ambient roll-to-roll fabrication of flexible solar cells based on small molecules
Lin, Y.; Dam, H. F.; Andersen, T. R.; Bundgaard, E.; Fu, W.; Chen, H.; Krebs, F. C.; Zhan, X. *J. Mater. Chem. C* **2013**, *1*, 8007–8010.

Abstract:

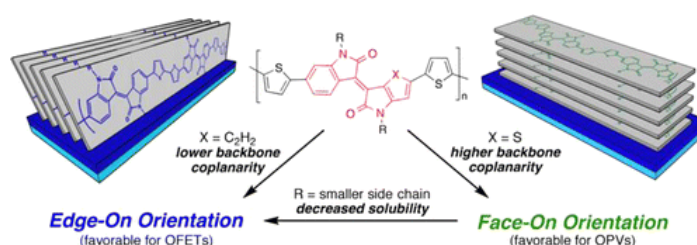


All solution-processed roll-to-roll flexible solar cells based on a star-shaped small molecule donor and PCBM acceptor were fabricated by slot-die coating, as the first successful example reported for small molecule roll-to-roll flexible solar cells.

- Control of Polymer-Packing Orientation in Thin Films through Synthetic Tailoring of Backbone Coplanarity

Chen, M. S.; Niskala, J. R.; Unruh, D. A.; Chu, C. K.; Lee, O. P.; Fréchet, J. M. *Chem. Mater.* **2013**, *25*, 4088–4096.

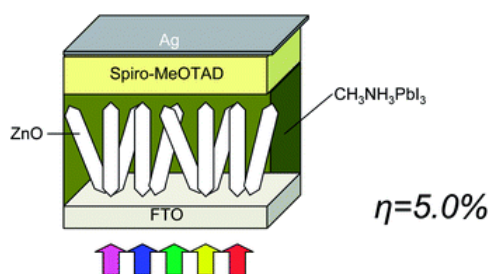
Abstract:



Controlling solid-state order of π -conjugated polymers through macromolecular design is essential for achieving high electronic device performance; yet, it remains a challenge, especially with respect to polymer-packing orientation. Our work investigates the influence of backbone coplanarity on a polymer's preference to pack face-on or edge-on relative to the substrate. Isoindigo-based polymers were synthesized with increasing planarity by systematically substituting thiophenes for phenyl rings in the acceptor comonomer. This increasing backbone coplanarity, supported by density functional theory (DFT) calculations of representative trimers, leads to the narrowing of polymer band gaps as characterized by ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy and cyclic voltammetry. Among the polymers studied, regiosymmetric II and TII polymers exhibited the highest hole mobilities in organic field-effect transistors (OFETs), while in organic photovoltaics (OPVs), TBII polymers that display intermediate levels of planarity provided the highest power conversion efficiencies. Upon thin-film analysis by atomic force microscopy (AFM) and grazing-incidence X-ray diffraction (GIXD), we discovered that polymer-packing orientation could be controlled by tuning polymer planarity and solubility. Highly soluble, planar polymers favor face-on orientation in thin films while the less soluble, nonplanar polymers favor an edge-on orientation. This study advances our fundamental understanding of how polymer structure influences nanostructural order and reveals a new synthetic strategy for the design of semiconducting materials with rationally engineered solid-state properties.

- Efficient and stable $\text{CH}_3\text{NH}_3\text{PbI}_3$ -sensitized ZnO nanorod array solid-state solar cells
Bi, D.; Boschloo, G.; Schwarzmüller, S.; Yang, L.; Johansson, E. M. J.; Hagfeldt, A. *Nanoscale* **2013**, *5*, 11686–11691.

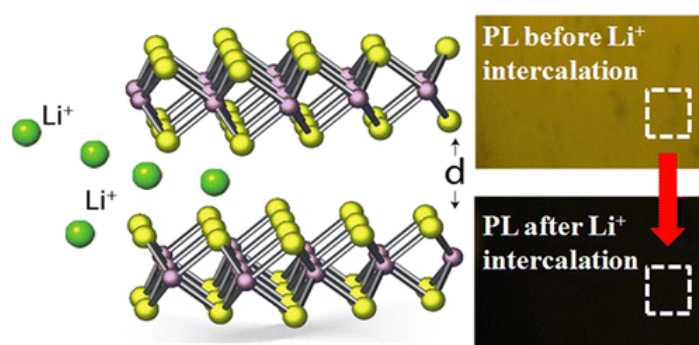
Abstract:



We report for the first time the use of a perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) absorber in combination with ZnO nanorod arrays (NRAs) for solar cell applications. The perovskite material has a higher absorption coefficient than molecular dye sensitizers, gives better solar cell stability, and is therefore more suited as a sensitizer for ZnO NRAs. A solar cell efficiency of 5.0% was achieved under 1000 W m^{-2} AM 1.5 G illumination for a solar cell with the structure: ZnO NRA/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-MeOTAD/Ag. Moreover, the solar cell shows a good long-term stability. Using transient photocurrent and photovoltage measurements it was found that the electron transport time and lifetime vary with the ZnO nanorod length, a trend which is similar to that in dye-sensitized solar cells, DSCs, suggesting a similar charge transfer process in ZnO NRA/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells as in conventional DSCs. Compared to $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ solar cells, ZnO shows a lower performance due to more recombination losses.

- Electrochemical Control of Photoluminescence in Two-Dimensional MoS_2 Nanoflakes
Wang, Y.; Ou, J. Z.; Balendhran, S.; Chrimes, A. F.; Mortazavi, M.; Yao, D. D.; Field, M. R.; Latham, K.; Bansal, V.; Friend, J. R.; Zhuiykov, S.; Medhekar, N. V.; Strano, M. S.; Kalantar-zadeh, K. *ACS Nano* **2013**, 7, 10083–10093.

Abstract:



Two-dimensional (2D) transition metal dichalcogenide semiconductors offer unique electronic and optical properties, which are significantly different from their bulk counterparts. It is known that the electronic structure of 2D MoS_2 , which is the most popular member of the family, depends on the number of layers. Its electronic structure alters dramatically at near atomically thin morphologies, producing strong photoluminescence (PL). Developing processes for controlling the 2D MoS_2 PL is essential to efficiently harness many of its optical capabilities. So far, it has been shown that this PL can be electrically or mechanically gated. Here, we introduce an electrochemical approach to actively control the PL of liquid-phase-exfoliated 2D MoS_2 nanoflakes by manipulating the amount of intercalated ions including Li^+ , Na^+ , and K^+ into and out of the 2D crystal structure. These ions are selected as they are crucial components in many bioprocesses. We show that this controlled intercalation allows for large PL modulations. The introduced electrochemically controlled PL will find

significant applications in future chemical and bio-optical sensors as well as optical modulators/switches.