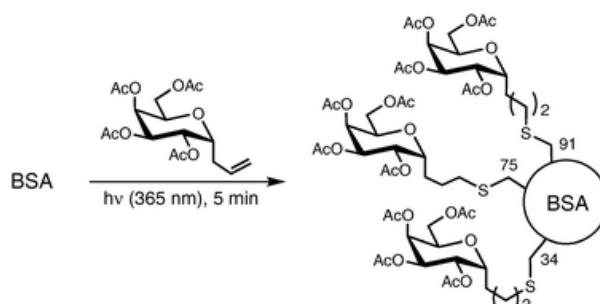


- Recent applications of thiol–ene coupling as a click process for glycoconjugation  
Dondoni, A.; Marra, A. *Chem. Soc. Rev.* **2012**, *41*, 573-586.

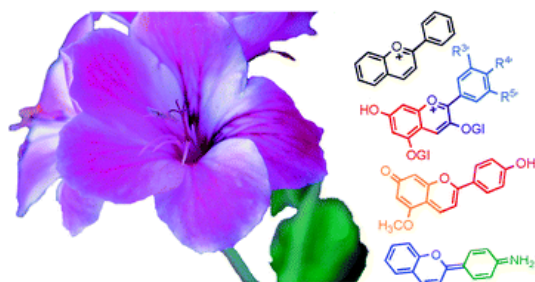
Abstract:



There has been over the past decades a resurgence of the free-radical thiol–ene coupling (TEC) as a method for assembling crosslinked networks and polymer functionalization. On the other hand the use of TEC in carbohydrate chemistry, a field of special importance due to the key role of carbohydrates in living organisms, is represented only by a handful of papers. Nevertheless it appears that TEC possesses many if not all the attributes of a click process proceeding with the assistance of the greenest catalyst such as visible light. This *tutorial review* focuses on the application of TEC on different topics, all related to glycochemistry, including: (a) carbohydrate modification, (b) oligosaccharide and glycosyl amino acid synthesis, (c) assembly of glycoclusters on rigid molecular platforms (calixarene, cyclodextrin, silsesquioxane, dendrimer), (d) peptide and protein glycosylation. Also the very recent development in peptide glycosylation by the closely related thiol–yne chemistry is described.

- Chemistry and applications of flavylum compounds: *a handful of colours*  
Pina, F.; Melo, M. J.; Laia, C. A. T.; Parola, A. J.; Lima, J. C. *Chem. Soc. Rev.* **2012**, *41*, 869-908.

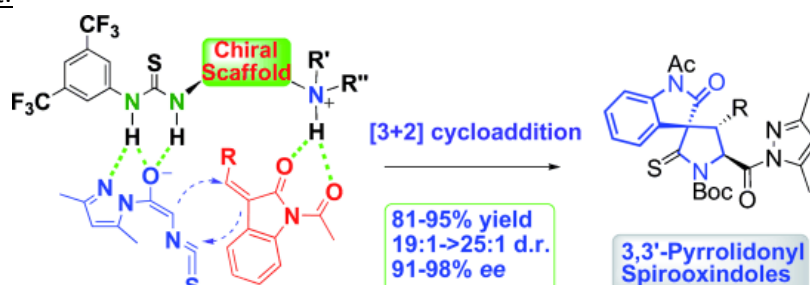
Abstract:



Flavylum compounds are versatile molecules that comprise anthocyanins, the ubiquitous colorants used by Nature to confer colour to most flowers and fruits. They have found a wide range of applications in human technology, from the millenary colour paints described by the Roman architect Vitruvius, to their use as food additives, combining colour and antioxidant effects, and even as light absorbers in solar cells aiming at a greener solar energy conversion. Their rich complexity derives in part from their ability to switch between a variety of species (flavylum cations, neutral quinoidal bases, hemiketals and chalcones, and negatively charged phenolates) by means of external stimuli, such as pH, temperature and light. This *critical review* describes (i) the historical advancements in the understanding of the equilibria of their chemical reaction networks; (ii) their thermodynamics and kinetics; (iii) the mechanisms underlying their colour development, such as co-pigmentation and host–guest interactions; (iv) the photophysics and photochemistry that lead to photochromism; and (v) applications in solar cells, models for optical memories, photochromic soft materials such as ionic liquids and gels, and their properties in solid state materials (274 references).

- Core Structure-Based Design of Organocatalytic [3+2]-Cycloaddition Reactions: Highly Efficient and Stereocontrolled Syntheses of 3,3'-Pyrrolidonyl Spirooxindoles  
Tan, B.; Zeng, X.; Leong, W. W. Y.; Shi, Z.; Barbas, C. F.; Zhong, G. *Chem. Eur. J.* **2012**, *18*, 63-67.

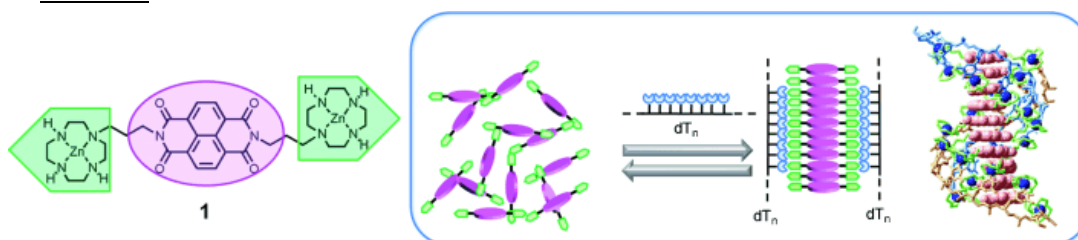
Abstract:



Extraordinary levels of stereocontrol were achieved in an efficient organocatalytic asymmetric [3+2]-cycloaddition reaction between an  $\alpha$ -isothiocyanato imide and various methyleneindolinones. Simple precursors were used for the rapid construction of spirocyclooxindole derivatives with high enantiopurity and structural diversity, thus providing a new avenue of significance to medicinal chemistry and diversity-oriented synthesis.

- DNA-Templated Assembly of Naphthalenediimide Arrays  
Nakamura, M.; Okaue, T.; Takada, T.; Yamana, K. *Chem. Eur. J.* **2012**, *18*, 196-201.

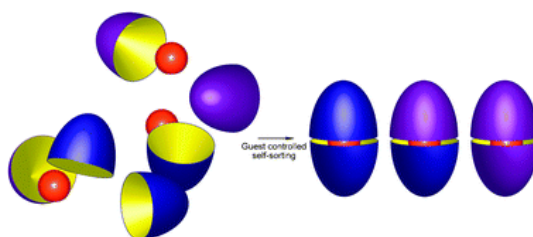
Abstract:



It stacks up: A naphthalenediimide (NDI) derivative (1) with two ZnII-cyclens that act as receptors for the thymine base in DNA has been synthesized. UV/Vis and CD spectroscopy, gel filtration, and molecular-modeling studies have shown that the bis(ZnII-cyclen)-NDI can be assembled in the presence of oligo-dT to form  $\pi$ -stacked NDI arrays (see scheme).

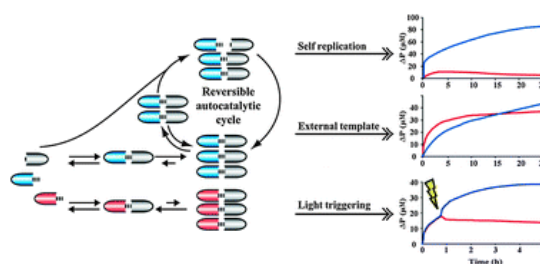
- Guest-controlled self-sorting in assemblies driven by the hydrophobic effect  
Gan, H.; Gibb, B. C. *Chem. Commun.* **2012**, *48*, 1656-1658

Abstract:



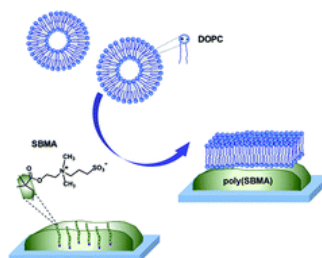
The extent of self-sorting in systems comprised of two different deep-cavity cavitands is investigated. The nature of the guest(s) encapsulated in the resulting assemblies is shown to profoundly influence the extent of self-sorting.

- Chemical and light triggering of peptide networks under partial thermodynamic control  
Dadon, Z.; Samiappan, M.; Wagner, N.; Ashkenasy, G. *Chem. Commun.* **2012**, *48*, 1419-1421  
Abstract:



The kinetics of novel dynamic libraries that operate *via* reversible replication is described. In these systems, selective product formation is governed by peptides autocatalytic efficiency and by differences in their unfolding stability. We suggest ways to significantly alter the network behavior by chemical inputs (templates) or physical triggers (light).

- Surface-grafted zwitterionic polymers as platforms for functional supported phospholipid membranes  
Santonicola, M.G.; Memesa, M.; Meszyńska, A.; Ma, Y.; Vancso, G. J. *Soft Matter*, **2012**, *8*, 1556-1562.  
Abstract:



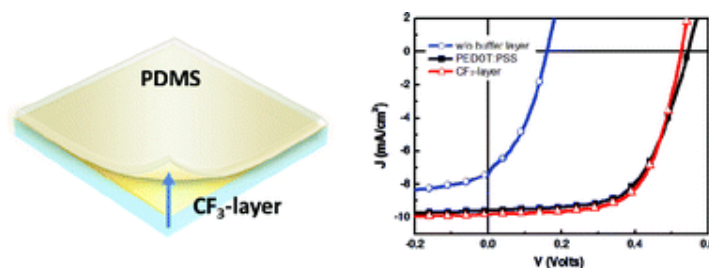
Polymer brushes grafted from surfaces using controlled polymerization techniques, most notably surface-initiated atom-transfer radical polymerization (SI-ATRP), provide robust and reproducible platforms with precise control of surface properties. These platforms are especially useful in biologically oriented applications involving the confinement of membrane proteins onto solid supports, including screening of pharmaceuticals and biosensing. Here we investigate a tunable zwitterion-based polymeric interface that can guide the assembly of neutral lipid membranes with high mechanical stability and reproducibility on various synthetic materials. By controlling the polymer architecture using ATRP, we show that phospholipid membranes can be made to self-assemble on thin layers of charge-balanced poly(sulfobetaine methacrylate) from fusion of DOPC vesicles under physiological conditions. The self-assembly kinetics and functionality of the polymer-supported lipid membranes are investigated using various surface sensitive techniques, including surface plasmon resonance, fluorescence microscopy, and atomic force microscopy. The growth of zwitterionic polymer layers with controlled length and grafting density allows for modulation of the adhesion of the lipid bilayers to surfaces, thus offering unique advantages for the design and synthesis of bioactive surfaces.

- Self-assembled multilayers of modified ITO in polymer solar cells by soft-imprinting

Huang, L. C.; Liu, H. W.; Liang, C. W.; Chou, T. R.; Wang, L.; Chao, C. Y. *Soft Matter* **2012**, *8*, 1467-1472.

4

Abstract:

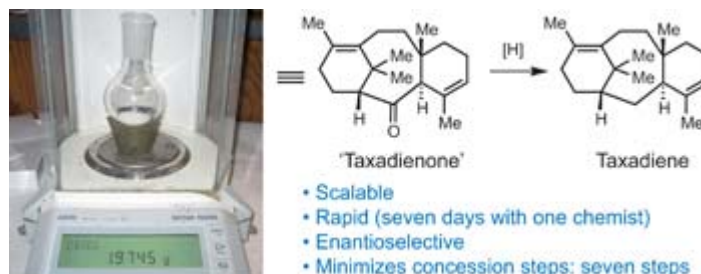


Optimized performances of polymer solar cells has been of magnificent interest in recent years. A variety of approaches have been reported to alter or replace the polymer buffer layers in solar device structures. In this present work, surface modification of indium tin oxide (ITO)-coated substrates through the use of self-assembled multilayers by the soft-imprinting method has been applied to adjust the anode work function and device performance in polymer solar cells based on a P3HT:PCBM heterojunction. The efficiency and morphology of the solar device with  $\text{CF}_3$ -terminal group materials as a buffer layer have been measured and investigated. These results demonstrate that the soft-imprinting method is an effective and rapid procedure that enhances the quality of polymer solar cells and indicates potential implications for other organic devices containing an interface between a blended organic active layer and an electrode layer.

- Scalable enantioselective total synthesis of taxanes

Mendoza, A.; Ishihara, Y.; Baran, P. S. *Nature Chem.* **2011**, *4*, 21-25.

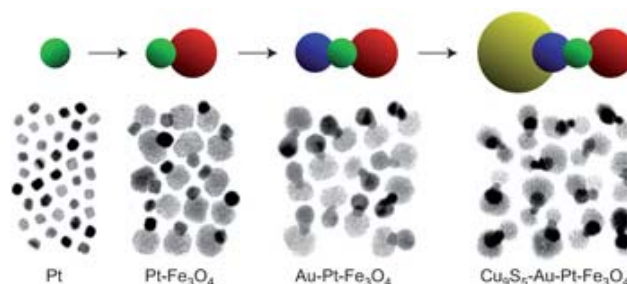
Abstract:



Taxanes form a large family of terpenes comprising over 350 members, the most famous of which is Taxol (paclitaxel), a billion-dollar anticancer drug. Here, we describe the first practical and scalable synthetic entry to these natural products via a concise preparation of (+)-taxa-4(5),11(12)-dien-2-one, which has a suitable functional handle with which to access more oxidized members of its family. This route enables a gram-scale preparation of the 'parent' taxane—taxadiene—which is the largest quantity of this naturally occurring terpene ever isolated or prepared in pure form. The characteristic 6-8-6 tricyclic system of the taxane family, containing a bridgehead alkene, is forged via a vicinal difunctionalization/Diels–Alder strategy. Asymmetry is introduced by means of an enantioselective conjugate addition that forms an all-carbon quaternary centre, from which all other stereocentres are fixed through substrate control. This study lays a critical foundation for a planned access to minimally oxidized taxane analogues and a scalable laboratory preparation of Taxol itself.

- A total-synthesis framework for the construction of high-order colloidal hybrid nanoparticles  
Buck, M. R.; Bondi, J. F.; Schaak, R. E. *Nature Chem.* **2011**, *4*, 37-44.

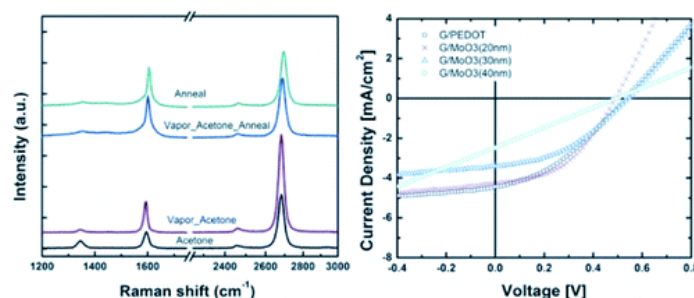
Abstract:



Colloidal hybrid nanoparticles contain multiple nanoscale domains fused together by solid-state interfaces. They represent an emerging class of multifunctional lab-on-a-particle architectures that underpin future advances in solar energy conversion, fuel-cell catalysis, medical imaging and therapy, and electronics. The complexity of these ‘artificial molecules’ is limited ultimately by the lack of a mechanism-driven design framework. Here, we show that known chemical reactions can be applied in a predictable and stepwise manner to build complex hybrid nanoparticle architectures that include  $M$ -Pt- $\text{Fe}_3\text{O}_4$  ( $M = \text{Au}, \text{Ag}, \text{Ni}, \text{Pd}$ ) heterotrimers,  $M_x\text{S}$ -Au-Pt- $\text{Fe}_3\text{O}_4$  ( $M = \text{Pb}, \text{Cu}$ ) heterotetramers and higher-order oligomers based on the heterotrimeric Au-Pt- $\text{Fe}_3\text{O}_4$  building block. This synthetic framework conceptually mimics the total-synthesis approach used by chemists to construct complex organic molecules. The reaction toolkit applies solid-state nanoparticle analogues of chemoselective reactions, regiospecificity, coupling reactions and molecular substituent effects to the construction of exceptionally complex hybrid nanoparticle oligomers.

- Graphene As Transparent Conducting Electrodes in Organic Photovoltaics: Studies in Graphene Morphology, Hole Transporting Layers, and Counter Electrodes  
Park, H.; Brown, P. R.; Bulović, V.; Kong, J. *Nano Lett.* **2012**, *12*, 133–140.

Abstract:

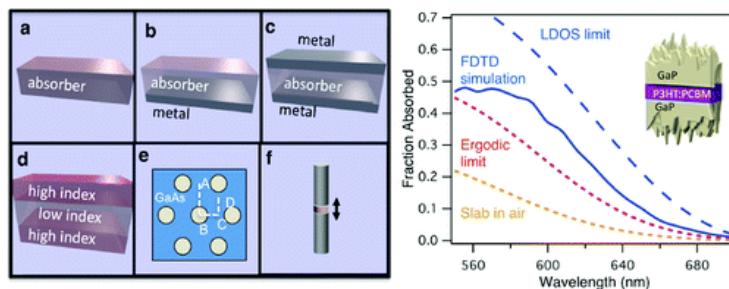


In this work, organic photovoltaics (OPV) with graphene electrodes are constructed where the effect of graphene morphology, hole transporting layers (HTL), and counter electrodes are presented. Instead of the conventional poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) PEDOT:PSS HTL, an alternative transition metal oxide HTL (molybdenum oxide ( $\text{MoO}_3$ )) is investigated to address the issue of surface immiscibility between graphene and PEDOT:PSS. Graphene films considered here are synthesized via low-pressure chemical vapor deposition (LPCVD) using a copper catalyst and experimental issues concerning the transfer of synthesized graphene onto the substrates of OPV are discussed. The morphology of the graphene electrode and HTL wettability on the graphene surface are shown to play important roles in the successful integration of graphene films into the OPV devices. The effect of various cathodes on the device performance is also studied. These factors (i.e., suitable HTL, graphene surface morphology and residues, and the choice of well-matching counter electrodes) will provide better understanding in utilizing graphene films as transparent conducting electrodes in future solar cell applications.

- Solar Cell Light Trapping beyond the Ray Optic Limit

Callahan, D. M.; Munday, J. N.; Atwater, H. A. *Nano Lett.* **2012**, *12*, 214–218.

Abstract:

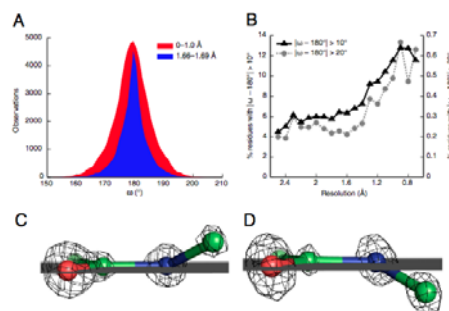


In 1982, Yablonovitch proposed a thermodynamic limit on light trapping within homogeneous semiconductor slabs, which implied a minimum thickness needed to fully absorb the solar spectrum. However, this limit is valid for geometrical optics but not for a new generation of subwavelength solar absorbers such as ultrathin or inhomogeneously structured cells, wire-based cells, photonic crystal-based cells, and plasmonic cells. Here we show that the key to exceeding the conventional ray optic or so-called ergodic light trapping limit is in designing an elevated local density of optical states (LDOS) for the absorber. Moreover, for any semiconductor we show that it is always possible to exceed the ray optic light trapping limit and use these principles to design a number of new solar absorbers with the key feature of having an elevated LDOS within the absorbing region of the device, opening new avenues for solar cell design and cost reduction.

- Nonplanar peptide bonds in proteins are common and conserved but not biased toward active sites

Berkholz, D. S.; Driggers, C. M.; Shapovalov, M. V.; Dunbrack, R. L.; Karplus, P. A. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 449-453.

Abstract :



**Fig. 1.** Observed nonplanarity in peptide bonds increases at atomic resolution. (A) Histogram of the distribution of  $\omega$  angles for two resolution ranges (5.1, 0.0 Å and 1.66–1.69 Å). Observation numbers and means of the two histograms are 32,549/179.1° and 17,001/179.3°, respectively. (B) The percent of general peptides that are modeled as highly nonplanar ( $\geq 10^\circ$  and  $\geq 20^\circ$  as noted in figure) are plotted as a function of resolution in 0.1 Å resolution slices. (C, D) Two well defined highly nonplanar peptide bonds (one rotated in each direction) located outside of protein active sites. Shown are the peptide bonds between (C) residues Ile102-Asp103 from a carboxylic esterase (PDB code 1q4w) (21) with ( $\omega = 180^\circ$ ) =  $-26^\circ$  (electron density at 6.6 $\sigma_{\text{max}}$ ), and (D) residues Asp105-Asn106 from a  $\beta$ -glycosidase (PDB code 7a3 h) (22) with ( $\omega = 180^\circ$ ) =  $23^\circ$  (electron density at 4.6 $\sigma_{\text{max}}$ ). In a planar peptide bond, all five atoms would lie in the plane shown in gray. Searches were done with the PGD (18) for dipeptides, using a 90% sequence-identity threshold and otherwise default search parameters.

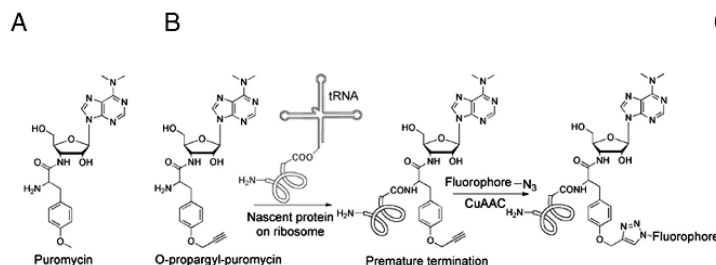
The planarity of peptide bonds is an assumption that underlies decades of theoretical modeling of proteins. Peptide bonds strongly deviating from planarity are considered very rare features of protein structure that occur for functional reasons. Here, empirical analyses of atomic-resolution protein structures reveal that *trans* peptide groups can vary by more than 25° from planarity and that the true extent of nonplanarity is underestimated even in 1.2 Å resolution structures. Analyses as a function of the  $\varphi, \psi$ -backbone dihedral angles show that the expected value deviates by  $\pm 8^\circ$  from planar as a systematic function of conformation, but that the large majority of variation in planarity depends on tertiary effects. Furthermore, we show that those peptide bonds in proteins that are most nonplanar, deviating by over 20° from planarity, are not strongly associated with active sites. Instead, highly nonplanar peptides are simply integral components of protein structure related to local and tertiary structural features that tend to be conserved among homologs. To account for

the systematic  $\varphi, \psi$ -dependent component of nonplanarity, we present a conformation-dependent library that can be used in crystallographic refinement and predictive protein modeling.

7

- Imaging protein synthesis in cells and tissues with an alkyne analog of puromycin  
Liu, J.; Xu, Y.; Stoleru, D.; Salic, A. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 413-418.

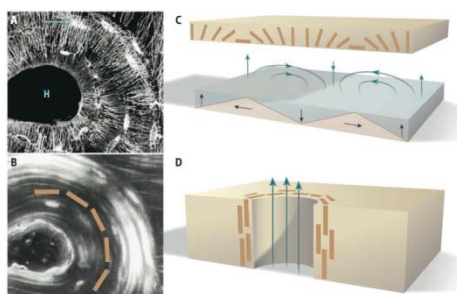
Abstract :



Synthesis of many proteins is tightly controlled at the level of termination of translation, and plays an essential role in fundamental processes such as cell growth and proliferation, signaling, differentiation, or death. Methods that allow imaging and identification of nascent proteins are critical for dissecting regulation of translation, both spatially and temporally, particularly in whole organisms. We introduce a simple and robust chemical method to image and affinity-purify nascent proteins in cells and in animals, based on an alkyne analog of puromycin, O-propargyl-puromycin (OP-puro). OP-puro forms covalent conjugates with nascent polypeptide chains, which are rapidly turned over by the proteasome and can be visualized or captured by copper(I)-catalyzed azide-alkyne cycloaddition. Unlike methionine analogs, OP-puro does not require methionine-free conditions and, uniquely, can be used to label and assay nascent proteins in whole organisms. This strategy should have broad applicability for imaging protein synthesis and for identifying proteins synthesized under various physiological and pathological conditions in vivo.

- A Composite Matter of Alignment  
Fratzl, P. *Science* **2012**, *335*, 177-178.

Abstract:



**Tougher surfaces inspired by bones.** (A and B) Cross-sectional view of an osteon in equine bone, based on data from [25]. (A) Osteocyte cells (blue arrow) form a dense network visualized by a fluorescent stain (white) around the Haversian canal (labeled H), which houses the blood vessel supplying nutrients to the cells. (B) A polarized-light image of the same bone section reveals that cells have deposited the bone matrix, consisting of collagen fibrils and plate-like mineral particles, with a concentric fiber arrangement around the Haversian canal (the orientation of inclusions is schematically shown by brown rectangles). (C and D) Erb et al. fabricated unusual three-dimensional reinforcement architectures through orientational and spatial magnetic control, shown here schematically. (C) A gradually varying particle alignment generated by a standard refrigerator magnet's domain structure. (D) A cross section of a spatial gradient in magnetized particles that were aligned preferentially around a channel in the material.

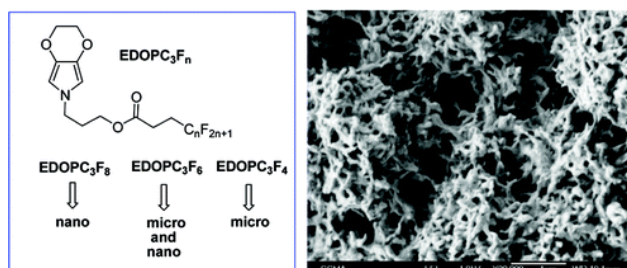
If you have had an eyeglass frame break, it likely did so at the point where the temple is screwed to a hinge. The holes in the frame create local stress concentrations that can initiate cracks that limit the durability of the material. Local reinforcements can be a cost-effective solution against fracture at sites such as bolt holes, where the performance of the material is challenged by additional stresses. This approach can be simple to implement in isotropic materials such as metals, but simple ways to reinforce such materials as fiber-polymer composites have been lacking. On page 199 of this issue,

Erb *et al.* (1) propose a new method to align fibers or platelets in a polymer for the near-surface reinforcement of polymeric composites. In their approach, these inclusions are decorated with magnetic nanoparticles and oriented by a magnetic field in the production process in which the solution polymerizes to form a solid composite.

- Surface Structuration (Micro and/or Nano) Governed by the Fluorinated Tail Lengths toward Superoleophobic Surfaces

Bellanger, H.; Darmanin, T.; Guittard, F. *Langmuir* **2012**, *28*, 186-192.

Abstract:

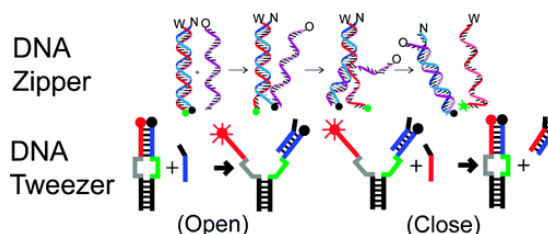


As compared to superhydrophobic surfaces, the challenge to obtain superoleophobic properties, surfaces against low-surface-tension probe liquids such as hexadecane, is very important because of their high tendency to wet. From the molecular design of the monomer, it is possible to obtain in one step superoleophobic surfaces by electrodeposition. Hence, we report the synthesis and the characterization of an original series of fluorinated 3,4-ethylenedioxy-pyrrole (EDOP) derivatives. The electrodeposited polymer films are characterized by contact angle measurements (static and dynamic with various probe liquids), optical profilometry, and scanning electron microscopy. In the view toward reaching superoleophobic properties, a common approach is to increase the number of fluoromethylene units of the surface post-treatment agent. Here, surprisingly, it is possible, in one step, to reach more efficient antioil surface properties by decreasing the length of the fluorinated tail (F-octyl to F-hexyl). This fact can be explained by a double scale of structuration (micro and nano) induced using only F-hexyl tails.

- DNA Zipper-Based Tweezers

Landon, P. B.; Ramachandran, S.; Gillman, A.; Gidron, T.; Yoon, D.; Lal, R. *Langmuir* **2012**, *28*, 534-540.

Abstract:



Here we report the design and development of DNA zippers and tweezers. Essentially a zipper system consists of a normal strand (**N**), a weak strand (**W**), and an opening strand (**O**). **N** strand is made up of normal DNA bases, while **W** is engineered to have inosine substituting for guanine. By altering the number and order of inosine, **W** is engineered to provide less than natural bonding affinities to **N** in forming the [**N:W**] helix. When **O** is introduced (a natural complement of **N**), it competitively displaces **W** from [**N:W**] and forms [**N:O**]. This principle is incorporated in the development of a molecular device that can perform the functions of tweezers (sense, hold, and



release). Tweezers were constructed by holding **N** and **W** together using a hinge at one end. Thus, when the tweezers open, **N** and **W** remain in the same vicinity. This allows the tweezers to cycle among open and close positions by their opening and closing strands. Control over their opening and closing kinetics is demonstrated. In contrast to the previously reported DNA tweezers, the zipper mechanism makes it possible to operate them with opening strands that do not contain single-stranded DNA overhangs. Our approach yields a robust, compact, and regenerative tweezer system that could potentially be integrated into complex nanomachines.

- Triphenylamine Dendronized Iridium(III) Complexes: Robust Synthesis, Highly Efficient Nondoped Orange Electrophosphorescence and the Structure-Property Relationship.

Zhu, M.; Zou, J.; He, X.; Yang, C.; Wu, H.; Zhong, C.; Qin, J.; Cao, Y. *Chem. Mater.* **2012**, *24*, 174-180.

Abstract:

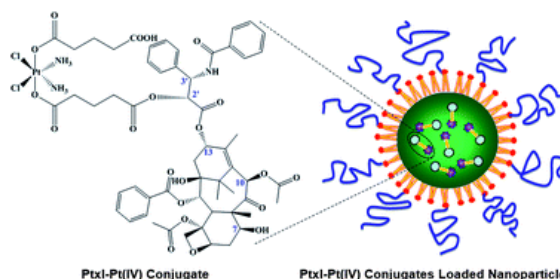


New triphenylamine dendronized homoleptic Ir(III) complexes, namely Ir-G1, Ir-G2, and Ir-G3, with six, eighteen, and up to forty-two triphenylamine units, respectively, are designed and efficiently synthesized through convergent strategy. Both linear enlargement of the dendritic arms and the “double-dendron” strategy are applied to maximize the degree of site-isolation of the emissive center. The relationship between the dendritic structures and their photophysical, electrochemical, and electrophosphorescent performances is investigated. Phosphorescent organic light-emitting diodes (PhOLEDs) employing the dendrimers as solution-processed emitters are fabricated. The nondoped devices with Ir-G1 and Ir-G2 as emitters display very high efficiencies and small values of efficiency roll-off. For example, a device with Ir-G1 as emitter exhibits the best results ever reported for solution-processed orange phosphorescent devices with maximum luminous efficiency of 40.9 cd A<sup>-1</sup> and power efficiency of 39.5 lm W<sup>-1</sup>. Moreover, the maximum power efficiency of the nondoped device is nearly three times higher than that of the doped control device by doping Ir-G1 into the general polymer matrix. This indicates that incorporation of triphenylamine moieties into the sphere of iridium(III) core is a simple and effective approach to develop highly efficient host-free dendritic phosphors.

- Nanoparticle drug delivery enhances the cytotoxicity of hydrophobic-hydrophilic drug conjugates.

Aryal, S.; Jack Hu, C. E.; Fu, V.; Zhang, L. *J. Mater. Chem.* **2012**, *22*, 994-999.

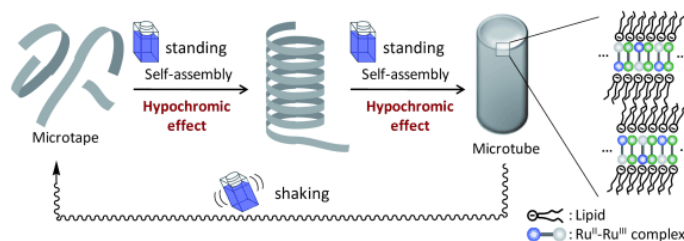
Abstract:



We report a drug conjugation approach to concurrently load both hydrophobic and hydrophilic drugs into the same drug delivery nanocarrier in a precisely controllable manner. Using paclitaxel as a model hydrophobic drug and cisplatin as a model hydrophilic drug, we demonstrate the synthesis and characterization of a paclitaxel-cisplatin conjugate via a hydrolysable linker and its easy encapsulation by a lipid-polymer hybrid nanoparticle with controllable drug loading yield and drug release profile. The cytotoxicity of the resulting drug conjugate loaded nanoparticles against human ovarian cancer cells is investigated and compared to that of unencapsulated free drug conjugates. It is found that the cellular cytotoxicity of the hydrophobic-hydrophilic drug conjugates is significantly improved after being encapsulated into the nanoparticles. This is likely because the nanoparticles facilitate the intracellular entry of the amphiphilic drug conjugates and thus overcome their poor transport ability across the lipid bilayer structured cellular membranes.

- Self-Assembly of Tubular Microstructures from Mixed-Valence Metal Complexes and Their Reversible Transformation by External Stimuli  
Kuroiwa, K.; Yoshida, M.; Masaoka, S.; Kaneko, K.; Sakai, K.; Kimizuka, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 656-659.

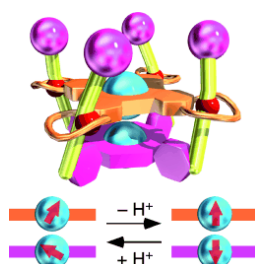
Abstract:



Mix and shake: Lipid packaged dinuclear ruthenium(II,III) complexes of class III mixed-valence state produce a reversible hypochromic effect upon external physical stimuli, such as shaking, due to the arrangement of transition dipole moments. The effect is accompanied by tubular-to-ribbon structural changes (see scheme).

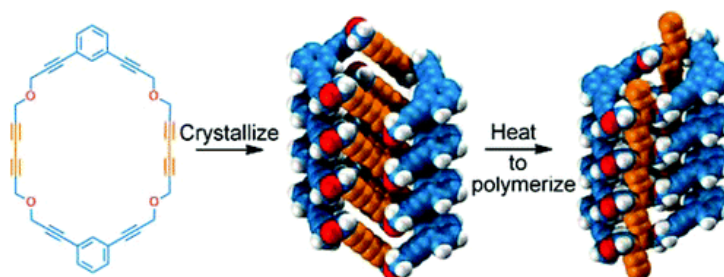
- Switchable Intermolecular Communication in a Four-Fold Rotaxane  
Yamada, Y.; Okamoto, M.; Furukawa, K.; Kato, T.; Tanaka, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 709-713.

Abstract:



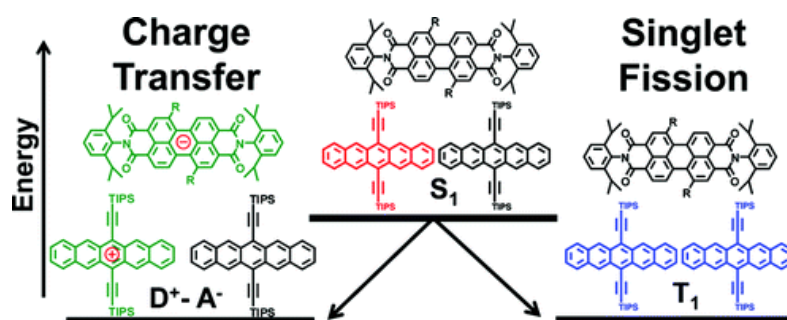
Firmly tied: A four-fold rotaxane was prepared from a porphyrin unit with four alkylammonium chains and a phthalocyanine unit with four peripheral crown ethers. In a dinuclear  $\text{Cu}^{2+}$  complex of the four-fold rotaxane, the  $\text{Cu}^{2+}$ -porphyrin and the  $\text{Cu}^{2+}$ -phthalocyanine moieties were stacked efficiently on one another to afford spin-spin communication. The spin states were switched reversibly (see picture).

- Preparation and Structure of a Tubular Addition Polymer: A True Synthetic Nanotube  
Hsu, T.-J.; Fowler, F. W.; Lauher, J. W.; Michl, J. *J. Am. Chem. Soc.* **2012**, *134*, 142–145.  
Abstract:



The structure of a synthetic nanotube prepared by the solid-state polymerization of a stacked column of diacetylene-based macrocycles has been determined. A polyether macrocycle monomer with two parallel diacetylene functionalities was prepared. Its crystal structure revealed that the compound crystallizes with structural parameters suitable for topo chemical polymerization. Slow annealing of a single crystal for 35 days brought about a single-crystal-to-single-crystal polymerization resulting in the first experimentally determined structure of a tubular addition polymer.

- Competition between Singlet Fission and Charge Separation in Solution-Processed Blend Films of 6,13-Bis(triisopropylsilylethynyl)pentacene with Sterically-Encumbered Perylene-3,4:9,10-bis(dicarboximide)s  
Ramanan, C.; Smeigh, A. L.; Anthony, J. E.; Marks, T. J.; Wasielewski, M. *J. Am. Chem. Soc.* **2012**, *134*, 386–397.  
Abstract:

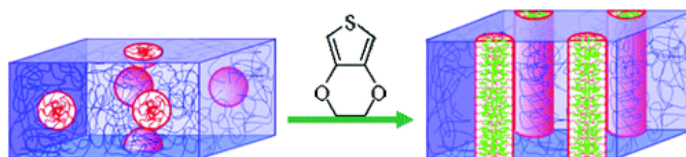


The photophysics and morphology of thin films of *N,N*-bis(2,6-diisopropylphenyl)perylene-3,4:9,10-bis(dicarboximide) (1) and the 1,7-diphenyl (2) and 1,7-bis(3,5-di-*tert*-butylphenyl) (3) derivatives blended with 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn) were studied for their potential use as photoactive layers in organic photovoltaic (OPV) devices. Increasing the steric bulk of the 1,7-substituents of the perylene-3,4:9,10-bis(dicarboximide) (PDI) impedes aggregation in the solid state. Film characterization data using both atomic force microscopy and X-ray diffraction showed that decreasing the PDI aggregation by increasing the steric bulk in the order 1 < 2 < 3 correlates with a decrease in the density/size of crystalline TIPS-Pn domains. Transient absorption spectroscopy was

performed on  $\sim$ 100 nm solution-processed TIPS-Pn:PDI blend films to characterize the charge separation dynamics. These results showed that selective excitation of the TIPS-Pn results in competition between ultrafast singlet fission ( $1^* \text{TIPS-Pn} + \text{TIPS-Pn} \rightarrow 2 \text{ } 3^* \text{TIPS-Pn}$ ) and charge transfer from  $1^* \text{TIPS-Pn}$  to PDI (1–3). As the blend films become more homogeneous across the series TIPS-Pn:PDI 1  $\rightarrow$  2  $\rightarrow$  3, charge separation becomes competitive with singlet fission. Ultrafast charge separation forms the geminate radical ion pair state  $1(\text{TIPS-Pn}^{\bullet+} - \text{PDI}^{\bullet-})$  that undergoes radical pair intersystem crossing to form  $3(\text{TIPS-Pn}^{\bullet+} - \text{PDI}^{\bullet-})$ , which then undergoes charge recombination to yield either  $3^* \text{PDI}$  or  $3^* \text{TIPS-Pn}$ . Energy transfer from  $3^* \text{PDI}$  to TIPS-Pn also yields  $3^* \text{TIPS-Pn}$ . These results show that multiple pathways produce the  $3^* \text{TIPS-Pn}$  state, so that OPV design strategies based on this system must utilize this triplet state for charge separation.

- Block Copolymer Supramolecular Assembly beyond Hydrogen Bonding  
Hagaman, D.; Enright, T. P.; Sidorenko, A. *Macromolecules* **2012**, *45*, 275–282.

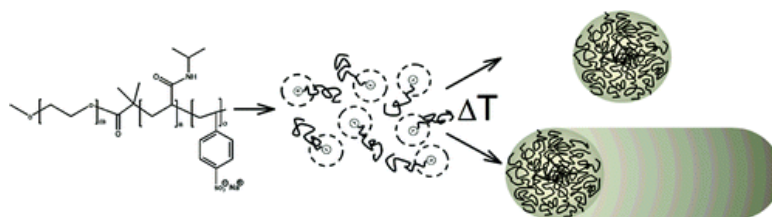
Abstract:



Supramolecular assemblies of block copolymers (BSAs) with low molecular weight additives require preferential interactions between the additive and one of the blocks. So far, only hydrogen bonds (HB) were explored to obtain BSAs. We report on three novel BSAs of block copolymer PS-block-P4VP with commercially valuable additives of the EDOT family. Two of the additives ((3,4-ethylenedioxythiophene) (EDOT) and 3,4-(2,2-dimethylpropylenedioxy)thiophene (ProDOT)) form the BSAs based on interactions other than HB. The morphology and some properties of the BSAs were studied by means of AFM, FTIR, and spectroscopic ellipsometry. The BSAs reveal cylindrical morphology with periodicity of 30 nm. In thin films the orientation of the cylinders can be switched from perpendicular to parallel by annealing in vapors of a suitable solvent. Extraction with a selective solvent results in porous films with porosity of 15%. These non-HB BSAs were compared with the HB BSA of HMeDOT as well as HABA BSA reported recently. The nature of the non-HB interactions is briefly discussed.

- Small-Angle X-ray Scattering Study of Charged Triblock Copolymers as a Function of Polymer Concentration, Temperature, and Charge Screening  
Behrens, M. A.; Kjønksen, A.; Zhu, K.; Nyström, B.; Pedersen, J. S. *Macromolecules* **2012**, *45*, 246–255.

Abstract:



In the current study, the influence of electrostatic interaction on micelle formation has been investigated by characterizing a series of charged thermo-responsive triblock copolymers by densitometry and small-angle X-ray scattering in a wide temperature range from 20 to 90 °C and by varying the salt concentration of the solvent. The copolymers, MPEG45-b-P(NIPAAm)<sub>n</sub>-b-P(SSS)<sub>22</sub>,

were composed of methoxypoly(ethylene glycol) (MPEG, hydrophilic), poly(N-isopropylacrylamide) (PNIPAAm, temperature sensitive), and poly(4-styrenesulfonic acid sodium) (PSSS, charged). The PNIPAAm block constituted between 20 and 50% of the polymer repeat units. The single polymers were described with a Gaussian chain model, where the repulsive interchain interactions were taken into account in aqueous solution. Above the critical micelle temperature (CMT) the polymer with the medium PNIPAAm block formed spherical micelles, whereas the copolymer with the largest PNIPAAm block formed cylindrical micelles. Addition of salt to the solution affected the formed micelles as well as the CMT of the system.