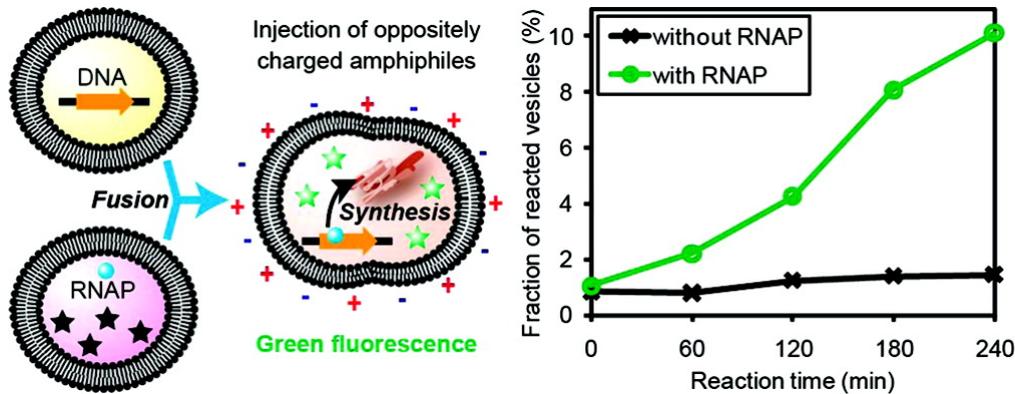


- Programmed Vesicle Fusion Triggers Gene Expression

Caschera, F.; Sunami, T.; Matsuura, T.; Suzuki, H.; Hanczyc, M. H.; Yomo, T. *Langmuir* **2011**, 27, 13082-13090.

1

Abstract:

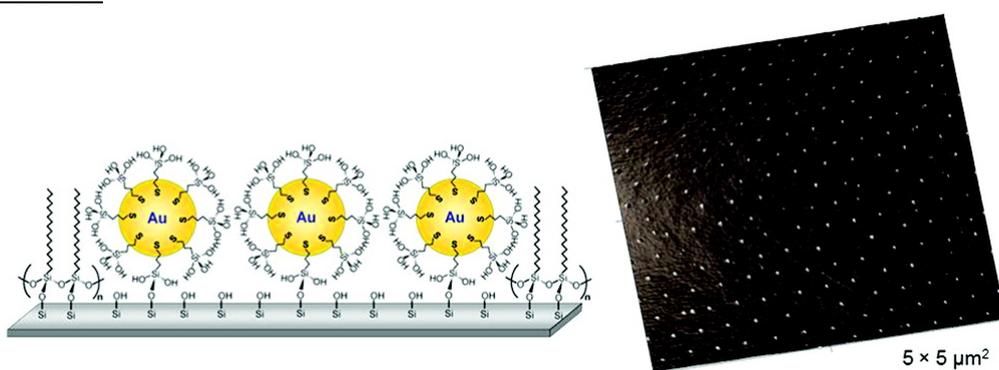


The membrane properties of phospholipid vesicles can be manipulated to both regulate and initiate encapsulated biochemical reactions and networks. We present evidence for the inhibition and activation of reactions encapsulated in vesicles by the exogenous addition of charged amphiphiles. While the incorporation of cationic amphiphile exerts an inhibitory effect, complementation of additional anionic amphiphiles revitalize the reaction. We demonstrated both the simple hydrolysis reaction of  $\beta$ -glucuronidase and the *in vitro* gene expression of this enzyme from a DNA template. Furthermore, we show that two vesicle populations decorated separately with positive and negative amphiphiles can fuse selectively to supply feeding components to initiate encapsulated reactions. This mechanism could be one of the rudimentary but effective means to regulate and maintain metabolism in dynamic artificial cell models.

- Nanostructures of Functionalized Gold Nanoparticles Prepared by Particle Lithography with Organosilanes

Lusker, K. L.; Li, J.-R.; Garno, J. C. *Langmuir* **2011**, 27, 13269-13275.

Abstract:



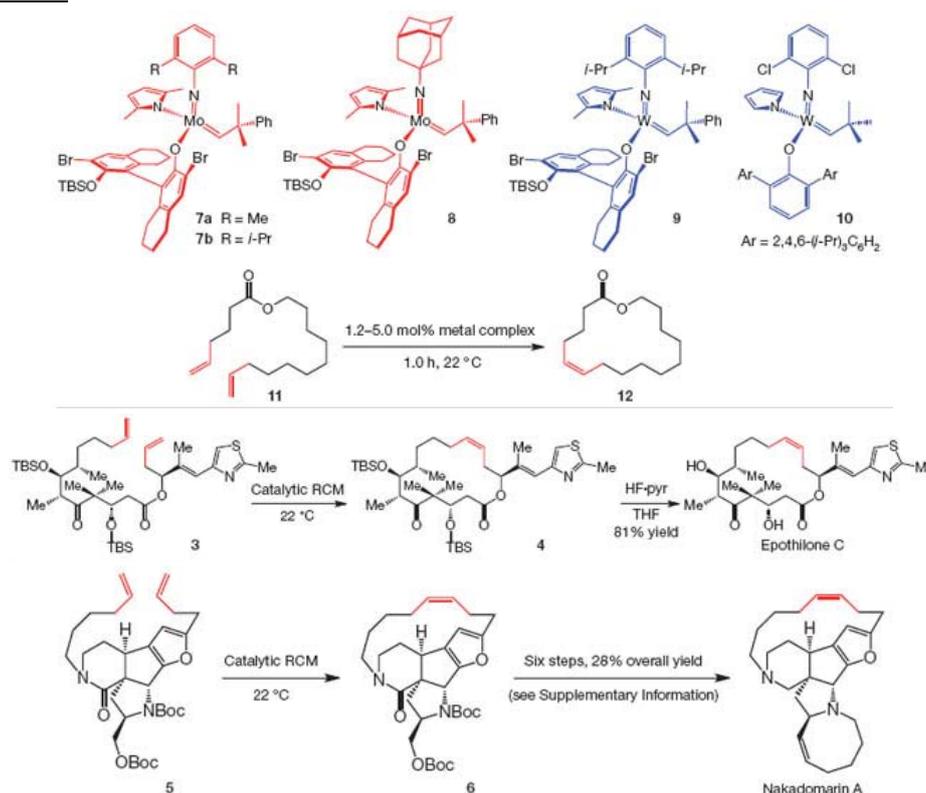
Periodic arrays of organosilane nanostructures were prepared with particle lithography to define sites for selective adsorption of functionalized gold nanoparticles. Essentially, the approach for nanoparticle lithography consists of procedures with two masks. First, latex mesospheres were used as a surface mask for deposition of an organosilane vapor, to produce an array of holes within a covalently bonded, organic thin film. The latex particles were readily removed with solvent rinses to expose discrete patterns of nanosized holes of uncovered substrate. The nanostructured film of organosilanes was then used as a surface mask for a second patterning step, with immersion in a

solution of functionalized nanoparticles. Patterned substrates were fully submerged in a solution of surface-active gold nanoparticles coated with 3-mercaptopropyltrimethoxysilane. Regularly shaped, nanoscopic areas of bare substrate produced by removal of the latex mask provided sites to bind silanol-terminated gold nanoparticles, and the methyl-terminated areas of the organosilane film served as an effective resist, preventing nonspecific adsorption on masked areas. Characterizations with atomic force microscopy demonstrate the steps for lithography with organosilanes and functionalized nanoparticles. Patterning was accomplished for both silicon and glass substrates, to generate nanostructures with periodicities of 200–300 nm that match the diameters of the latex mesospheres of the surface masks. Nanoparticles were shown to bind selectively to uncovered, exposed areas of the substrate and did not attach to the methyl-terminal groups of the organosilane mask. Billions of well-defined nanostructures of nanoparticles can be generated using this high-throughput approach of particle lithography, with exquisite control of surface density and periodicity at the nanoscale.

- Synthesis of macrocyclic natural products by catalyst-controlled stereoselective ring-closing metathesis

Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88–93.

Abstract:



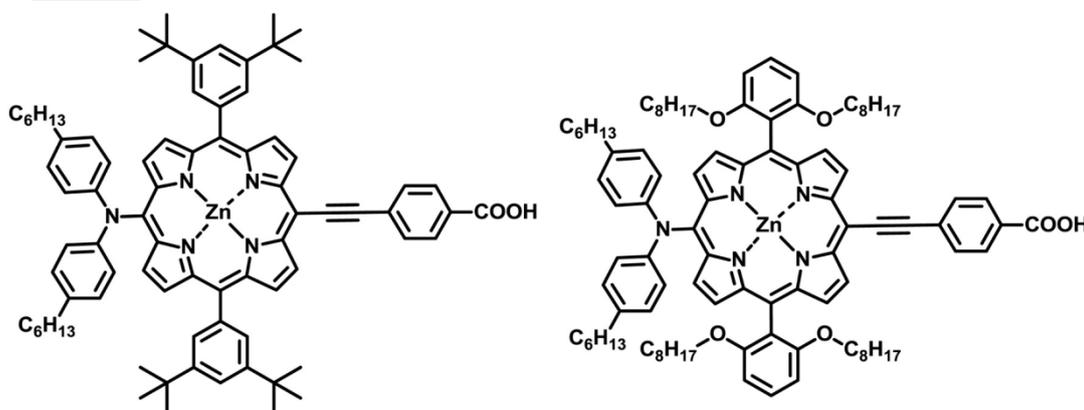
Many natural products contain a C = C double bond through which various other derivatives can be prepared; the stereochemical identity of the alkene can be critical to the biological activities of such molecules. Catalytic ring-closing metathesis (RCM) is a widely used method for the synthesis of large unsaturated rings; however, cyclizations often proceed without control of alkene stereochemistry. This shortcoming is particularly costly when the cyclization reaction is performed after a long sequence of other chemical transformations. Here we outline a reliable, practical and general approach for the efficient and highly stereoselective synthesis of macrocyclic alkenes by catalytic

RCM; transformations deliver up to 97% of the Z isomer owing to control induced by a tungsten-based alkylidene. Utility is demonstrated through the stereoselective preparation of epothilone C and nakadomarin A, the previously reported syntheses of which have been marred by late-stage, non-selective RCM. The tungsten alkylidene can be manipulated in air, delivering the products in useful yields with high stereoselectivity. As a result of efficient RCM and re-incorporation of side products into the catalytic cycle with minimal alkene isomerization, desired cyclizations proceed in preference to alternative pathways, even under relatively high substrate concentration.

- Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency

Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diao, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. *Science* **2011**, *334*, 629-634.

Abstract:

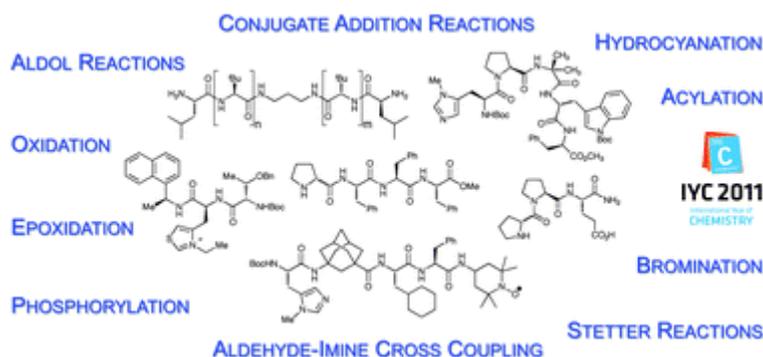


The iodide/triiodide redox shuttle has limited the efficiencies accessible in dye-sensitized solar cells. Here, we report mesoscopic solar cells that incorporate a Co<sup>(II/III)</sup>tris(bipyridyl)-based redox electrolyte in conjunction with a custom synthesized donor- $\pi$ -bridge-acceptor zinc porphyrin dye as sensitizer (designated **YD2-o-C8**). The specific molecular design of **YD2-o-C8** greatly retards the rate of interfacial back electron transfer from the conduction band of the nanocrystalline titanium dioxide film to the oxidized cobalt mediator, which enables attainment of strikingly high photovoltages approaching 1 volt. Because the **YD2-o-C8** porphyrin harvests sunlight across the visible spectrum, large photocurrents are generated. Cosensitization of **YD2-o-C8** with another organic dye further enhances the performance of the device, leading to a measured power conversion efficiency of 12.3% under simulated air mass 1.5 global sunlight.

- Asymmetric catalysis with peptides

Wennemers, H. *Chem. Commun.* **2011**, *47*, 12036-12041.

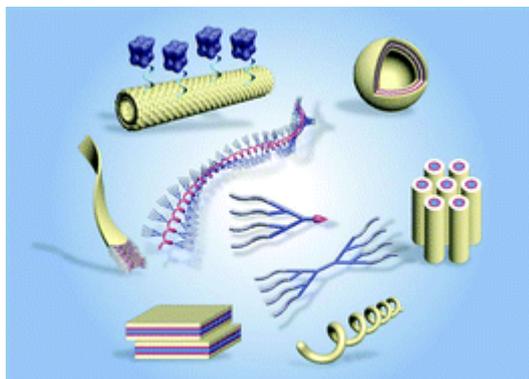
Abstract:



Over the past decade several peptides have been developed as effective asymmetric catalysts for a range of synthetically useful reactions. Many have properties that are difficult to achieve with other catalysts. The article highlights features that render peptidic organocatalysts unique and attractive for future applications. Challenges such as the design of peptidic catalysts are discussed.

- Functional supramolecular assemblies derived from dendritic building blocks  
Park, C.; Lee, J.; Kim, C. *Chem. Commun.* **2011**, 47, 12042-12056.

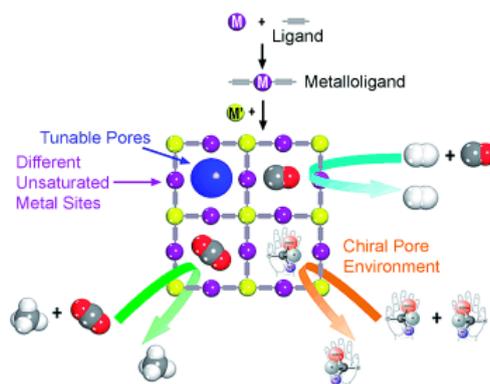
Abstract:



Control of the structure and function of self-assembled materials has been a significant issue in many areas of nanoscience. Among many different types of building blocks, dendritic ones have shown interesting self-assembly behaviour and functional performances due to their unique shape and multiple functionalities. Dendritic building blocks exhibit unique self-assembly behaviour in diverse environments such as aqueous and organic solutions, solid–liquid interfaces, and thermotropic solid conditions. Tuning the balance between hydrophilic and hydrophobic parts, as well as the external conditions for self-assembly, provides unique opportunities for control of supramolecular architectures. Furthermore, the introduction of suitable functional moieties into dendrons enables us to control self-assembly characteristics, allowing nanostructures to exhibit smart performances for electronic or biological applications. The self-assembly characteristics of amphiphilic dendrons under various conditions were investigated to elucidate how dendrons can assemble into nanoscopic structures and how these nanoassemblies exhibit unique properties. Well-defined nanostructures derived from self-assembly of dendrons provide an efficient approach for exhibition of unique functions at the nanoscale. This feature article describes the unique self-assembly characteristics of various types of dendritic building blocks and their potential applications as advanced materials.

- Functional Mixed Metal–Organic Frameworks with Metalloligands  
Das, M. C.; Xiang, S.; Zhang, Z.; Chen, B. *Angew. Chem. Int. Ed.* **2011**, 50, 10510–10520.

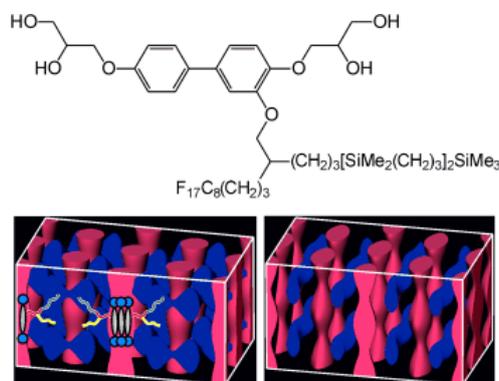
Abstract:



Immobilization of functional sites within metal–organic frameworks (MOFs) is very important for their ability to recognize small molecules and thus for their functional properties. The metalloligand approach has enabled us to rationally immobilize a variety of different functional sites such as open metal sites, catalytic active metal sites, photoactive metal sites, chiral pore environments, and pores of tunable sizes and curvatures into mixed metal–organic frameworks (M'MOFs). In this Minireview, we highlight some important functional M'MOFs with metalloligands for gas storage and separation, enantioselective separation, heterogeneous asymmetric catalysis, sensing, and as photoactive and nanoscale drug delivery and biomedical imaging materials.

- Two- and Three-Dimensional Liquid-Crystal Phases from Axial Bundles of Rodlike Polyphiles: Segmented Cylinders, Crossed Columns, and Ribbons between Sheets  
Liu, F.; Prehm, M.; Zeng, X.; Ungar, G.; Tschierske, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 10599–10602.

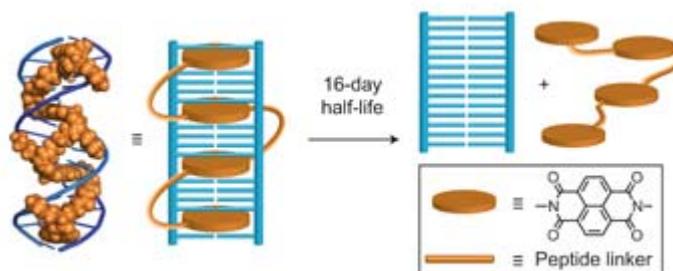
Abstract:



Pleated ribbons and bow ties: Rodlike mesogens (see scheme) with swallow-tail side chains arrange axially in ribbonlike bundles. At high temperatures the ribbons rotate, resulting in a novel 3D hexagonal liquid-crystal phase (see picture, left). At lower temperature, rotation locks in giving a structure of crossed aromatic and fluorinated columns (right). On further cooling the ribbons fuse into aromatic sheets with fluorinated columns intercalated.

- A sequence-specific threading tetra-intercalator with an extremely slow dissociation rate constant  
Holman, G. G.; Zewail-Foote, M.; Smith, A. R.; Johnson, K. A.; Iverson, B. L. *Nature Chem.* **2011**, *3*, 875-881.

Abstract:

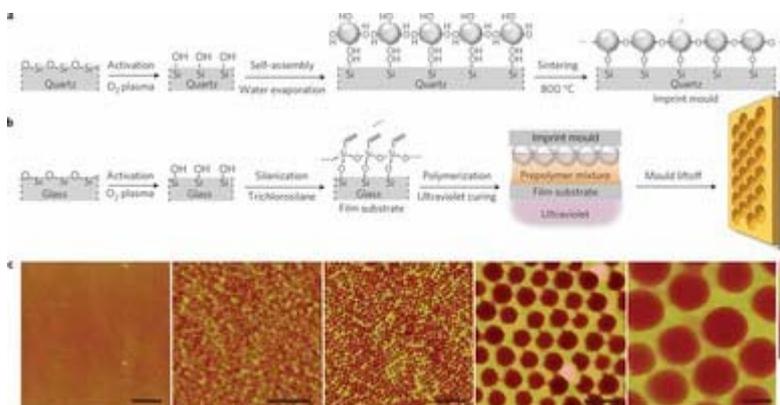


A long-lived and sequence-specific ligand–DNA complex would make possible the modulation of biological processes for extended periods. For this purpose, we are investigating a polyintercalation approach to DNA recognition in which flexible chains of aromatic units thread back and forth repeatedly through the double helix. Here we describe the DNA-binding behaviour of a threading tetra-intercalator. Specific binding was observed on a relatively long DNA strand that strongly favoured a predicted 14 base-pair sequence. Kinetic studies revealed a multistep association process, with sequence specificity that primarily derives from large differences in dissociation rates. The rate-limiting dissociation rate constant of the tetra-intercalator complex dissociating from its preferred binding site was extremely slow, corresponding to a half-life of 16 days. This is one of the longest non-covalent complex half-lives yet reported and, to the best of our knowledge, the longest for a DNA-binding molecule.

- The role of nanopore shape in surface-induced crystallization

Diao, Y.; Harada, T.; Myerson, A. S.; Hatton, T. A.; Trout, B. L. *Nature Mater.* **2011**, *10*, 867–871.

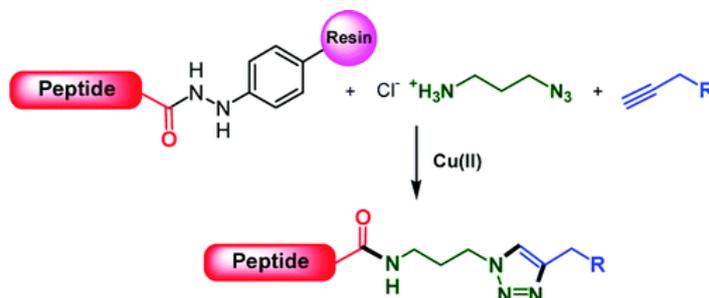
Abstract:



Crystallization of a molecular liquid from solution often initiates at solid–liquid interfaces, and nucleation rates are generally believed to be enhanced by surface roughness. Here we show that, on a rough surface, the shape of surface nanopores can also alter nucleation kinetics. Using lithographic methods, we patterned polymer films with nanopores of various shapes and found that spherical nanopores 15–120nm in diameter hindered nucleation of aspirin crystals, whereas angular nanopores of the same size promoted it. We also show that favourable surface–solute interactions are required for angular nanopores to promote nucleation, and propose that pore shape affects nucleation kinetics through the alteration of the orientational order of the crystallizing molecule near the angles of the pores. Our findings have clear technological implications, for instance in the control of pharmaceutical polymorphism and in the design of ‘seed’ particles for the regulation of crystallization of fine chemicals.

- Three-Component Synthesis of Neoglycopeptides Using a Cu(II)-Triggered Aminolysis of Peptide Hydrazide Resin and an Azide–Alkyne Cycloaddition Sequence  
Ebran, J.-P.; Dendane, N.; Melnyk, O. *Org. Lett.* **2011**, *13*, 4336–4339.

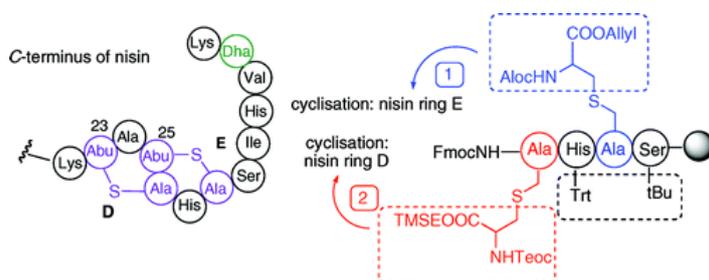
Abstract:



Copper(II)-induced oxidative aminolysis of hydrazides generates Cu(I), the catalyst of the azide–alkyne cycloaddition. This feature was exploited to design a novel solid phase detaching three-component reaction permitting the conversion of supported peptide hydrazides into 1,2,3-triazole linked C-terminal neoglycopeptides.

- Synthesis of Peptides Containing Overlapping Lanthionine Bridges on the Solid Phase: An Analogue of Rings D and E of the Lantibiotic Nisin  
Mothia, B.; Appleyard, A. N.; Wadman, S.; Tabor, A. B. *Org. Lett.* **2011**, *13*, 4216–4219.

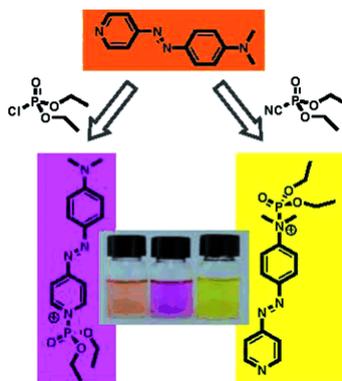
Abstract:



A methodology for the solid-phase synthesis of the overlapping lanthionine bridges found in many lantibiotics has been developed. A novel Teoc/TMSE-protected lanthionine derivative has been synthesized, and this lanthionine, and an Aloc/allyl-protected lanthionine derivative, have been incorporated into a linear peptide using solid-phase peptide synthesis. Selective deprotection of the silyl protecting groups, followed by sequential cyclization, deprotection of the allyl protecting groups, and further cyclization, enabled the regioselective formation of an analogue of rings D and E of nisin.

- Chromogenic, Specific Detection of the Nerve-Agent Mimic DCNP (a Tabun Mimic)  
Royo, S.; Costero, A. M.; Parra, M.; Gil, S.; Martínez-Mañez, R.; Sancenón, F. *Chem. Eur. J.* **2011**, *17*, 6931–6934.

Abstract:

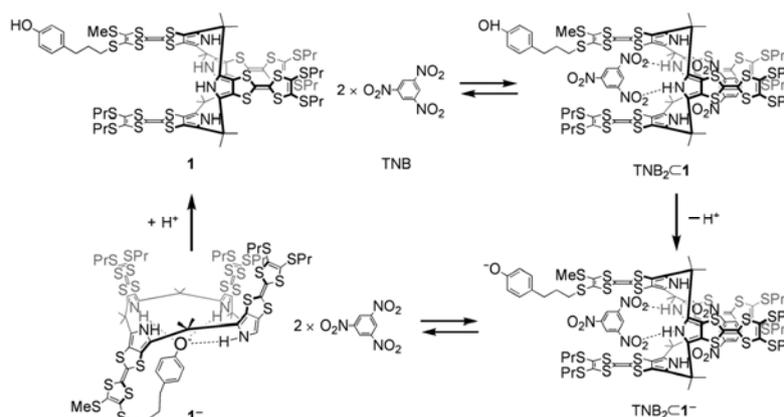


Nerve-gas detection: An azo dye with pyridine and aniline moieties can selectively detect diethylcyanophosphate (DCNP) from diisopropylfluorophosphate (DFP) and diethylchlorophosphate (DCP) by colour changes. Upon addition of DFP and DCP a phosphorylation in the pyridine occurs with a colour change from orange to magenta, whereas addition of DCNP phosphorylated the aniline ring with a colour change from orange to yellow (see figure).

- Acid/Base Controllable Molecular Recognition

Nielsen, K. A.; Bähring, S.; Jeppesen, J. O. *Chem. Eur. J* **2011**, *17*, 11001-11007.

Abstract:

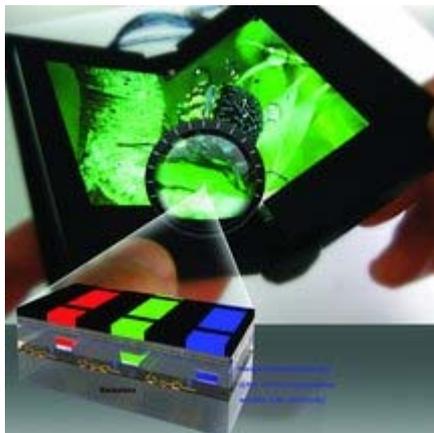


The study of controllable molecular recognition in supramolecular receptors is important for elucidating design strategies that can lead to external control of molecular recognition applications. In this work, we present the design and synthesis of an asymmetric (TTF) tetrathiafulvalene-calix[4]pyrrole receptor and show that its recognition of 1,3,5-trinitrobenzene (TNB) can be controlled by an acid/base input. The new receptor is composed of three identical TTF units and a fourth TTF unit appended with a phenol moiety. Investigation of the host-guest complexation taking place between the TTF-calix[4]pyrrole receptor and the TNB guests was studied by means of absorption and  $^1\text{H}$  NMR spectroscopy; this revealed that the conformation of the molecular receptor can be switched between locked and unlocked states by using base and acid as the input. In the unlocked state, the receptor is able to accommodate two TNB guest molecules, whereas the guests are not able to bind to the receptor in the locked state. This work serves to illustrate how external control (acid/base) of a receptor may be used to direct the molecular recognition of guests (TNBs). It has led to a new controllable molecular recognition system that functions as an acid/base switch.

- Low-Power Flexible Organic Light-Emitting Diode Display Device

Kim, S.; Kwon, H.-J.; Lee, S.; Shim, H.; Chun, Y.; Choi, W.; Kwack, J.; Han, D.; Song, M.; Kim, S.; Mohammadi, S.; Kee, I.; Lee, S. Y. *Adv. Mater.* **2011**, *23*, 3511–3516.

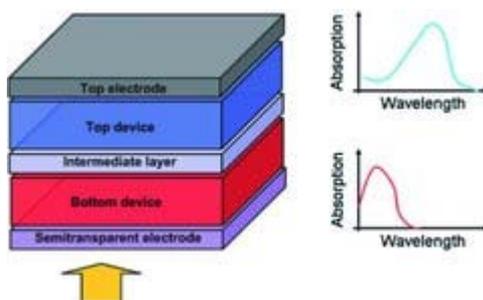
Abstract:



**A low-power flexible organic light-emitting diode (OLED) display device** based on low temperature color filters with a thin film encapsulated RGB OLED microcavity is achieved with high contrast ratios (up to 150 000:1 in dark ambient) and low power consumption (34% power saving compared to polarization film). Furthermore, a mechanical 10 000 times folding experiment with a folding radius of 1 mm demonstrates the mechanical reliability of the flexible OLED device.

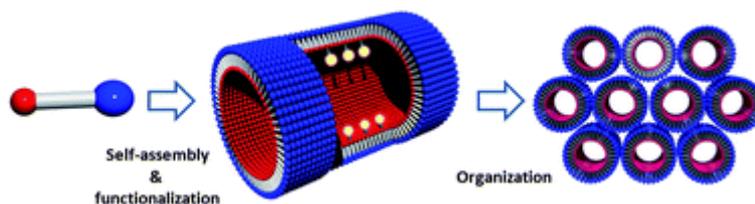
- Polymer–Fullerene Bulk-Heterojunction Solar Cells  
Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. *Adv. Mater.* **2010**, *22*, 3839–3856.

Abstract:



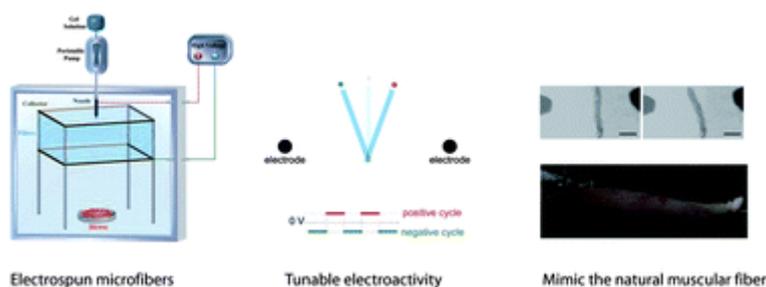
Solution-processed bulk heterojunction organic photovoltaic (OPV) devices have gained serious attention during the last few years and are established as one of the leading next generation photovoltaic technologies for low cost power production. This article reviews the OPV development highlights of the last two decades, and summarizes the key milestones that have brought the technology to today's efficiency performance of over 7%. An outlook is presented on what will be required to drive this young photovoltaic technology towards the next major milestone, a 10% power conversion efficiency, considered by many to represent the efficiency at which OPV can be adopted in wide-spread applications. With first products already entering the market, sufficient lifetime for the intended application becomes more and more critical, and the status of OPV stability as well as the current understanding of degradation mechanisms will be reviewed in the second part of this article.

- Supramolecular organic nanotubes: how to utilize the inner nanospace and the outer space  
Kameta, N.; Minamikawa, H.; Masuda, M. *Soft Matter* **2011**, *7*, 4539-4561.

Abstract:

Organic nanotubes (ONTs) are tubular nanostructures prepared from small organic molecules or macromolecules. These structures have attracted growing attention because their inner and outer spaces exhibit unique properties that may be exploited for potential applications. In the first part of this review, we describe methodologies to construct well-defined ONTs: how to control the dimensions, discriminate the inner and outer surfaces, and functionalize the nanostructures. The well-defined ONTs contain cylindrical nanospaces that can capture, store, and release various nanomaterials, from small molecules to macromolecules. The ONTs' outer spaces and surfaces play critical roles in dispersibility, organization, and manipulation of the ONTs. In the second part, we describe the ONTs' physicochemical properties and utilization of the inner and outer spaces, emphasizing the advantages of ONTs over other types of nanomaterials. Smaller nanomaterials can be efficiently captured in the nanospaces of the ONTs *via* selective surface interactions. For example, encapsulation of proteins in the ONT nanospaces prevents them from chemical or thermal denaturation. Furthermore, the encapsulated materials can be released in response to external stimuli, such as pH or temperature, which can alter the surface charge and/or fluidity. These unique properties of ONTs allow them to be utilized for biomaterials and drug delivery applications.

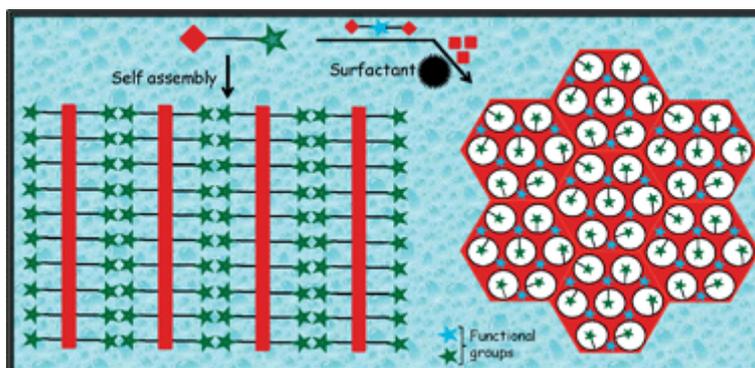
- Artificial muscular microfibers: hydrogel with high speed tunable electroactivity  
Bassil, M.; Ibrahim, M.; El Tahchi, M. *Soft Matter* **2011**, 7, 4833-4838.

Abstract:

The advancement in polymer muscle-like actuator technologies is of immense importance in the development of biologically inspired designs for tissue substitutes where the mechanical robustness is combined with fast physico-chemical responsiveness, biocompatibility and electroactivity. The multiformability (films, fibres, tubules,...) and the multifunctionality (response to temperature, pH, electromagnetic excitation,...) of hydrogels make them a great candidate for electro-bio-active artificial implantable muscular fibers and as soft actuators for gentle micro-scale manipulations. With an end objective to conceive and fabricate a system with instantaneous response to external stimuli, we present the results of an experimental method used to prepare long thin self-assembled hydrogel fibers with aspect ratio greater than  $10^5$  (length/diameter). We show for the first time that these fibers are electroactive and dynamically tunable under low applied electric field (as low as  $500 \text{ V m}^{-1}$ ) with high potential in instantaneous sensing of pH and ionic strength variations in their surrounding medium.

- From molecular chemistry to hybrid nanomaterials. Design and functionalization  
Mehdi, A.; Reye, C.; Corriu, R. *Chem. Soc. Rev.* **2011**, *40*, 563-574.

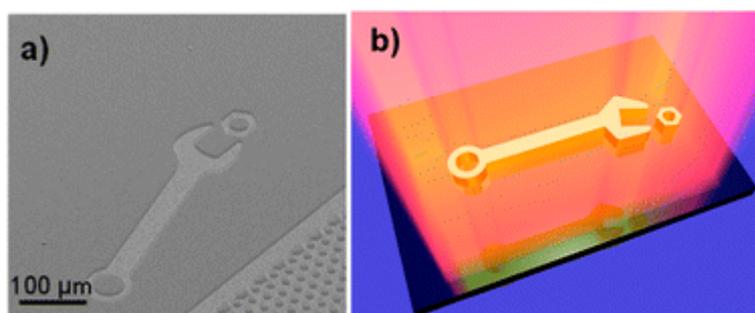
Abstract:



This *tutorial review* reports upon the organisation and functionalization of two families of hybrid organic–inorganic materials. We attempted to show in both cases the best ways permitting the organisation of materials in terms of properties at the nanometric scale. The first family concerns mesoporous hybrid organic–inorganic materials prepared in the presence of a structure-directing agent. We describe the functionalization of the channel pores of ordered mesoporous silica, that of the silica framework, as well as the functionalization of both of them simultaneously. This family is currently one of the best supports for exploring polyfunctional materials, which can provide a route to interactive materials. The second family concerns lamellar hybrid organic–inorganic materials which is a new class of nanostructured materials. These materials were first obtained by self-assembly, as a result of van der Waals interactions of bridged organosilica precursors containing long alkylene chains during the sol–gel process, without any structure directing agent. This methodology has been extended to functional materials. It is also shown that such materials can be obtained from monosilylated precursors.

- Hybrid materials for optics and photonics  
Lebeau, B.; Innocenzi, P. *Chem. Soc. Rev.* **2011**, *40*, 886-906.

Abstract:



The interest in organic–inorganic hybrids as materials for optics and photonics started more than 25 years ago and since then has known a continuous and strong growth. The high versatility of sol–gel processing offers a wide range of possibilities to design tailor-made materials in terms of structure, texture, functionality, properties and shape modelling. From the first hybrid material with optical functional properties that has been obtained by incorporation of an organic dye in a silica matrix, the research in the field has quickly evolved towards more sophisticated systems, such as multifunctional and/or multicomponent materials, nanoscale and self-assembled hybrids and devices for integrated optics. In the present *critical review*, we have focused our attention on three main research areas:

passive and active optical hybrid sol–gel materials, and integrated optics. This is far from exhaustive but enough to give an overview of the huge potential of these materials in photonics and optics (254 references).

- Materials chemistry of fullerene C<sub>60</sub> derivatives

Montellano López, A.; Mateo-Alonso, A.; Prato, M. *J. Mater. Chem.* **2011**, *21*, 1305-1318.

Abstract:

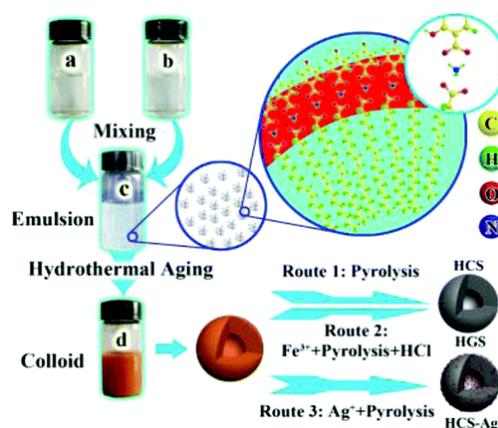


Despite the increasing interest of the scientific community in carbon nanotubes and graphene, fullerene C<sub>60</sub> still plays an important role in the family of nanocarbons. A quarter of a century of research on fullerenes has been dedicated to understanding the way to produce stable, well-characterized and highly soluble fullerene derivatives, which retain the original properties of C<sub>60</sub>. The applications in a wide number of fields, especially on new materials design, have enriched the literature with fascinating examples where fullerenes are directly involved. We report here a brief summary of recent achievements in some exciting applications of fullerene derivatives.

- Weak Acid–Base Interaction Induced Assembly for the Synthesis of Diverse Hollow Nanospheres

Wang, G.-H.; Sun, Q.; Zhang, R.; Li, W.-C.; Zhang, X.-Q.; Lu, A.-H. *Chem. Mater.* **2011**, *23*, 4537–4542.

Abstract:



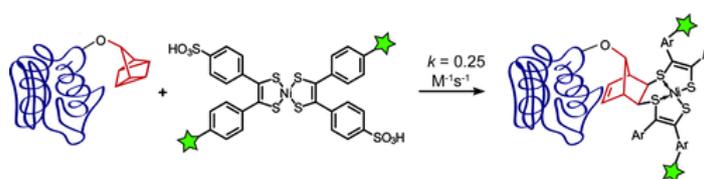
We have established a novel and generalizable hydrothermal synthesis for diverse hollow nanospheres, which cover polymer, carbon, graphitic carbon, and metal-doped carbon hollow nanospheres. The synthesis principle is based on the weak acid–base interaction ( $-\text{COO}^-/-\text{NH}_4^+/-\text{COO}^-$ ) induced assembly. That is, the ammonium cations from the reactant ammonia act as a trigger for the assembly of  $-\text{COO}^-$  group-containing polymer around surfactant oleic acid micelles through

the weak interaction between carboxylate anion and ammonium ion. Consequently, hollow polymer nanospheres (HPSs) with diameters ranging from 100 to 200 nm and hollow core sizes ranging from 30 to 80 nm can be synthesized. It was determined that approximately 61% of the added amount of  $\text{NH}_3$  participates is retained in the HPS product. Taking these HPSs as the precursor, hollow carbon nanospheres (HCSs) with tunable surface areas can be obtained by varying the preparation conditions. More importantly, owing to the presence of the  $-\text{COO}^-$  functional groups, a wide range of metal cations (e.g.,  $\text{Fe}^{3+}$  and  $\text{Ag}^+$ ) can be successfully introduced into these HPSs, so that they can then be converted to hollow graphitized nanospheres and Ag-doped catalytically active HCSs.

- A Bioorthogonal Quadricyclane Ligation

Sletten, E. M.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2011**, *133*, 17570-17573.

Abstract:

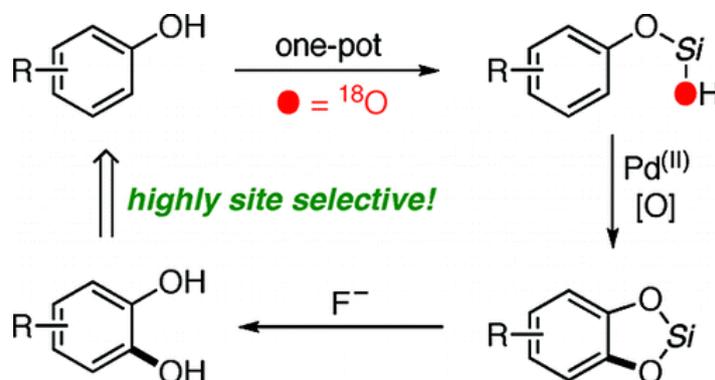


New additions to the bioorthogonal chemistry compendium can advance biological research by enabling multiplexed analysis of biomolecules in complex systems. Here we introduce the quadricyclane ligation, a new bioorthogonal reaction between the highly strained hydrocarbon quadricyclane and Ni bis(dithiolene) reagents. This reaction has a second-order rate constant of  $0.25 \text{ M}^{-1} \text{ s}^{-1}$ , on par with fast bioorthogonal reactions of azides, and proceeds readily in aqueous environments. Ni bis(dithiolene) probes selectively labeled quadricyclane-modified bovine serum albumin, even in the presence of cell lysate. We have demonstrated that the quadricyclane ligation is compatible with, and orthogonal to, strain-promoted azide–alkyne cycloaddition and oxime ligation chemistries by performing all three reactions in one pot on differentially functionalized protein substrates. The quadricyclane ligation joins a small but growing list of tools for the selective covalent modification of biomolecules.

- Synthesis of Catechols from Phenols via Pd-Catalyzed Silanol-Directed C–H Oxygenation

Huang, C.; Ghavtadze, N.; Chattopadhyay, B.; Gevorgyan, V. *J. Am. Chem. Soc.* **2011**, *133*, 17630-17633.

Abstract:



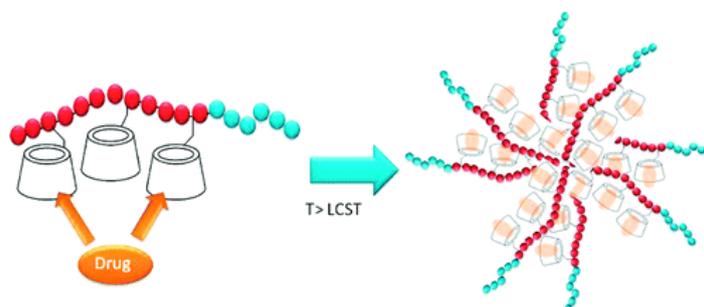
A silanol-directed, Pd-catalyzed C–H oxygenation of phenols into catechols is presented. This method is highly site selective and general, as it allows for oxygenation of not only electron-neutral but also electron-poor phenols. This method operates via a silanol-directed acetoxylation, followed by a

subsequent acid-catalyzed cyclization reaction into a cyclic silicon-protected catechol. A routine desilylation of the silacyle with TBAF uncovers the catechol product.

- Development of Micellar Novel Drug Carrier Utilizing Temperature-Sensitive Block Copolymers Containing Cyclodextrin Moieties

Yhaya, F.; Lim, J.; Kim, Y.; Liang, M.; Gregory, A. M.; Stenzel, M. H. *Macromolecules* **2011**, *44*, 8433–8445.

Abstract:

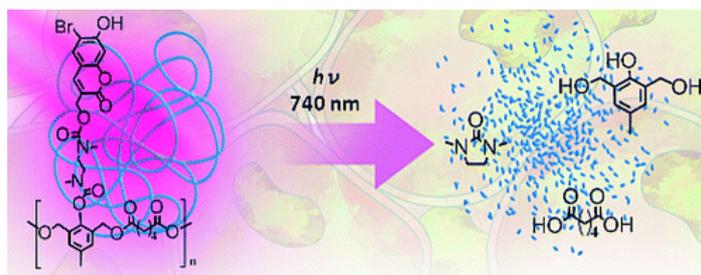


A drug-delivery system for albendazole (ABZ) based on  $\beta$ -cyclodextrin has been synthesized. Well-defined statistical copolymers, composed of N-isopropylacrylamide (NIPAAm) and trimethylsilylpropargyl acrylate (TMSPA), have been prepared by reversible addition–fragmentation chain transfer (RAFT) polymerization. The reactivity ratios were determined to be  $r_{\text{TMSPA}} = 1.12$  and  $r_{\text{NIPAAm}} = 0.49$ , in the absence of RAFT agent, and  $r_{\text{TMSPA}} = 1.35$  and  $r_{\text{NIPAAm}} = 0.35$ , in the presence of RAFT agent using the average of different techniques. Block copolymers were prepared using a PEOGMEA40 macro-RAFT agent chain extended with NIPAAm and TMSPA in various feed ratios. After deprotection, the polymers were reacted with 6I-azido-6I-deoxy- $\beta$ -cyclodextrin via Huisgen azide–alkyne 1,3-dipolar cycloaddition, resulting in thermo-responsive block copolymers with pendant  $\beta$ -cyclodextrin groups, which were then acetylated to modify the polarity and inclusion-complex formation of  $\beta$ -cyclodextrin with the drug albendazole (ABZ). Only block copolymers with small amounts of cyclodextrin were observed to have an LCST while the copolymers containing higher  $\beta$ -cyclodextrin fractions increased the LCST of PNIPAAm beyond measurable temperature ranges. Encapsulation of ABZ increased the LCST. The loading efficiency increased in the polymer  $\beta$ -cyclodextrin conjugate compared to native  $\beta$ -cyclodextrin with the highest loading observed in the block copolymer after all remaining cyclodextrin hydroxyl groups had been acetylated. While  $\beta$ -cyclodextrin is toxic, attachment of a polymer lowered the toxicity to nontoxic levels. The ABZ-loaded polymers were all observed to be highly toxic to OVCAR-3 ovarian cancer cell lines with the acetylated polymer showing the highest toxicity.

- Low Power, Biologically Benign NIR Light Triggers Polymer Disassembly

Fomina, N.; McFearin, C. L.; Sermsakdi, M.; Morachis, J. M.; Almutairi, A. *Macromolecules* **2011**, *44*, 8590–8597.

Abstract:



Near infrared (NIR) irradiation can penetrate up to 10 cm deep into tissues and be remotely applied with high spatial and temporal precision. Despite its potential for various medical and biological applications, there is a dearth of biomaterials that are responsive at this wavelength region. Herein we report a polymeric material that is able to disassemble in response to biologically benign levels of NIR irradiation upon two-photon absorption. The design relies on the photolysis of the multiple pendant 4-bromo-7-hydroxycoumarin protecting groups to trigger a cascade of cyclization and rearrangement reactions leading to the degradation of the polymer backbone. The new material undergoes a 50% Mw loss after 25 s of ultraviolet (UV) irradiation by single photon absorption and 21 min of NIR irradiation via two-photon absorption. Most importantly, even NIR irradiation at a biologically benign laser power is sufficient to cause significant polymer disassembly. Furthermore, this material is well tolerated by cells both before and after degradation. These results demonstrate for the first time a NIR sensitive material with potential to be used for in vivo applications.