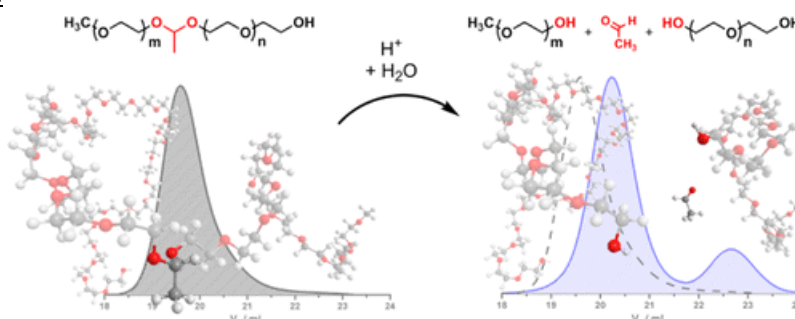


- Universal Concept for the Implementation of a Single Cleavable Unit at Tunable Position in Functional Poly(ethylene glycol)s

1

Dingels, C.; Müller, S. S.; Steinbach, T.; Tonhauser, C.; Frey, H. *Biomacromolecules* **2013**, *14*, 448-459.

Abstract:

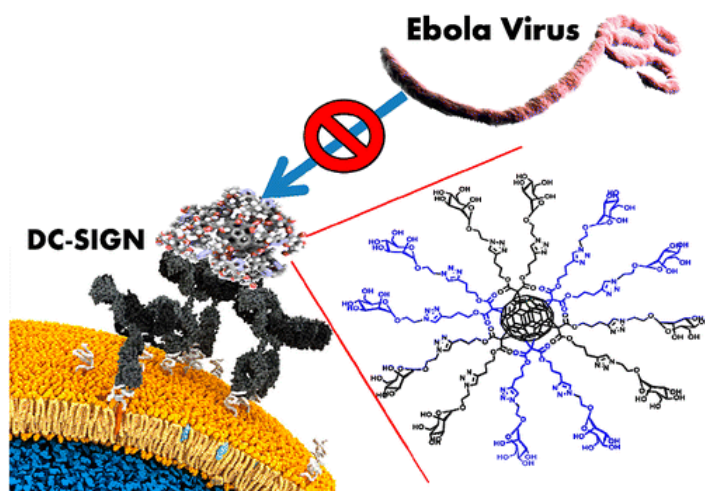


Poly(ethylene glycol) (PEG) with acid-sensitive moieties gained attention particularly for various biomedical applications, such as the covalent attachment of PEG (PEGylation) to protein therapeutics, the synthesis of stealth liposomes, and polymeric carriers for low-molecular-weight drugs. Cleavable PEGs are favored over their inert analogues because of superior pharmacodynamic and/or pharmacokinetic properties of their formulations. However, synthetic routes to acetal-containing PEGs published up to date either require enormous efforts or result in ill-defined materials with a lack of control over the molecular weight. Herein, we describe a novel methodology to implement a single acetaldehyde acetal in well-defined (hetero)functional poly(ethylene glycol)s with total control over its position. To underline its general applicability, a diverse set of initiators for the anionic polymerization of ethylene oxide (cholesterol, dibenzylamino ethanol, and poly(ethylene glycol) monomethyl ether (mPEG)) was modified and used to synthesize the analogous labile PEGs. The polyether bearing the cleavable lipid had a degree of polymerization of 46, was amphiphilic and exhibited a critical micelle concentration of $4.20 \text{ mg}\cdot\text{L}^{-1}$. From dibenzylamino ethanol, three heterofunctional PEGs with different molecular weights and labile amino termini were generated. The transformation of the amino functionality into the corresponding squaric acid ester amide demonstrated the accessibility of the cleavable functional group and activated the PEG for protein PEGylation, which was exemplarily shown by the attachment to bovine serum albumin (BSA). Furthermore, turning mPEG into a macroinitiator with a cleavable hydroxyl group granted access to a well-defined poly(ethylene glycol) derivative bearing a single cleavable moiety within its backbone. All the acetal-containing PEGs and PEG/protein conjugates were proven to degrade upon acidic treatment.

- Glycofullerenes Inhibit Viral Infection

Luczkowiak, J.; Muñoz, A.; Sánchez-Navarro, M.; Ribeiro-Viana, R.; Ginieis, A.; Illescas, B. M.; Martín, N.; Delgado, R.; Rojo, J. *Biomacromolecules* **2013**, *14*, 431-437.

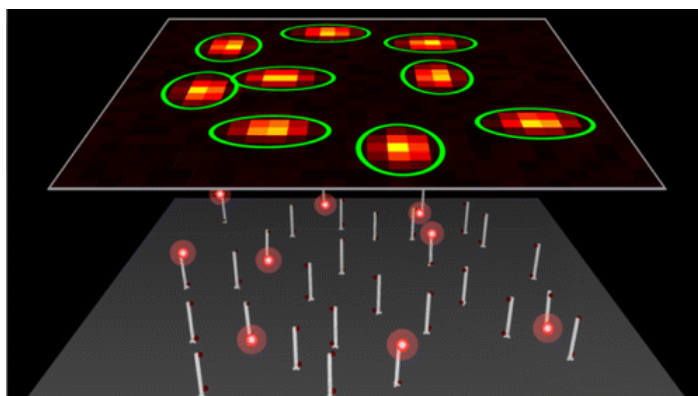
Abstract:



Water-soluble glycofullerenes based on a hexakis-adduct of [60]fullerene with an octahedral addition pattern are very attractive compounds providing a spherical presentation of carbohydrates. These tools have been recently described and they have been used to interact with lectins in a multivalent manner. Here, we present the use of these glycofullerenes, including new members with 36 mannoses, as compounds able to inhibit a DC-SIGN-dependent cell infection by pseudotyped viral particles. The results obtained in these experiments demonstrate for the first time that these glycoconjugates are adequate to inhibit efficiently an infection process, and therefore, they can be considered as very promising and interesting tools to interfere in biological events where lectins such as DC-SIGN are involved.

- DNA Origami Nanopillars as Standards for Three-Dimensional Super resolution Microscopy
Schmied, J. J.; Forthmann, C.; Pibiri, E.; Lalkens, B.; Nickels, P.; Liedl, T.; Tinnefeld, P. *Nano Lett.* **2013**, *13*, 781–785.

Abstract:

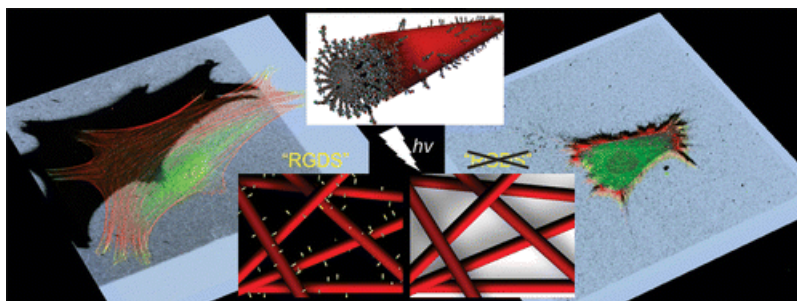


Nanopillars are promising nanostructures composed of various materials that bring new functionalities for applications ranging from photovoltaics to analytics. We developed DNA nanopillars with a height of 220 nm and a diameter of 14 nm using the DNA origami technique. Modifying the base of the nanopillars with biotins allowed selective, upright, and rigid immobilization on solid substrates. With the help of site-selective dye labels, we visualized the structure and determined the orientation of the nanopillars by three-dimensional fluorescence superresolution microscopy. Because of their rigidity and nanometer-precise addressability, DNA origami nanopillars qualify as scaffold for the assembly of plasmonic devices as well as for three-dimensional superresolution standards.

- Photodynamic Control of Bioactivity in a Nanofiber Matrix

Sur, S.; Matson, J. B.; Webber, M. J.; Newcomb, C. J.; Stupp, S. I. *ACS Nano* **2012**, 6, 10776-10785.

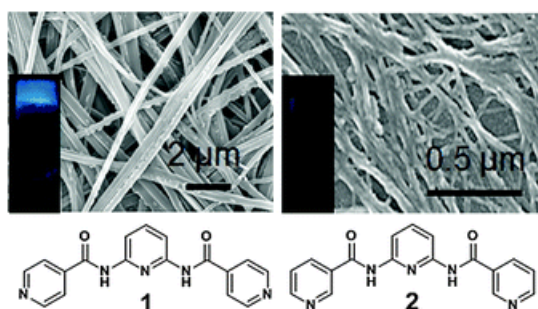
Abstract:



Self-assembling peptide materials have been used extensively to mimic natural extracellular matrices (ECMs) by presenting bioactive epitopes on a synthetic matrix. Although this approach can facilitate a desired response from cells grown in the matrix, it lacks the capacity for spatial or temporal regulation of the presented signals. We describe here a photoresponsive, synthetic ECM using a supramolecular platform composed of peptide amphiphiles (PAs) that self-assemble into cylindrical nanofibers. A photocleavable nitrobenzyl ester group was included in the peptide backbone using a novel Fmoc-amino acid that is compatible with microwave-assisted solid-phase peptide synthesis. The placement of the photolabile group on the peptide backbone enabled efficient removal of the ECM-derived cell adhesion epitope RGDS from PA molecules upon exposure to light (half-life of photolysis 1.9 min) without affecting the nanofiber assembly. Fibroblasts cultured on RGDS-presenting PA nanofiber substrates demonstrated increased cell spreading and more mature focal adhesions compared with unfunctionalized and control (RGES-presenting) surfaces, as determined by immunostaining and cell morphological analysis. Furthermore, we observed an arrest in fibroblast spreading on substrates containing a cleavable RGDS epitope when the culture was exposed to light; in contrast, this dynamic shift in cell response was absent when the RGDS epitope was attached to the PA molecule by a light-insensitive control linker. Light-responsive bioactive materials can contribute to the development of synthetic systems that more closely mimic the dynamic nature of native ECM.

- Fluorescent hydrogels formed by CH- π and π - π interactions as the main driving forces: an approach toward understanding the relationship between fluorescence and structure
Ahn, J.; Park, S.; Lee, J. H.; Jung, S. H.; Moon, S.-J.; Jung, J. H. *Chem. Commun.* **2013**, 49, 2109-2111.

Abstract:

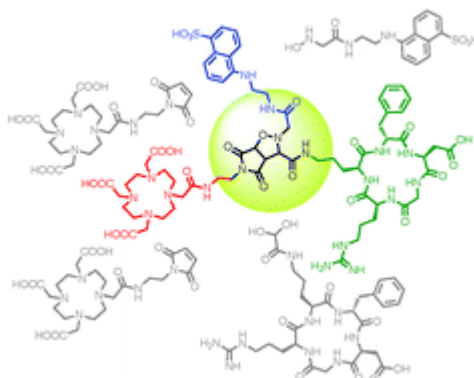


Amide-linked tripyridine derivatives **1**, with a para-substituent, and **2**, with a meta-substituent, were

gelated in water or water–DMSO. The gelation capabilities of 1 and 2 were attributed to the cooperative effects of mainly CH– π and π – π stacking or strong intermolecular hydrogen bonding interactions between the amide groups. The fluorescence properties of gels 1 and 2 were dependent on the binding strength of the π – π stacking.

- Site-selective three-component reaction for dual-functionalization of peptides
Munch, H. K.; Rasmussen, J. E.; Popa, G.; Christensen, J. B.; Jensen, K. J. *Chem. Commun.* **2013**, 49, 1936–1938.

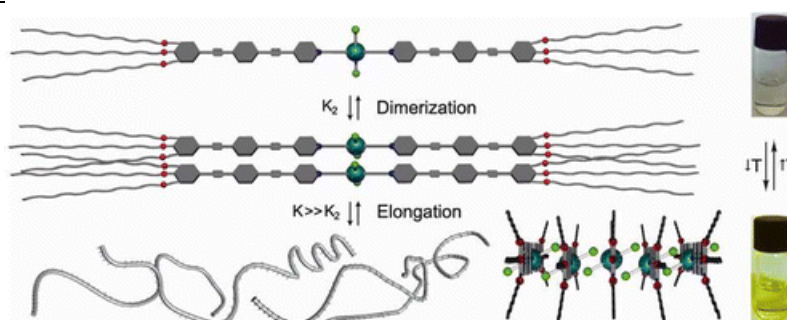
Abstract:



A site-selective dual-functionalization of peptides is presented, involving readily available maleimides as well as N-hydroxylamines. The modification proceeds through a three component 1,3-dipolar cycloaddition, forming a stable product. This was exemplified by the one-pot attachment of two molecular imaging moieties to a tumor binding cyclic peptide, and was extended to the conjugation of a DOTA chelator to a 12 kDa protein.

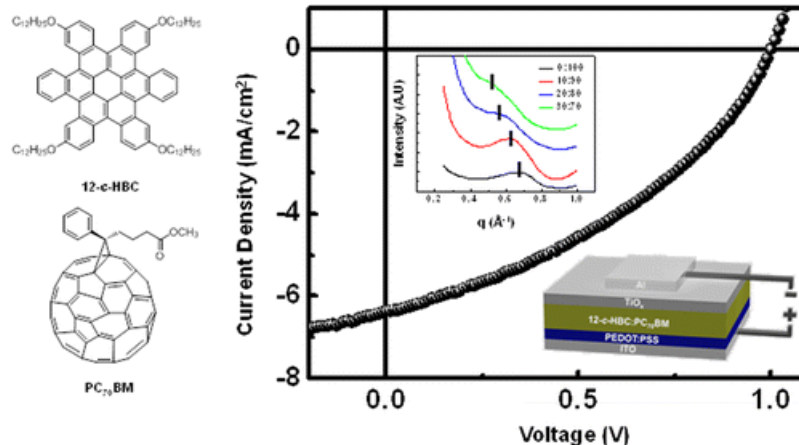
- Cooperative Supramolecular Polymerization Driven by Metallophilic Pd...Pd Interactions
Mayoral, M. J.; Rest, C.; Stepanenko, V.; Schellheimer, J.; Albuquerque, R. Q.; Fernández, G. J. *Am. Chem. Soc.* **2013**, 135, 2148–2151.

Abstract :



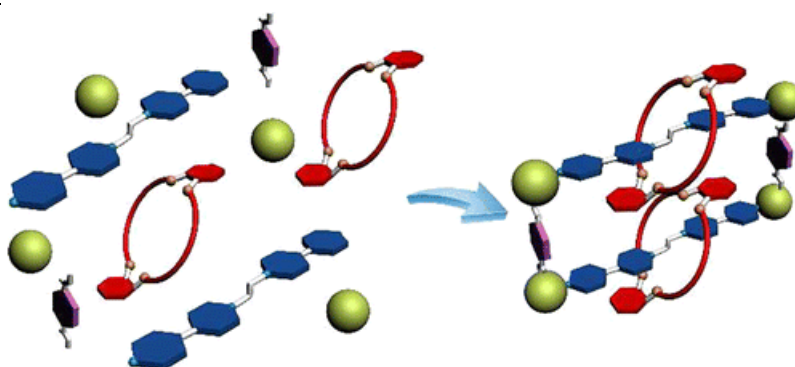
A new oligophenyleneethynylene (OPE)-based Pd(II) pyridyl complex has been synthesized, and its self-assembly has been investigated in solution, in the bulk state, and on surfaces. Detailed analysis of concentration- and temperature-dependent UV–vis studies in methylcyclohexane supported by DFT calculations demonstrate for the first time that cooperative supramolecular polymerization processes can be driven by metallophilic interactions.

- Using Self-Organization To Control Morphology in Molecular Photovoltaics
Kang, S. J.; Ahn, S.; Kim, J. B.; Schenck, C.; Hiszpanski, A. M.; Oh, S.; Schiros, T.; Loo, Y.-L.; Nuckolls, C. J. *Am. Chem. Soc.* **2013**, 135, 2207–2212.

Abstract:

This work explores the formation of well-defined molecular p–n junctions in solution-processed self-assembled heterojunction solar cells using dodecyloxy-substituted contorted hexabenzocoronene (12-c-HBC) as a donor material and phenyl-C70-butyl ester (PC71BM) as an acceptor. We find that the contorted 12-c-HBC molecules effectively assemble in solution to form a nested structure with the ball-shaped PC71BM. The result is a self-assembled molecular-scale p–n junction. When this well-defined p–n junction is embedded in active films, we can make efficient self-assembled solar cells with minimal amounts of donor material relative to the acceptor. The power conversion efficiency is drastically enhanced by the mode of donor and acceptor assembly within the film.

- Formation of [3]Catenanes from 10 Precursors via Multicomponent Coordination-Driven Self-Assembly of Metallarectangles
Li, S.; Huang, J.; Cook, T. R.; Pollock, J. B.; Kim, H.; Chi, K.-W.; Stang, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 2084-2087.

Abstract:

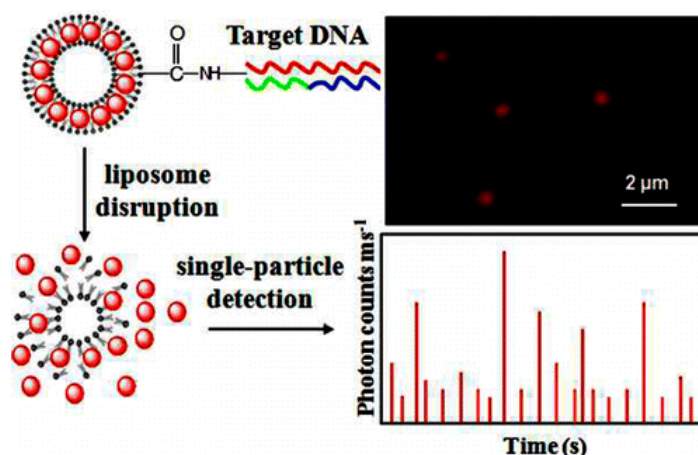
We describe the formation of a suite of [3]catenanes via multicomponent coordination-driven self-assembly and host–guest complexation of a rectangular scaffold comprising a 90° Pt-based acceptor building block with a pseudorotaxane bis(pyridinium)ethane/dibenzo-24-crown-8 linear dipyrindyl ligand and three dicarboxylate donors. The doubly threaded [3]catenanes are formed from a total of 10 molecular components from four unique species. Furthermore, the dynamic catenation process is reversible and can be switched off and on in a controllable manner by successive addition of KPF_6 and 18-crown-6, as monitored by ^1H and ^{31}P NMR spectroscopy.

- Liposome–Quantum Dot Complexes Enable Multiplexed Detection of Attomolar DNAs

without Target Amplification

Zhou, J.; Wang, Q.-X.; Zhang, C.-Y. *J. Am. Chem. Soc.* **2013**, *135*, 2056-2059.

Abstract:

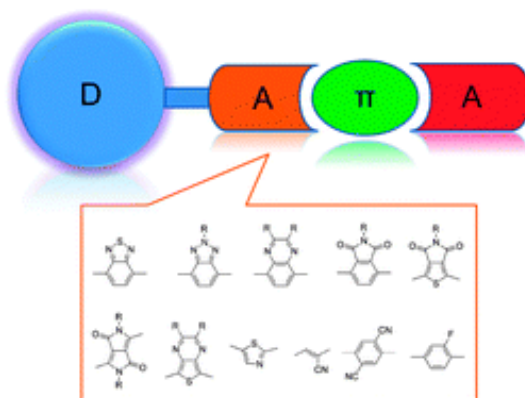


Sensitive detection of DNA usually relies on target amplification approaches such as polymerase chain reaction and rolling circle amplification. Here we describe a new approach for sensitive detection of low-abundance DNA using liposome–quantum dot (QD) complexes and single-particle detection techniques. This assay allows for detection of single-stranded DNA at attomolar concentrations without the involvement of target amplification. Importantly, this strategy can be employed for simultaneous detection of multiple DNA targets.

- Organic sensitizers from D– π –A to D–A– π –A: effect of the internal electron-withdrawing units on molecular absorption, energy levels and photovoltaic performances

Wu, Y.; Zhu, W. *Chem. Soc. Rev.* **2013**, *42*, 2039-2058.

Abstract:

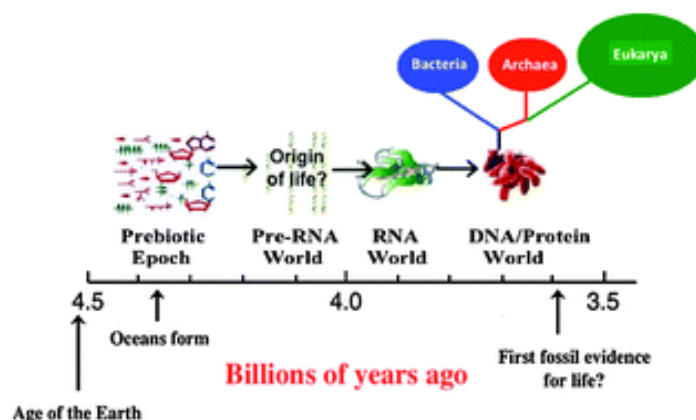


The high performance and low cost of dye-sensitized solar cells (DSSCs) have drawn great interest from both academic and industrial circles. The research on exploring novel efficient sensitizers, especially on inexpensive metal-free pure organic dyes, has never been suspended. The donor– π –acceptor (D– π –A) configuration is mainstream in the design of organic sensitizers due to its convenient modulation of the intramolecular charge-transfer nature. Recently, it has been found that incorporation of additional electron-withdrawing units (such as benzothiadiazole, benzotriazole, quinoxaline, phthalimide, diketopyrrolopyrrole, thienopyrazine, thiazole, triazine, cyanovinyl, cyano- and fluoro-substituted phenyl) into the π bridge as internal acceptors, termed the D–A– π –A configuration, displays several advantages such as tuning of the molecular energy levels, red-shift of the charge-transfer absorption band, and distinct improvement of photovoltaic performance and

stability. We apply the D–A– π –A concept broadly to the organic sensitizers containing additional electron-withdrawing units between electron donors and acceptors. This review is projected to summarize the category of pure organic sensitizers on the basis of the D–A– π –A feature. By comparing the structure–property relationship of typical photovoltaic D–A– π –A dyes, the important guidelines in the design of such materials are highlighted.

- New insights into prebiotic chemistry from Stanley Miller's spark discharge experiments Bada, J. L. *Chem. Soc. Rev.* **2013**, 42, 2186-2196.

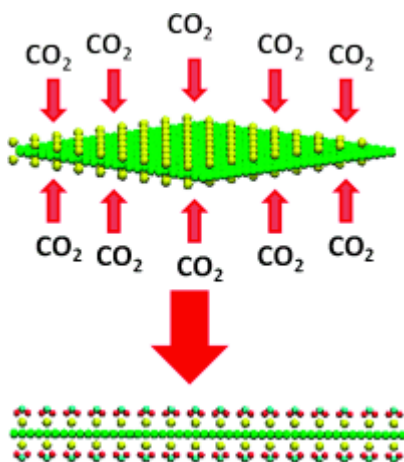
Abstract:



1953 was a banner year for biological chemistry: The double helix structure of DNA was published by Watson and Crick, Sanger's group announced the first amino acid sequence of a protein (insulin) and the synthesis of key biomolecules using simulated primordial Earth conditions has demonstrated by Miller. Miller's studies in particular transformed the study of the origin of life into a respectable field of inquiry and established the basis of prebiotic chemistry, a field of research that investigates how the components of life as we know it can be formed in a variety of cosmochemochemical environments. In this review, I cover the continued advances in prebiotic syntheses that Miller's pioneering work has inspired. The main focus is on recent state-of-the-art analyses carried out on archived samples of Miller's original experiments, some of which had never before been analyzed, discovered in his laboratory material just before his death in May 2007. One experiment utilized a reducing gas mixture and an apparatus configuration (referred to here as the "volcanic" apparatus) that could represent a water-rich volcanic eruption accompanied by lightning. Another included H₂S as a component of the reducing gas mixture. Compared to the limited number of amino acids Miller identified, these new analyses have found that over 40 different amino acids and amines were synthesized, demonstrating the potential robust formation of important biologic compounds under possible cosmochemochemical conditions. These experiments are suggested to simulate long-lived volcanic island arc systems, an environment that could have provided a stable environment for some of the processes thought to be involved in chemical evolution and the origin of life. Some of the alternatives to the Miller-based prebiotic synthesis and the "primordial soup" paradigm are evaluated in the context of their relevance under plausible planetary conditions.

- Interaction Mechanism of CO₂ Ambient Adsorption on Transition-Metal-Coated Boron Sheets Tai, T. B.; Nguyen, M. T. *Chem. Eur. J.* **2013**, 19, 2942-2946.

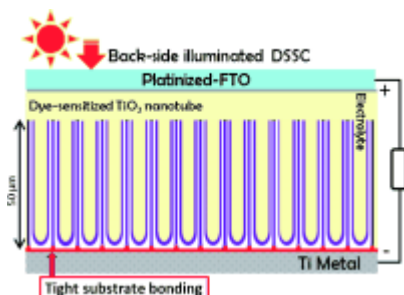
Abstract:



Getting attached: Ca- and Sc-coated α -boron sheets are excellent absorbents for ambient CO_2 capture with remarkably high adsorption energies (E_{ads}) up to 3.0 eV (see figure). More importantly, the interaction mechanism between Sc and boron substrate and CO_2 in chemisorption configurations is nonclassical and emerges in a two-step process.

- High-Aspect-Ratio Dye-Sensitized Solar Cells Based on Robust, Fast-Growing TiO_2 Nanotubes
So, S.; Lee, K.; Schmuki, P. *Chem. Eur. J.* **2013**, *19*, 2966-2970.

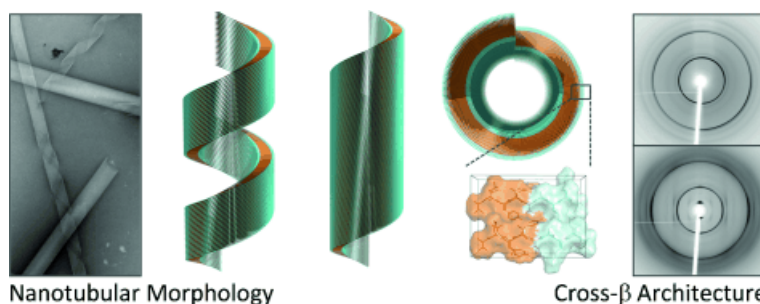
Abstract:



Get attached: The mechanical attachment of TiO_2 nanotube layers to a substrate can be a determining factor for the performance of these layers in dye-sensitized solar cells (DSSCs). Self-organized TiO_2 nanotube layers grown in an electrolyte that contained lactic acid are shown to have considerably improved anchoring on the Ti metal substrate, which allows the construction of stable and efficient solar cells with $>50 \mu\text{m}$ nanotube length (see figure).

- The Structure of Cross- β Tapes and Tubes Formed by an Octapeptide, $\alpha\text{S}\beta 1$
Morris, K. L.; Zibae, S.; Chen, L.; Goedert, M.; Sikorski, P.; Serpell, L. C. *Angew. Chem. Int. Ed.* **2013**, *8*, 2279–2283.

Abstract:



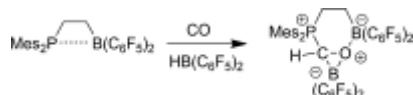
Elaborate morphology: The $\alpha\text{S}\beta 1$ peptide, a fragment of α -synuclein, assembles into flat tapes

consisting of a peptide bilayer, which can be modeled based on the cross- β structure found in amyloid proteins. The tapes are stabilized by hydrogen bonding, whilst the amphiphilic nature of the peptide results in the thin bilayer structure. To further stabilize the structure, these tapes may twist to form helical tapes, which subsequently close into nanotubes.

- Facile Carbon Monoxide Reduction at Intramolecular Frustrated Phosphane/Borane Lewis Pair Templates

Sajid, M.; Elmer, L.-M.; Rosorius, C.; Daniliuc, C. G.; Grimme, S.; Kehr, G.; Erker, G. *Angew. Chem. Int. Ed.* **2013**, *8*, 2243-2246.

Abstract:

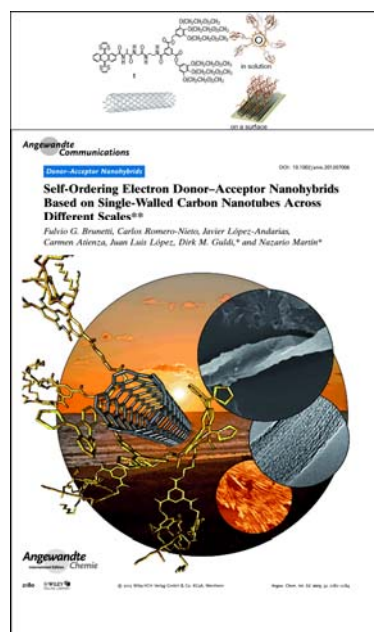


A new reaction pathway: Carbon monoxide is readily reduced by Piers' borane at a frustrated Lewis pair (FLP) to yield a formylborane stabilized by the FLP (see picture). This reaction may be considered a typical example of efficient activation of a small molecule by a FLP.

- Self-Ordering Electron Donor–Acceptor Nanohybrids Based on Single-Walled Carbon Nanotubes Across Different Scales

Brunetti, F. G.; Romero-Nieto, C.; López-Andarias, J.; Atienza, C.; López, J. L.; Guldi, D. M.; Martín, N. *Angew. Chem. Int. Ed.* **2013**, *8*, 2180–2184.

Abstract:



From nano- to macroscale: The immobilization of photo- and redox-active 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene-based dipeptide **1** onto SWCNTs resulted in a high order of self-alignment among **1**/SWCNTs (see picture). The assembly of the **1**/SWCNTs is the key for stabilizing long-lived charge-separated states that are formed upon photoexcitation of the SWCNTs.

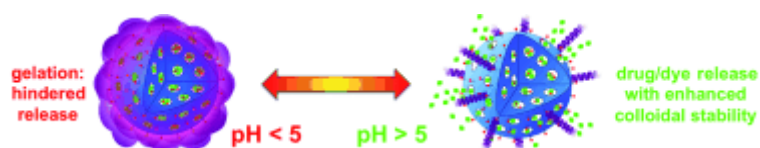
- pH-Responsive Nutraceutical–Mesoporous Silica Nanoconjugates with Enhanced Colloidal Stability

Guillet-Nicolas, R.; Popat, A.; Bridot, J.-L.; Monteith, G.; Qiao, S. Z.; Kleitz, F. *Angew. Chem. Int.*

Ed. **2013**, 8, 2318-2322.

Abstract:

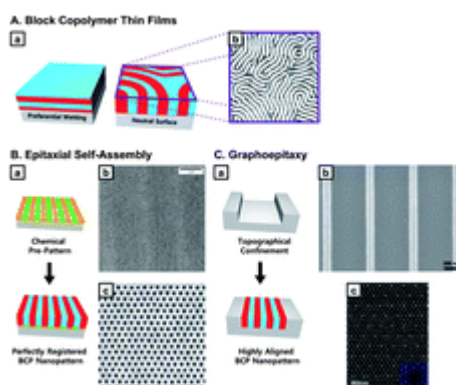
10



An innovative platform for targeted oral drug delivery is proposed based on the functionalization of drug/dye-loaded mesoporous silica nanoparticles (MSNs) with a biodegradable nutraceutical (β -lactoglobulin). The attachment of the nutraceutical not only protects the drug/dye from leaching in acidic environment, but also effectively allows their release in desired basic sites (pH 7.4).

- Directed self-assembly of block copolymers for universal nanopatterning
Kim, B. H.; Kim, J. Y.; Kim, S. O. *Soft Matter* **2013**, 9, 2780-2786.

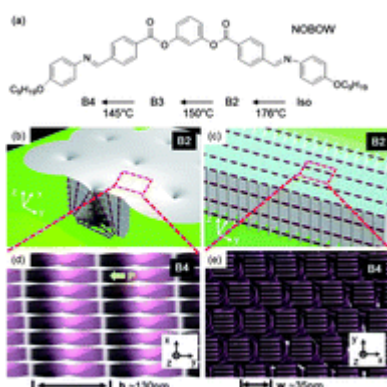
Abstract:



Block copolymers (BCP) are self-assembling polymeric materials that have been extensively investigated for several decades. Recently, directed self-assembly (DSA) of BCPs has received enormous research attention from both academia and industry as next-generation nanolithography technology. This article provides a brief introduction to (i) the spontaneous and directed self-assembly of BCPs, (ii) the orientation and lateral ordering of BCP nanopatterns and their relationships with DSA strategies, (iii) various potential applications of BCP nanopatterning, and (iv) mussel-inspired BCP nanopatterning for arbitrary substrate materials including low surface energy materials.

- Self-assembled hydrophobic surface generated from a helical nanofilament (B4) liquid crystal phase
Kim, H.; Yi, Y.; Chen, D.; Korblova, E.; Walba, D. M.; Clark, N. A.; Yoon, D. K. *Soft Matter* **2013**, 9, 2793-2797.

Abstract:

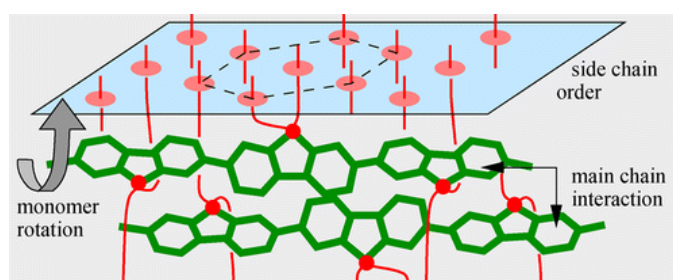


Hydrophobic air/liquid crystal (LC) surfaces exhibiting self-assembled dual scale roughness have been made by simple cooling of a bent-core mesogen from its high temperature isotropic melt through two liquid crystal phases. The transition to the fluid smectic B2 phase generates micron-scale toric focal conic domains (TFCDs) at the surface. Upon further cooling into the hexatic smectic B4 phase these TFCD structures are preserved and become textured by the nanometer-sized helical nanofilaments (HNFs) of the B4. The resulting TFCD/HNF surface is hydrophobic and shows clear evidence for surface tension reduction characteristic of dual-scale roughness, suggesting a simple self-assembly-based approach to low surface tension surfaces using LC morphology.

- Crystalline and Noncrystalline Forms of Poly(9,9-diheptylfluorene)

Knaapila, M.; Torkkeli, M.; Galbrecht, F.; Scherf, U. *Macromolecules* **2013**, 46, 836-843.

Abstract:

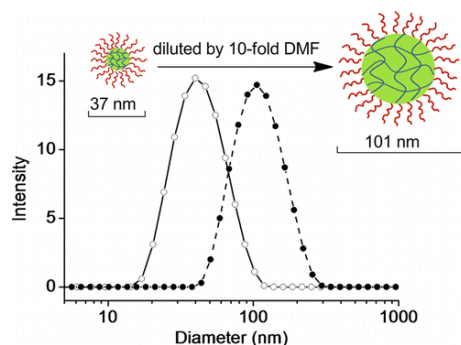


The formation of ordered morphologies in poly(9,9-diheptylfluorene) (PF7) was investigated using X-ray diffraction and grazing incidence X-ray diffraction. Two crystalline phases were found. The α -phase is orthorhombic with $a = 2.60$ nm, $b = 2.25$ nm, and $c = 3.34$ nm, and it is structurally very close to the α -phase in poly(9,9-dioctylfluorene) (PF8). The γ -phase is monoclinic with $a = 2.88$ nm, $b = 0.96$ nm, and $c = 1.68$ nm, and the oblique angle is close to 90° . The γ -phase is the stable form in the bulk while the α -phase preferentially forms in thin films. Well-ordered and aligned crystalline films were produced from both good (toluene) and moderate (methylcyclohexane, MCH) solvent. Preparing films from MCH without annealing resulted in mesoscopic crystal with decreased order along the a -axis. This mesoscopic structure differs from the β -phase found in PF8 and is more related to the crystalline γ -phase. This difference may explain why mesoscopic PF8 has a phase transition into the α -phase, whereas the mesoscopic PF7 rather into the γ -phase.

- Redox-Responsive, Core Cross-Linked Polyester Micelles

Zhang, Z.; Yin, L.; Tu, C.; Song, Z.; Zhang, Y.; Xu, Y.; Tong, R.; Zhou, Q.; Ren, J.; Cheng, J. *ACS Macro Lett.* **2013**, 2, 40-44.

Abstract:

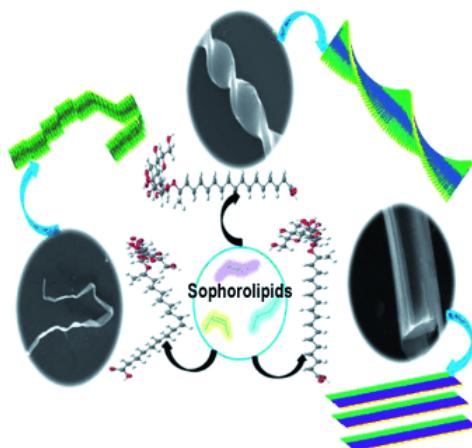


Monomethoxy poly(ethylene glycol)-*b*-poly(Tyr(alkynyl))-OCA, a biodegradable amphiphilic block copolymer, was synthesized by means of ring-opening polymerization of 5-(4-(prop-2-yn-1-

ylloxy)benzyl)-1,3-dioxolane-2,4-dione (Tyr(alkynyl)-OCA) and used to prepare core cross-linked polyester micelles via click chemistry. Core cross-linking not only improved the structural stability of the micelles, but also allowed controlled release of cargo molecules in response to the reducing reagent. This new class of core cross-linked micelles can potentially be used in controlled release and drug delivery applications.

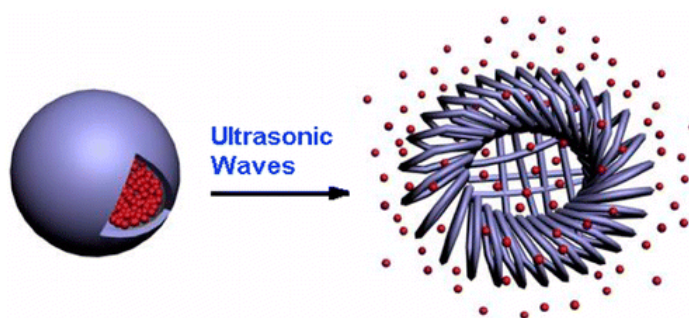
12

- Influence of the Sophorolipid Molecular Geometry on their Self-Assembled Structures
Dhasaiyan, P.; Banerjee, A.; Visaveliya, N.; Prasad, B. L. V. *Chem. Asian J.* **2013**, 8, 369 – 372.
Abstract:



The remarkable influence of a small change in the molecular geometry on the self-assembled structures of the acidic form of sophorolipids (SLs) derived from oleic, elaidic, and stearic acid is demonstrated. Most interestingly helical structures were seen only from SLs derived from elaidic acid (the *trans* conformer).

- Hollow Spheres Self-Assembled by a Tetraphenylethylene Macrocycle and Their Transformation to Bird Nests under Ultrasound
Song, S.; Zheng, Y. S. *Org. Lett.* **2013**, 15, 820-823.
Abstract:



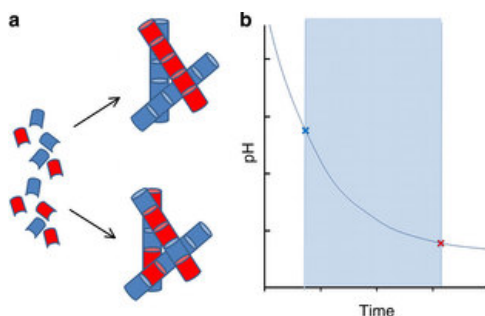
A new tetraphenylethylene macrocycle easily self-assembled into both intrinsic pores and extrinsic pores in crystal and hollow spheres in precipitates. The hollow spheres could be transformed into bird nests composed of nanorods under ultrasound, which could be used to load and controllably release anticancer drugs.

- Chemically programmed self-sorting of gelator networks
Morris, K. L.; Chen, L.; Raeburn, J.; Sellick, O. R.; Cotanda, P.; Paul, A.; Griffiths, P. C.; King, S. M.; O'Reilly, R. K.; Serpell, L. C.; Adams, D. J. *Nature Communications* **2013**, 4,

1480.

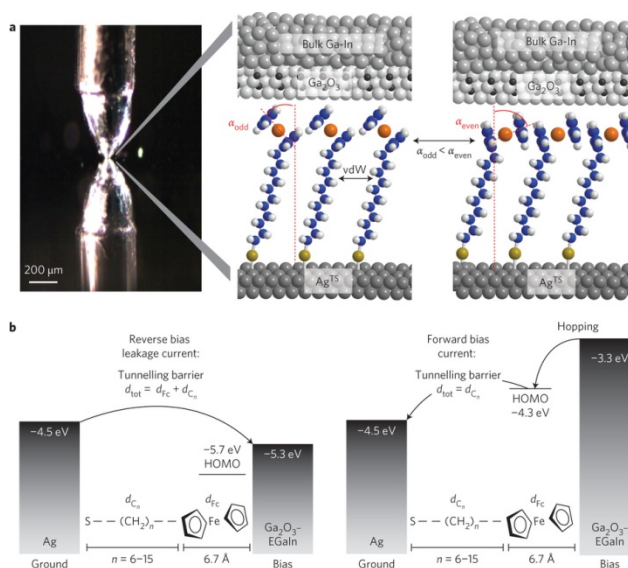
Abstract:

13



Controlling the order and spatial distribution of self-assembly in multicomponent supramolecular systems could underpin exciting new functional materials, but it is extremely challenging. When a solution of different components self-assembles, the molecules can either coassemble, or self-sort, where a preference for like-like intermolecular interactions results in coexisting, homomolecular assemblies. A challenge is to produce generic and controlled 'one-pot' fabrication methods to form separate ordered assemblies from 'cocktails' of two or more self-assembling species, which might have relatively similar molecular structures and chemistry. Self-sorting in supramolecular gel phases is hence rare. Here we report the first example of the pH-controlled self-sorting of gelators to form self-assembled networks in water. Uniquely, the order of assembly can be predefined. The assembly of each component is preprogrammed by the pK_a of the gelator. This pH-programming method will enable higher level, complex structures to be formed that cannot be accessed by simple thermal gelation.

- The role of van der Waals forces in the performance of molecular diodes
Nerngchamnong, N.; Yuan, L.; Qi, D.-C.; Li, J.; Thompson, D.; Nijhuis, C. A. *Nature Nanotechnology* **2013**, 8, 113–118.

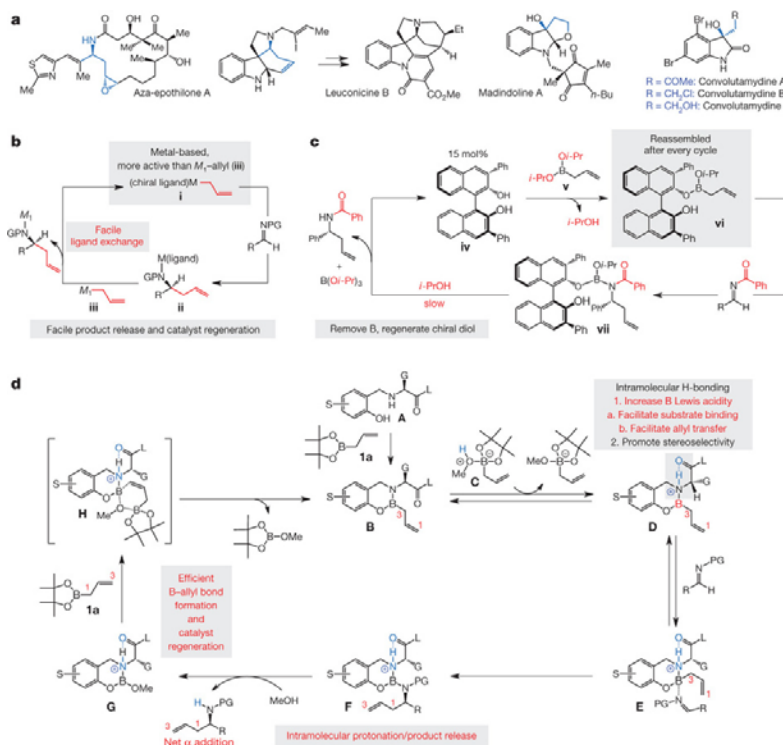
Abstract:

One of the main goals of organic and molecular electronics is to relate the performance and electronic function of devices to the chemical structure and intermolecular interactions of the organic component inside them, which can take the form of an organic thin film, a self-assembled monolayer or a single molecule. This goal is difficult to achieve because organic and molecular electronic devices are complex physical-organic systems that consist of at least two electrodes, an organic component

and two (different) organic/inorganic interfaces. Singling out the contribution of each of these components remains challenging. So far, strong π - π interactions have mainly been considered for the rational design and optimization of the performances of organic electronic devices, and weaker intermolecular interactions have largely been ignored. Here, we show experimentally that subtle changes in the intermolecular van der Waals interactions in the active component of a molecular diode dramatically impact the performance of the device. In particular, we observe an odd-even effect as the number of alkyl units is varied in a ferrocene-alkanethiolate self-assembled monolayer. As a result of a more favourable van der Waals interaction, junctions made from an odd number of alkyl units have a lower packing energy (by ~ 0.4 - 0.6 kcal mol⁻¹), rectify currents 10 times more efficiently, give a 10% higher yield in working devices, and can be made two to three times more reproducibly than junctions made from an even number of alkyl units.

- Simple organic molecules as catalysts for enantioselective synthesis of amines and alcohols
Silverio, D. L.; Torker, S.; Pilyugina, T.; Vieira, E. M.; Snapper, M. L.; Haeffner, F.; Hoveyda, A. H. *Nature* **2013**, *494*, 216-221.

Abstract:



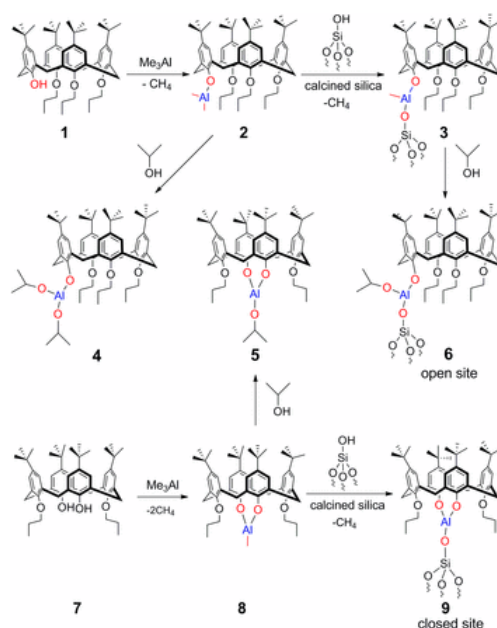
The discovery of catalysts that can be used to synthesize complex organic compounds by enantioselective transformations is central to advances in the life sciences; for this reason, many chemists aim to discover catalysts that allow for preparation of chiral molecules as predominantly one mirror-image isomer. The ideal catalyst should not contain precious elements and should bring reactions to completion in a few hours through operationally simple procedures. Here we introduce a set of small organic molecules that can catalyse reactions of unsaturated organoboron reagents with imines and carbonyls; the products of the reactions are enantiomerically pure amines and alcohols, which might serve as intermediates in the preparation of biologically active molecules. A distinguishing feature of this catalyst class is the presence of a 'key' proton embedded within their structure. Catalysts are derived from the abundant amino acid valine and are prepared in large quantities in four steps with inexpensive reagents. Reactions are scalable, do not demand stringent

conditions, and can be performed with as little as 0.25 mole per cent catalyst in less than six hours at room temperature to generate products in more than 85 per cent yield and $\geq 97:3$ enantiomeric ratio. The efficiency, selectivity and operational simplicity of the transformations and the range of boron-based reagents are expected to render this advance important for future progress in syntheses of amines and alcohols, which are useful in chemistry, biology and medicine.

- Catalytic consequences of open and closed grafted Al(III)-calix[4]arene complexes for hydride and oxo transfer reactions

Nandi, P.; Tang, W.; Okrut, A.; Kong, X.; Hwang, S.-J.; Neurock, M.; Katz, A. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 2484-2489.

Abstract:

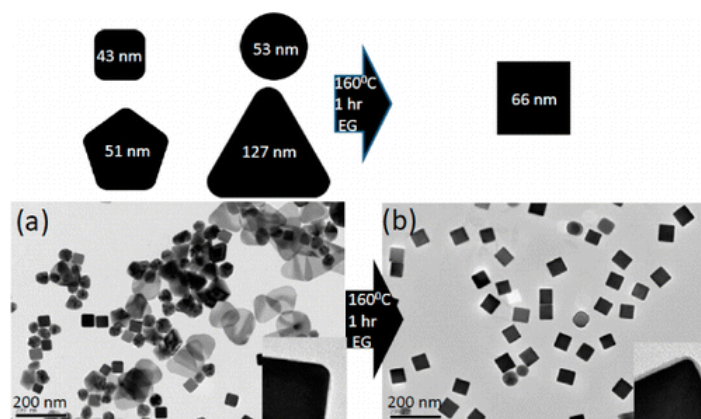


An approach for the control and understanding of supported molecular catalysts is demonstrated with the design and synthesis of open and closed variants of a grafted Lewis acid active site, consisting of Al(III)-calix[4]arene complexes on the surface of silica. The calixarene acts as a molecular template that enforces open and closed resting-state coordination geometries surrounding the metal active sites, due to its lower-rim substituents as well as site isolation by virtue of its steric bulk. These sites are characterized and used to elucidate mechanistic details and connectivity requirements for reactions involving hydride and oxo transfer. The consequence of controlling open versus closed configurations of the grafted Lewis acid site is demonstrated by the complete lack of observed activity of the closed site for Meerwein-Ponndorf-Verley (MPV) reduction; whereas, the open variant of this catalyst has an MPV reduction activity that is virtually identical to previously reported soluble molecular Al(III)-calix[4]arene catalysts. In contrast, for olefin epoxidation using *tert*-butylhydroperoxide as oxidant, the open and closed catalysts exhibit similar activity. This observation suggests that for olefin epoxidation catalysis using Lewis acids as catalyst and organic hydroperoxide as oxidant, covalent binding of the hydroperoxide is not required, and instead dative coordination to the Lewis acid center is sufficient for catalytic oxo transfer. This latter result is supported by density functional theory calculations of the transition state for olefin epoxidation catalysis, using molecular analogs of the open and closed catalysts.

- Does Morphology of a Metal Nanoparticle Play a Role in Ostwald Ripening Processes?

Kuo, C. L.; Hwang, K. C. *Chem. Mater.* **2013**, *25*, 365-371.

Abstract:

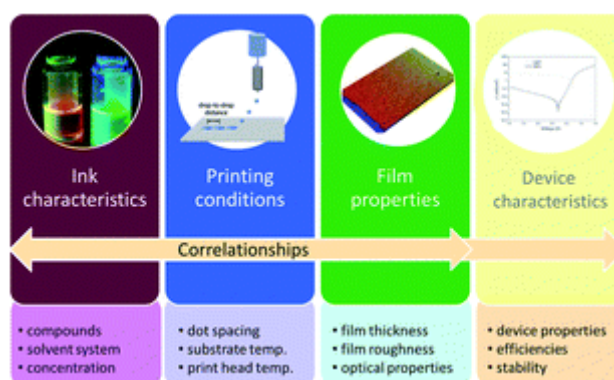


The Ostwald ripening theory is commonly adopted to rationalize the growth of large metal nanoparticles that are formed at the expense of small-sized nanoparticles of higher chemical potential energies. This classical theory did not describe whether the morphology of a metal nanoparticle plays a role in controlling the shape evolution in the ripening processes. Here we show the direct observation of shape evolution among Ag nanoparticles of different morphologies in solutions, and experimental measurements of the relative chemical potential energies (or the electrochemical oxidation potentials) of Ag NPs of different morphologies, including, nanocubes, nanospheres, triangular plates, and decahedral nanoparticles. Theoretical calculation shows that when the diameter of a metal NP is beyond 35 nm, the influence of particle sizes on the oxidation potentials becomes very small. Chemical etching of Ag NPs by $\text{Fe}(\text{NO}_3)_3$ results in preferential removal of atoms at sharp edges/corners, and negative shift in the oxidation potentials. The measured electrochemical oxidation potentials of Ag NPs are in following orders: nanocubes (43 nm in length, 346 $\text{mV}_{\text{Ag}/\text{AgCl}}$) > nanospheres (53 nm in diameter, 337 $\text{mV}_{\text{Ag}/\text{AgCl}}$) > penta-twinned decahedrons (86 nm in edge length, 315 $\text{mV}_{\text{Ag}/\text{AgCl}}$) > triangular nanoplates (127 nm in edge length and 11 nm in thickness, 293 $\text{mV}_{\text{Ag}/\text{AgCl}}$).

- Inkjet printing of organic electronics – comparison of deposition techniques and state-of-the-art developments

Teichler, A.; Perelaer, J.; Schubert, U. S. *J. Mater. Chem. C* **2013**, *1*, 1910-1925.

Abstract:

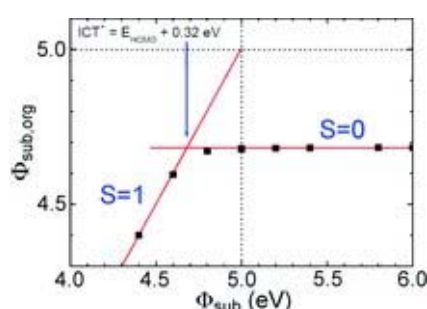


Inkjet printing represents a solution dispensing technique that is characterized by its non-contact, material-efficient and reproducible processing. This critical review discusses the use of inkjet printing

for organic electronics with a focus on the applicability as well as the drying behavior. The nascent inkjet printing technique is compared to commonly used solution deposition methods, like spin-coating and doctor blading. Basic drying principles of inkjet printed features are understood and fundamental correlations between processing properties and film characteristics can be drawn. It is, however, a long way to gain a full understanding of the complete drying process, since the process conditions as well as the ink properties correlate in a complex relation with the final device properties. Nevertheless, inkjet printing has the potential to evolve as one of the most promising film preparation techniques in the future and has already been applied successfully in combinatorial screening workflows and for the preparation of organic solar cell devices.

- Calculating the Universal Energy-Level Alignment of Organic Molecules on Metal Oxides
Ley, L.; Smets, Y.; Pakes, C. I.; Ristein, J. *Adv. Funct. Mater.* **2013**, 23, 794–805.

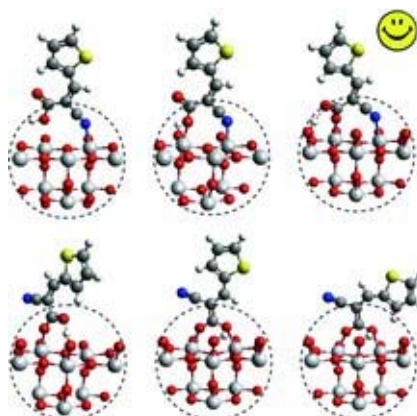
Abstract:



A model that describes the universal energy alignment of organic molecules on metal oxides is developed. The approach explains why the level alignment is rather independent of the experimental details, such as the electronic structure of the oxide, defects in the oxide, and the thickness of the oxide and the overlayer.

- Structure–Property Relations in All-Organic Dye-Sensitized Solar Cells
Jiao, Y.; Zhang, F.; Grätzel, M.; Meng, S. *Adv. Funct. Mater.* **2013**, 23, 424–429.

Abstract:

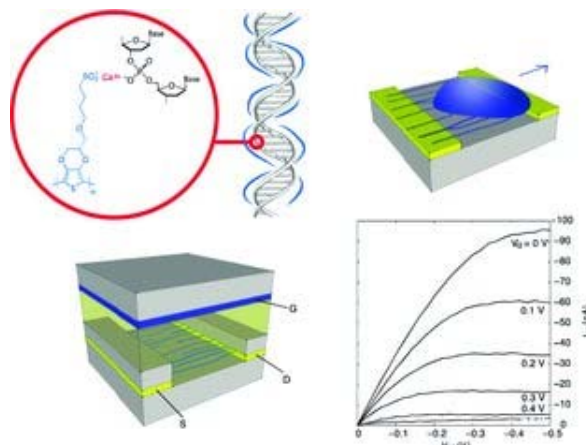


An important structural feature at the interface, Ti–N anchoring, is inferred from energetics, vibrational, and electronic data for a broad group of all-organic dyes on TiO₂. This feature contributes to the observed efficiency improvement in all-organic cyanoacrylate dye-sensitized solar cells. The main results are based on first-principles molecular dynamics and real-time time-dependent density functional theory simulations, accompanied with experimental confirmation.

- Water-Dispersible Fullerene Aggregates as a Targeted Anticancer Prodrug with both Chemo- and Photodynamic Therapeutic Actions

Fan, J.; Fang, G.; Zeng, F.; Wang, X.; Wu, S. *Small* **2013**, 9, 613–621.

Abstract:

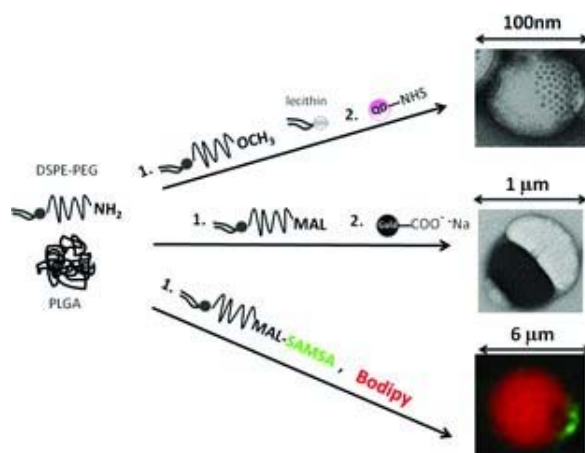


Prodrug therapy is one strategy to deliver anticancer drugs in a less reactive manner to reduce nonspecific cytotoxicity. A new multifunctional anticancer prodrug system based on water-dispersible fullerene (C60) aggregates is introduced; this prodrug system demonstrates active targeting, pH-responsive chemotherapy, and photodynamic therapeutic (PDT) properties. Incorporating (via a cleavable bond) an anticancer drug, which is doxorubicin (DOX) in this study, and a targeting ligand (folic acid) onto fullerene while maintaining an overall size of approximately 135 nm produces a more specific anticancer prodrug. This prodrug can enter folate receptor (FR)-positive cancer cells and kill the cells via intracellular release of the active drug form. Moreover, the fullerene aggregate carrier exhibits PDT action; the cytotoxicity of the system towards FR-positive cancer cells is increased in response to light irradiation. As the DOX drug molecules are conjugated onto fullerene, the DOX fluorescence is significantly quenched by the strong electron-accepting capability of fullerene. The fluorescence restores upon release from fullerene, so this fluorescence quenching–restoring feature can be used to track intracellular DOX release. The combined effect of chemotherapy and PDT increases the therapeutic efficacy of the DOX–fullerene aggregate prodrug. This study provides useful insights into designing and improving the applicability of fullerene for other targeted cancer prodrug systems.

- Spontaneous Formation of Heterogeneous Patches on Polymer–Lipid Core–Shell Particle Surfaces during Self-Assembly

Salvador-Morales, C.; Valencia, P. M.; Gao, W.; Karnik, R.; Farokhzad, O. C. *Small* **2013**, 9, 511–517.

Abstract:



Spontaneous formation of heterogeneous patches on the surface of lipid-based nanoparticles (NPs)

and microparticles (MPs) due to the segregation of two different functional groups. Patch formation is observed when tracing the functional groups with quantum dots, gold nanoparticles, and fluorescent dyes. This discovery could have important implications for the future design of self-assembled NPs and MPs for different biomedical applications.