
Abstract:

Two in one: Two pseudorotaxanes can be combined to form a twin-axial hetero[7]rotaxane (see picture) by using the copper-catalyzed alkyne–azide “click” reaction. The synthetic route, in which twin-axial and single-axial rotaxanes are formed, combines self-assembly and the formation of covalent bonds to ensure the correct positioning of the two types of rings in the final product.

Halochromic Phenolate Perylene Bisimides with Unprecedented NIR Spectroscopic Properties

Abstract:

C — C coupling of 1,7-dibromoperylene bisimide with sterically hindered 2,6-di-tert-butylphenol by a carbon nucleophilic substitution reaction in the absence of transition-metal catalysts gave novel halochromic perylene bisimides (see picture). The corresponding phenolate ions of these compounds exhibit unprecedented NIR spectroscopic properties including strong absorption with maxima at around 1200 nm.

Biofunctionalization of nanoparticles for cytosensing and cell surface carbohydrate assay

Abstract:

Developing sensitive and specific sensing strategies for probing the chemical and biological events in/at a living cell can ultimately contribute to the understanding of life processes. These strategies
are also beneficial to early diagnosis of diseases for early and successful treatment. Biofunctionalization of nanoparticles can integrate remarkable properties of both biological components and nanoparticles, thus providing a promising platform for tracing the recognition and transduction processes and improving the sensing performance. This Feature Article reviews the current research regarding the biofunctionalization strategies, and the usage of the bionanocomposites in the arena of cytosensing and cell surface carbohydrate assay.

  
  Abstract:

Fibers of micrometer and submicrometer diameters have been of significant interest in recent years owing to their advanced applications in diverse fields such as optoelectronics, regenerative medicine, piezoelectrics, ceramic materials, etc. There are a number of processes to make thin fibers including electrospinning, melt blowing, and recently developed Forcespinning. However, use of solvents or heat to lower viscosity for processing is common to all existing polymer fiber manufacturing methods, and a greener approach to making fibers remains a challenge. Interestingly, nature has engineered spiders and silkworms with a benign way of making mechanically strong and tough fibers through an intricate self-assembly of protein constituents during the fiber formation process. Comprehending the biosynthetic process and precisely replicating it has been a challenging task. However, we find that extruding small functional segments into solid fibrillar structures, through mediation of chemical interactions between the subunits, is a design approach that can be broadly adapted from nature to realize a greener fiber manufacturing process. Using the robust chemistry of thiol-ene photopolymerization, we demonstrate here that a photocurable mixture of a multifunctional acrylate, a tetrafuctional thiol, and a photoinitiator can be processed into continuous fibers by in situ photopolymerization during electrospinning under ambient conditions. The fibers are mechanically robust and have excellent chemical and thermal stability. While electrospinning has been used to demonstrate this concept, the chemistry could be broadly adapted into other fiber manufacturing methods to produce fibers without using solvents or heat.

  
  Abstract:
Macroscopic molecular recognition observations were realized using polyacrylamide-based gels modified with α-cyclodextrin (α-CD), β-cyclodextrin (β-CD), 1-naphthylmethyl (1Np), and 2-naphthylmethyl (2Np) moieties, which are denoted as αCD(x)-gel, βCD(x)-gel, 1Np(y)-gel, and 2Np(y)-gel, where x and y indicate the mol % of CD and Np moieties, respectively. The αCD(5)-gel did not adhere to either the 1Np(5)-gel or 2Np(5)-gel, whereas the βCD(5)-gel interacted with both to form alternating or checkered assemblies. Although the difference in the association constants of β-CD for the model polymers was small, the βCD(x)-gel successfully discriminated between 1Np(y)-gel and 2Np(y)-gel at the appropriate x and y.

- **Molecular Patterning at a Liquid/Solid Interface: The Foldamer Approach**
  
  **Abstract:**
  Molecular patterning has received a lot of attention in the past decade; however, the functionalization of these surface-confined 2D patterns on the nanoscale level remains a challenge. Assembling 2D patterns from oligomeric foldamers turns out to be an interesting approach to accomplishing the controlled positioning of functional elements. We designed a family of peptidomimetic foldamers bearing a 2D turn element folding at the liquid/solid interface. The turning element was developed while studying derivatives with one turning unit. Furthermore, folding was found to be induced by the confinement of the surface. This achievement paves the way for the design of foldamers with multiple turns, providing a higher versatility in the functionalization of nanopatterns.

- **Electrically driven directional motion of a four-wheeled molecule on a metal surface**
  
  **Abstract:**
Propelling single molecules in a controlled manner along an unmodified surface remains extremely challenging because it requires molecules that can use light, chemical or electrical energy to modulate their interaction with the surface in a way that generates motion. Nature’s motor proteins have mastered the art of converting conformational changes into directed motion, and have inspired the design of artificial systems such as DNA walkers and light- and redox-driven molecular motors. But although controlled movement of single molecules along a surface has been reported, the molecules in these examples act as passive elements that either diffuse along a preferential direction with equal probability for forward and backward movement or are dragged by an STM tip. Here we present a molecule with four functional units—our previously reported rotary motors—that undergo continuous and defined conformational changes upon sequential electronic and vibrational excitation. Scanning tunnelling microscopy confirms that activation of the conformational changes of the rotors through inelastic electron tunnelling propels the molecule unidirectionally across a Cu(111) surface. The system can be adapted to follow either linear or random surface trajectories or to remain stationary, by tuning the chirality of the individual motor units. Our design provides a starting point for the exploration of more sophisticated molecular mechanical systems with directionally controlled motion.

- Two types of luminescence blinking revealed by spectroelectrochemistry of single quantum dots

Abstract:
Photoluminescence blinking—random switching between states of high (ON) and low (OFF) emissivities—is a universal property of molecular emitters found in dyes, polymers, biological molecules and artificial nanostructures such as nanocrystal quantum dots, carbon nanotubes and nanowires. For the past 15 years, colloidal nanocrystals have been used as a model system to study this phenomenon. The occurrence of OFF periods in nanocrystal emission has been commonly attributed to the presence of an additional charge, which leads to photoluminescence quenching by non-radiative recombination (the Auger mechanism). However, this ‘charging’ model was recently challenged in several reports. Here we report time-resolved photoluminescence studies of individual nanocrystal quantum dots performed while electrochemically controlling the degree of their charging, with the goal of clarifying the role of charging in blinking. We find that two distinct types of blinking are possible: conventional (A-type) blinking due to charging and discharging of the nanocrystal core, in which lower photoluminescence intensities correlate with shorter photoluminescence lifetimes; and a second sort (B-type), in which large changes in the emission intensity are not accompanied by significant changes in emission dynamics. We attribute B-type blinking to charge fluctuations in the electron-accepting surface sites. When unoccupied, these sites intercept ‘hot’ electrons before they relax into emitting core states. Both blinking mechanisms can be electrochemically controlled and completely suppressed by application of an appropriate potential.

- Toward optomechanics: Maximizing the photodeformation of individual molecules
  Abstract:
Designing soft organic materials able to directly convert light into macroscopic motion represents one of the grand challenges in modern chemistry. Optomechanical properties originate from the collection and amplification of many local deformation events in individual photoswitching entities due to their 3D organization. The basic concept of optomechanics is introduced, related recent achievements in the photoactuation of soft materials are highlighted, and a new approach, based on the optimization of the individual photoresponse at the single-molecule level, is outlined. Optomechanical systems constitute a fundamental approach to alternative utilization of solar energy and a platform for the development of future responsive soft materials and composites.

- Oligoazobenzenophanes—synthesis, photochemistry and properties
  Abstract:

  \[
  \frac{hN^1}{\Delta \text{ or } hN^2}
  \]

  The possibility to modulate molecules reversibly by light has been fascinating chemists early on. One of the most powerful photochromic classes of compounds are azobenzenes, which have been incorporated in multiple molecular systems to alter their functionality. Recently, the incorporation of azobenzenes into macrocyclic scaffolds, azobenzenophanes, revealed a novel aspect of this interesting photoswitch. Especially, the build-in of more than one azobenzene moiety into the structure creates photochromic compounds with multiple accessible states. The cyclic arrangement also leads to a change in the photochemical properties, which offer new opportunities for functional molecular devices. In this article the synthesis as well as the photochemistry including applications of macrocyclic azobenzenes, containing more than one azobenzene unit, oligoazobenzenophanes, are reviewed.

- Engineered hydrogen-bonded polymer multilayers: from assembly to biomedical applications
  Abstract:
Over the last two decades the layer-by-layer (LbL) assembly technique has become a highly versatile platform for the synthesis of nanoengineered thin films and particles. The widespread need for highly functional and responsive materials for applications in biomedicine—such as drug and gene delivery—has recently led to considerable efforts in the assembly of LbL materials, particularly films that can be subsequently stabilised and functionalised through a range of chemistries. In this tutorial review, recent developments in hydrogen-bonded LbL-assembled materials will be discussed, focusing on the design of materials with enhanced stimuli-responsive characteristics. Emphasis will be given to materials engineered for biomedical applications, specifically films/capsules that afford controlled loading and release of therapeutic cargo for application in vitro and in vivo.

- **Solution-phase counterion effects in supramolecular and mechanostereochemical systems**
  **Abstract:**

  The self-assembly of molecular components into complex superstructures involves the subtle interplay of various noncovalent forces. Charged species are often utilised in self-assembly processes as a result of the favorable π–π, cation–π, electrostatic, and hydrogen bonding interactions that form between these species. Although the counterions associated with these charged species can exert significant effects on the synthesis, stability, and operation of superstructures in solution, rarely are the counterions considered, leading to misinterpretations and misunderstandings of the studied systems. In this tutorial review, we discuss a variety of solution-phase counterion effects, from the fundamental origins to innovative ways in which these effects are exploited for useful functions.

- **Thiophene-Fused Tetracene Diimide with Low Band Gap and Ambipolar Behavior**
  **Abstract:**
The first tetracene diimide derivative fused with four thiophene rings, TT-TDI, was synthesized by an FeCl₃ mediated oxidative cyclodehydrogenation reaction. TT-TDI exhibited a low band gap of 1.52 eV and amphoteric redox behavior. TT-TDI also showed a liquid crystalline property and ambipolar charge transport in thin film field-effect transistors.

- Amino Acid Building Blocks for Efficient Fmoc Solid-Phase Synthesis of Peptides Adenylylated at Serine or Threonine
  **Abstract:**

  The first straightforward building block based (non-interassembly) synthesis of peptides containing adenylylated serine and threonine residues is described. Key features include final global acidolytic protective group removal as well as full compatibility with standard Fmoc solid-phase peptide synthesis (SPPS). The described Thr-AMP SPPS-building block has been employed in the synthesis of the Thr-adenylylated sequence of human GTPase CDC42 (Ac-SEYVP-T(AMP)-VFDNYGC-NH₂). Further, we demonstrate proof-of-concept for the synthesis of an Ser-adenylylated peptide (Ac-GSGA-S(AMP)-AGSGC-NH₂) from the corresponding adenylylated serine building block.

- Controlled self-assembly of α-helix-decorated peptide nanostructures
  **Abstract:**
This study describes a strategy to control the degree of α-helix stabilization and the shape of α-helix-decorated nanostructures. Coassembly of a macrocyclic peptide and a β-sheet peptide diminished steric clashes between helical peptide segments, further stabilizing α-helices.

- Amino acid based low-molecular-weight tris(bis-amido) organogelators
  Abstract:

  Two new amino acid based low-molecular-mass organic gelators were designed, synthesized, and examined for their ability to gelate various organic solvents. The gelator molecules were found to aggregate via N–H ⇌ O hydrogen bonding to form an interwinding 3D network which immobilized a large number of organic solvents. Among the different organic solvents used in the gelation study mesitylene is found to be the best solvent. The microstructure of organogels was studied with FESEM and optical micrographs. The involvement of hydrogen bonding in the aggregation of the gelator molecule was studied using temperature dependent ¹H NMR. The obtained organogels were found to exhibit significant mechanical strength.

- Solution-Processable Reduced Graphene Oxide as a Novel Alternative to PEDOT:PSS Hole Transport Layers for Highly Efficient and Stable Polymer Solar Cells
  Abstract:
The preparation of a reduced graphene oxide (pr-Go) is with a novel p-TosNHNH₂ reductant is demonstrated for use as an efficient anode interfacial layer for high-performance and high-stability organic solar cells (OSCs). The efficiency of the cells with pr-GO is highly comparable to those of the PEDOT:PSS-based devices. Furthermore, the pr-GO based OSCs show a much longer cell life time in air stability tests in comparison with PEDOT:PSS-based cells.

- **Organic Photorefractive Materials and Applications**
  **Abstract:**

  This review describes recent advances and applications in the field of organic photorefractive materials, an interesting area in the field of organic electronics and promising candidate for various aspects of photonic applications. We describe the current state of knowledge about the processes involved in the formation of photorefractive gratings in organic materials and focus on the chemical and photo-physical aspects of the material structures employed in low glass-transition temperature amorphous composites and organic photorefractive glasses. State-of-the art materials are highlighted and recent demonstrations of photonic applications relying on the reversible holographic nature of the photorefractive materials are discussed.

- **Increasing the Reactivity of Nitrogen Catalysts**
  **Abstract:**

\[ \text{\includegraphics[width=0.7\textwidth]{image}} \]
This review article presents how nitrogen-centred Lewis bases were modified in order to increase their reactivity in catalytic processes. As examples, we focus on alcohol acylation and Morita–Baylis–Hilman reactions in order to showcase the fundamental parameters at play in transformations initiated by catalysts bearing respectively an active sp2 or sp3 nitrogen atoms. These two aspects are epitomised by two leading compounds, the Steglich base 4-dimethylaminopyridine (DMAP), and 1,4-diazabicyclo[2.2.2]octane (DABCO). Throughout this review, we stress the role played and the information brought by physical organic chemistry. Comprehension of these complex transformations relies on the fundamental knowledge of parameters, such as, nucleophilicity, nucleofugality, Lewis basicity, and crucially also the knowledge of their divergent impacts on each elementary step of the catalytic cycle.

- **Synthesis, Characterisation and Application of Iridium(III) Photosensitisers for Catalytic Water Reduction**

  Abstract:

  ![Image](Image)

  The synthesis of novel, monocationic iridium(III) photosensitisers (Ir-PSs) with the general formula 
  \[ \text{[Ir}^{III}(\text{C}^\text{N})_2(\text{N}^\text{N})]^+ \] (\text{C}^\text{N}: cyclometallating phenylpyridine ligand, \text{N}^\text{N}: neutral bidentate ligand) is described. The structures obtained were examined by cyclic voltammetry, UV/Vis and photoluminescence spectroscopy and X-ray analysis. All iridium complexes were tested for their ability as photosensitisers to promote homogeneously catalysed hydrogen generation from water. In the presence of [HNEt$_3$][HFe$_3$(CO)$_{11}$] as a water-reduction catalyst (WRC) and triethylamine as a sacrificial reductant (SR), seven of the new iridium complexes showed activity. \[ \text{[Ir(6-iPr-bpy)(ppy)$_2$]PF}_6 \] (bpy: 2,2'-bipyridine, ppy: 2-phenylpyridine) turned out to be the most efficient photosensitiser. This complex was also tested in combination with other WRCs based on rhodium, platinum, cobalt and manganese. In all cases, significant hydrogen evolution took place. Maximum turnover numbers of 4550 for this Ir-PS and 2770 for the Fe WRC generated in situ from [HNEt$_3$][HFe$_3$(CO)$_{11}$] and tris[3,5-bis(trifluoromethyl)phenyl]phosphine was obtained. These are the highest overall efficiencies for any Ir/Fe water-reduction system reported to date. The incident photon to hydrogen yield reaches 16.4 % with the best system.

- **Imaging Mass Spectrometry and Genome Mining via Short Sequence Tagging Identified the Anti-Infective Agent Arylomycin in Streptomyces roseosporus**

  Abstract:
Here, we described the discovery of anti-infective agent arylomycin and its biosynthetic gene cluster in an industrial daptomycin producing strain *Streptomyces roseosporus*. This was accomplished via the use of MALDI imaging mass spectrometry (IMS) along with peptidogenomic approach in which we have expanded to short sequence tagging (SST) described herein. Using IMS, we observed that prior to the production of daptomycin, a cluster of ions (1–3) was produced by *S. roseosporus* and correlated well with the decreased staphylococcal cell growth. With a further adopted SST peptidogenomics approach, which relies on the generation of sequence tags from tandem mass spectrometric data and query against genomes to identify the biosynthetic genes, we were able to identify these three molecules (1–3) to arylomycins, a class of broad-spectrum antibiotics that target type I signal peptidase. The gene cluster was then identified. This highlights the strength of IMS and MS guided genome mining approaches in effectively bridging the gap between phenotypes, chemotypes, and genotypes.

- **Green Proteorhodopsin Reconstituted into Nanoscale Phospholipid Bilayers (Nanodiscs) as Photoactive Monomers**
  **Abstract:**

Over 4000 putative proteorhodopsins (PRs) have been identified throughout the oceans and seas of the Earth. The first of these eubacterial rhodopsins was discovered in 2000 and has expanded the family of microbial proton pumps to all three domains of life. With photophysical properties similar to those of bacteriorhodopsin, an archaeal proton pump, PRs are also generating interest for their potential use in various photonic applications. We perform here the first reconstitution of the minimal photoactive PR structure into nanoscale phospholipid bilayers (nanodiscs) to better understand how protein–protein and protein–lipid interactions influence the photophysical properties of PR. Spectral (steady-state and time-resolved UV–visible spectroscopy) and physical
(size-exclusion chromatography and electron microscopy) characterization of these complexes confirms the preparation of a photoactive PR monomer within nanodiscs. Specifically, when embedded within a nanodisc, monomeric PR exhibits a titratable $pK_a$ (6.5–7.1) and photocycle lifetime (100–200 ms) that are comparable to the detergent-solubilized protein. These ndPRs also produce a photoactive blue-shifted absorbance, centered at 377 or 416 nm, that indicates that protein–protein interactions from a PR oligomer are required for a fast photocycle. Moreover, we demonstrate how these model membrane systems allow modulation of the PR photocycle by variation of the discoidal diameter (i.e., 10 or 12 nm), bilayer thickness (i.e., 23 or 26.5 Å), and degree of saturation of the lipid acyl chain. Nanodiscs also offer a highly stable environment of relevance to potential device applications.

- **Synthesis of Well-Defined Photo-Cross-Linked Polymeric Nanocapsules by Surface-Initiated RAFT Polymerization**
  **Abstract:**

  Narrowly distributed hollow polymeric nanocapsules (PtBMA-co-PDIPM-b-PHPMA), with the size of 450 or 900 nm, were first synthesized by surface-initiated reversible addition–fragmentation chain transfer (RAFT) polymerization exploiting silica nanoparticles as sacrificial templates and 2,3-dimethylmaleic imidopropyl methacrylate (DIMIPM) as a photo-cross-linker. First, silica nanoparticles were amino functionalized by aminosilane agents, and then the dithiocarbonate chain transfer agent (CTA) was anchored via activated R-groups to the amino-functionalized surface of silica nanoparticles. This surface layer of CTA groups was then used to grow linear copolymers and block copolymers by RAFT polymerization leading to a core–shell morphology. TEM and GPC results indicated that the thickness of the shell can be well governed by simply controlling the molecular weight of the grafted copolymer. Finally, after photo-cross-linking and etching the silica core with NH4F/HF buffer, hollow nanocapsules were obtained, of which the morphology and composition were confirmed by employing a range of techniques, such as TEM, cryo-TEM, DLS, SEM, XPS, TGA, FTIR, GPC, and UV–vis spectroscopy. Thus, robust and narrowly distributed polymeric nanocapsules with size of 450 nm and a wall thickness 10 nm based on the grafted block copolymer PtBMA-co-PDIPM-b-PHPMA having $M_n = 19 \times 500$ g/mol (GPC) could be prepared.

- **Donor–Acceptor Random Copolymers Based on a Ladder-Type Nonacyclic Unit: Synthesis, Characterization, and Photovoltaic Applications**
  **Abstract:**
We have developed a ladder-type multifused thiophene–phenylene–thienylene–phenylene–thienyl (TPTPT) unit where each thiophene ring is covalently fastened with the adjacent benzene rings by a carbon bridge, forming four cyclopentadiene rings embedded in a nonacyclic structure. This rigid and coplanar TPTPT building block was copolymerized with electron-deficient acceptors, dibromobenzothiadiazole (BT) or dibromodithienyldiketopyrrolopyrrole (DPP), via Stille polymerization. By varying the feed ratio of the monomers, a new series of random copolymers PTPTPTBT11, PTPTPTBT12, PTPTPTDPP11, PTPTPTDPP12, and PTPTPTDPP13 with tunable optical and electronic properties were prepared. The PTPTPTDPP12/PC71BM (1:4, w/w) based device exhibited the highest short circuit current (Jsc) of 10.78 mA/cm² with a good power conversion efficiency (PCE) of 4.3% due to the much boarder absorption ability and the highest hole mobility of PTPTPTDPP12. The devices based on PTPTPTDPP13, PTPTPTDPP11, PTPTPTBT12, and PTPTPTBT11 polymers also displayed promising efficiencies of 4.1%, 3.6%, 3.1%, and 2.8%, respectively. Most importantly, PTPTPTDPP12 has been demonstrated as a superior low-band-gap material for polymer solar cell with inverted architecture, achieving a high PCE of 5.1%.

- Digitally tunable physicochemical coding of material composition and topography in continuous microfibers
  Abstract:

Heterotypic functional materials with compositional and topographical properties that vary spatiotemporally on the micro- or nanoscale are common in nature. However, fabricating such complex materials in the laboratory remains challenging. Here we describe a method to continuously create microfibres with tunable morphological, structural and chemical features using a microfluidic system consisting of a digital, programmable flow control that mimics the silk-spinning process of
spiders. With this method we fabricated hydrogel microfibres coded with varying chemical composition and topography along the fibre, including gas micro-bubbles as well as nanoporous spindle-knots and joints that enabled directional water collection. We also explored the potential use of the coded microfibres for tissue engineering applications by creating multifunctional microfibres with a spatially controlled co-culture of encapsulated cells.

- Electron microscopy of specimens in liquid

Abstract:

Imaging samples in liquids with electron microscopy can provide unique insights into biological systems, such as cells containing labelled proteins, and into processes of importance in materials science, such as nanoparticle synthesis and electrochemical deposition. Here we review recent progress in the use of electron microscopy in liquids and its applications. We examine the experimental challenges involved and the resolution that can be achieved with different forms of the technique. We conclude by assessing the potential role that electron microscopy of liquid samples can play in areas such as energy storage and bioimaging.