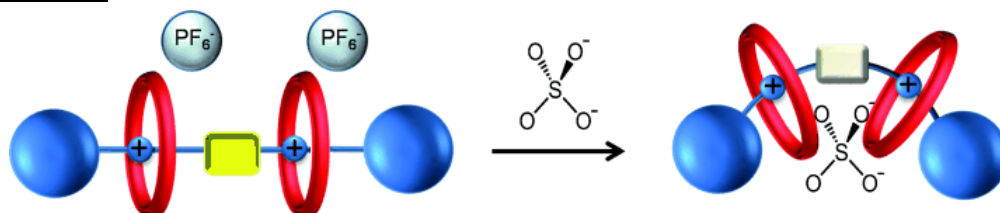


- Sulfate-Selective Binding and Sensing of a Fluorescent [3]Rotaxane Host System  
Langton, M. J.; Beer, D. *Chem. Eur. J.* **2012**, *18*, 14406 – 14412.

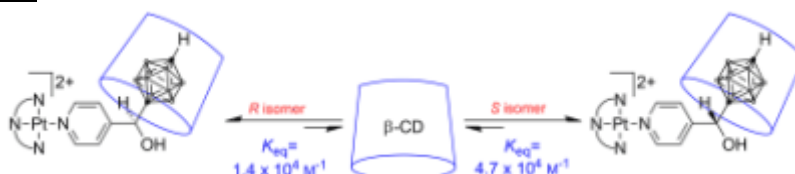
Abstract:



The chloride-templated synthesis of a novel [3]rotaxane, capable of binding anionic guests, and incorporating a naphthalene group for fluorescence sensing is reported. Extensive  $^1\text{H}$  NMR titration studies were used to probe the anion binding selectivity of the system. The rotaxane selectively recognises sulfate, undergoing an induced conformational change upon sulfate binding to form a 1:1 stoichiometric sandwich-type complex, concomitant with significant quenching of the fluorescence. Binding of mono-anionic guests results in the formation of a 2:1 stoichiometric guest–host complex, and a modest enhancement of the emission. Addition of an excess of sulfate in non-competitive solvent also results in a 2:1 emissive complex.

- Synthesis and Supramolecular Studies of Chiral Boronated Platinum(II) Complexes: Insights into the Molecular Recognition of Carboranes by  $\beta$ -Cyclodextrin  
Ching, H. Y. V.; Clifford, S.; Bhadbhade, M.; Clarke, R. J.; Rendina, L. M. *Chem. Eur. J.* **2012**, *18*, 14413 – 14425.

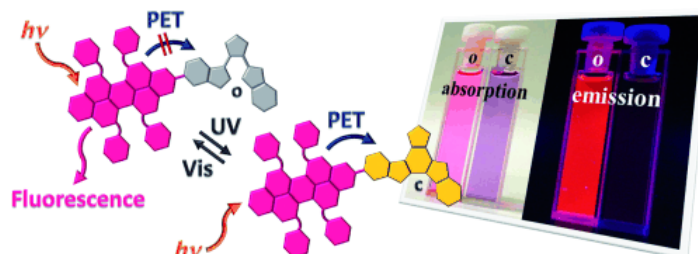
Abstract:



The synthesis and characterisation of a novel isomeric family of *closo*-carborane-containing  $\text{Pt}^{\text{II}}$  complexes ( $(R/S)\text{-(1-4)} \cdot 2\text{NO}_3$ ) are reported. Related complexes ( $5 \cdot \text{NO}_3$  and  $6 \cdot \text{NO}_3$ ) that contain the 7,8-*nido*-carborane cluster were obtained from the selective deboronation of the 1,2-*closo*-carborane analogues. The corresponding water-soluble supramolecular 1:1 host–guest  $\beta$ -cyclodextrin ( $\beta$ -CD) adducts ( $(R/S)\text{-(1-4)} \cdot \beta\text{-CD} \cdot 2\text{NO}_3$ ) were also prepared and fully characterised. HR-ESI-MS experiments confirmed the presence of the host–guest adducts, and 2D- $^1\text{H}\{^{11}\text{B}\}$  ROESY NMR studies showed that the boron clusters enter the  $\beta$ -CD from the side of the wider annulus. Isothermal titration calorimetry (ITC) experiments revealed enthalpically driven 1:1 and higher-order supramolecular interactions between  $\beta$ -CD and  $(R/S)\text{-(1-4)} \cdot 2\text{NO}_3$  in aqueous solution. A comparison of the predominate 1:1 binding mode established that the affinity of  $\beta$ -CD for the guest molecule is mainly influenced by the pyridyl ring substitution pattern and chirality of the host, whilst the nature of the *closo*-carborane isomer also plays some role, with the most favourable structural features for  $\beta$ -CD binding being the presence of the 4-pyridyl ring, 1,12-*closo*-carborane, and an *S* configuration. The results reported here represent the first comprehensive calorimetric study of the supramolecular interactions between *closo*-carborane compounds and  $\beta$ -CD, and it provides fascinating insights into the structural features influencing the thermodynamics of this phenomenon.

- Nondestructive Photoluminescence Read-Out by Intramolecular Electron Transfer in a Perylene Bisimide-Diarylethene Dyad  
Berberich, M.; Natali, M.; Spenst, P.; Chiorboli, C.; Scandola, F.; Würthner, F. *Chem. Eur. J.* **2012**, *18*, 13651–13664.

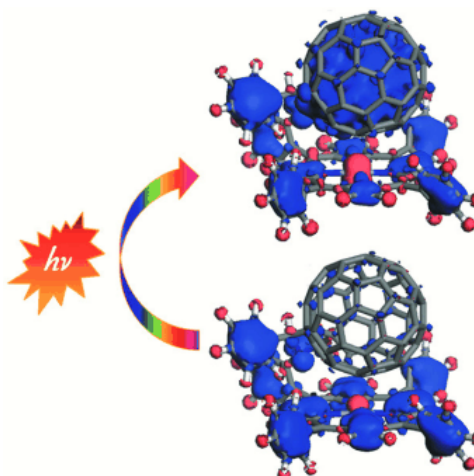
Abstract:



A novel, highly stable photochromic dyad **3** based on a perylene bisimide (PBI) fluorophore and a diarylethene (DAE) photochrome was synthesized and the optical and photophysical properties of this dyad were studied in detail by steady-state and time-resolved ultrafast spectroscopy. This photochromic dyad can be switched reversibly by UV-light irradiation of its ring-open form **3o** leading to the ring-closed form **3c**, and back reaction of **3c** to **3o** by irradiation with visible light. Solvent-dependent fluorescence studies revealed that the emission of ring-closed form **3c** is drastically quenched in solvents of medium (e.g., chloroform) to high (e.g., acetone) polarities, while the emission of the ring-open form **3o** is appreciably quenched only in highly polar solvents like DMF. The strong fluorescence quenching of **3c** is attributed to a photoinduced electron-transfer (PET) process from the excited PBI unit to ring-closed DAE moiety, as this process is thermodynamically highly favorable with a Gibbs free energy value of  $-0.34$  eV in dichloromethane. The electron-transfer mechanism for the fluorescence quenching of ring-closed **3c** is substantiated by ultrafast transient measurements in dichloromethane and acetone, revealing stabilization of charge-separated states of **3c** in these solvents. Our results reported here show that the new photochromic dyad **3** has potential for nondestructive read-out in write/read/erase fluorescent memory systems.

- A  $\pi$ -Stacked Porphyrin–Fullerene Electron Donor–Acceptor Conjugate That Features a Surprising Frozen Geometry  
Ciammaichella, A.; Dral, P. O.; Clark, T.; Tagliatesta, P.; Sekita, M.; Guldi, D. M. *Chem. Eur. J.* **2012**, *18*, 14008–14016.

Abstract:

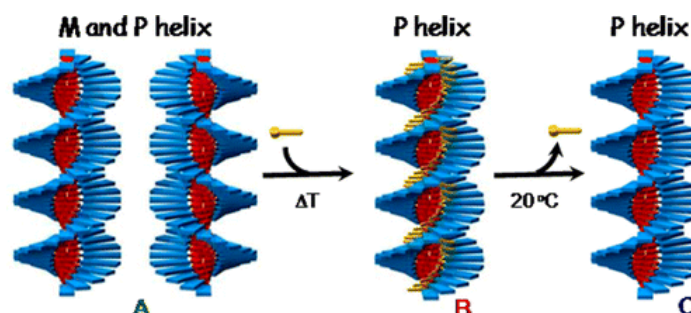


A “frozen” electron donor–acceptor array that bears porphyrin and fullerene units covalently linked through the *ortho* position of a phenyl ring and the nitrogen of a pyrrolidine ring, respectively, is reported. Electrochemical and photophysical features suggest that the chosen linkage supports both through-space and through-bond interactions. In particular, it has been found that the porphyrin singlet excited state decays within a few picoseconds by means of a photoinduced electron transfer to give the rapid formation of a long-lived charge-separated state. Density functional theory (DFT) calculations show HOMO and LUMO to be localized on the electron-donating porphyrin and the electron-accepting fullerene moiety, respectively, at this level of theory. More specifically, semiempirical molecular orbital (MO) configuration interaction (CI) and unrestricted natural orbital (UNO)-CI methods shed light on the nature of the charge-transfer states and emphasize the importance of the close proximity of donor and acceptor for effective electron transfer.

- Asymmetric Noncovalent Synthesis of Self-Assembled One-Dimensional Stacks by a Chiral Supramolecular Auxiliary Approach

George, S. J.; De Bruijn, R.; Tomović, Ž.; Van Averbek, B.; Beljonne, D.; Lazzaroni, R.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2012**, *134*, 17789–17796.

Abstract:



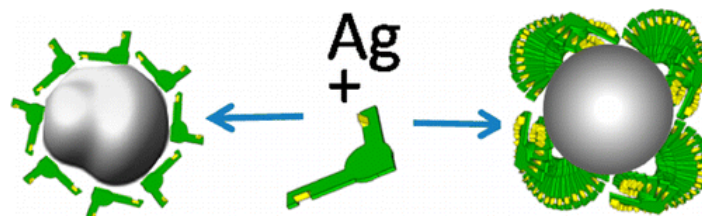
Stereoselective noncovalent synthesis of one-dimensional helical self-assembled stacks of achiral oligo(*p*-phenylenevinylene) ureidotriazine (AOPV3) monomers is obtained by a chiral supramolecular auxiliary approach. The racemic mixture of helical stacks of achiral AOPV3 molecules is converted into homochiral helical stacks, as shown by both spectroscopic measurements and molecular modeling simulations. The conversion is promoted by an orthogonal two-point ion-pair interaction with the chiral auxiliary dibenzoyl tartaric acid (d- or l-TA) molecules, which biases the angle population distribution and thereby the stack helicity. The induced preferred helicity is maintained by the OPV stacks even after the removal of the chiral auxiliary by extraction with ethylenediamine (EDA), due to the kinetic stability of the OPV stacks at room temperature. Spectroscopic probing of the helical self-assembly and the racemization process of these  $\pi$ -conjugated OPV chromophores shed further light into the mechanistic pathways of this chiral asymmetric noncovalent synthesis and the kinetic stability of the stacks produced. The racemization of the stacks follows first-order kinetics and no switch in mechanism is observed as a result of a temperature change; therefore, a racemization via disassembly assembly is proposed. Remarkably, the preferred helicity of the stacks of achiral AOPV3 can be retained almost completely after a heating–cooling cycle where the stacks first partially depolymerize and then polymerize again with the still existing stacks being the seeds for self-assembly of achiral AOPV3. Only after a fully dissociated state is obtained at high temperatures, the optical activity of the supramolecular stack self-assembled at room temperature is lost.

- Plasmonic Chiroptical Response of Silver Nanoparticles Interacting with Chiral Supramolecular Assemblies

4

Maoz, B. M.; Van der Weegen, R.; Fan, Z.; Govorov, A. O.; Ellestad, G.; Berova, N.; Meijer, E. W.; Markovich, G. *J. Am. Chem. Soc.* **2012**, *134*, 17807–17813.

Abstract:

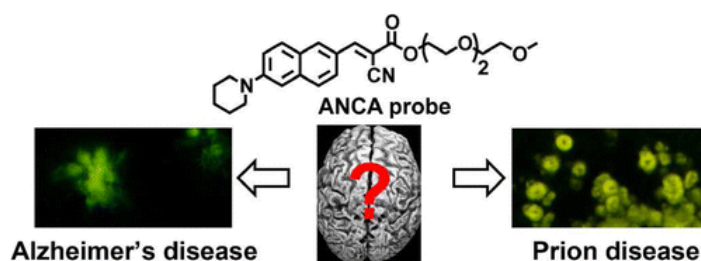


Silver nanoparticles were prepared in aqueous solutions of chiral supramolecular structures made of chiral molecular building blocks. While these chiral molecules display negligible circular dichroism (CD) as isolated molecules, their stacking produced a significant CD response at room temperature, which could be eliminated by heating to 80 °C due to disordering of the stacks. The chiral stack-plasmon coupling has induced CD at the surface plasmon resonance absorption band of the silver nanoparticles. Switching between two plasmonic CD induction mechanisms was observed: (1) Small Ag nanoparticles coated with large molecular stacks, where the induced plasmonic CD decayed together with the UV molecular CD bands on heating the solution, indicating some type of electromagnetic or dipole coupling mechanism. (2) Larger Ag nanoparticles coated with about a monolayer of molecules exhibited induced plasmonic CD that was temperature-independent. In this case it is estimated that the low chiroptical response of a molecular monolayer is incapable of inducing such a large chiroptical effect, and a model calculation shows that the plasmonic CD response may be the result of a slight chiral shape distortion of the silver nanoparticles.

- Aminonaphthalene 2-Cyanoacrylate (ANCA) Probes Fluorescently Discriminate between Amyloid- $\beta$  and Prion Plaques in Brain

Cao, K.; Farahi, M.; Dakanali, M.; Chang, W. M.; Sigurdson, C. J.; Theodorakis, E. A.; Yang, J. J. *Am. Chem. Soc.* **2012**, *134*, 17338–17341.

Abstract:



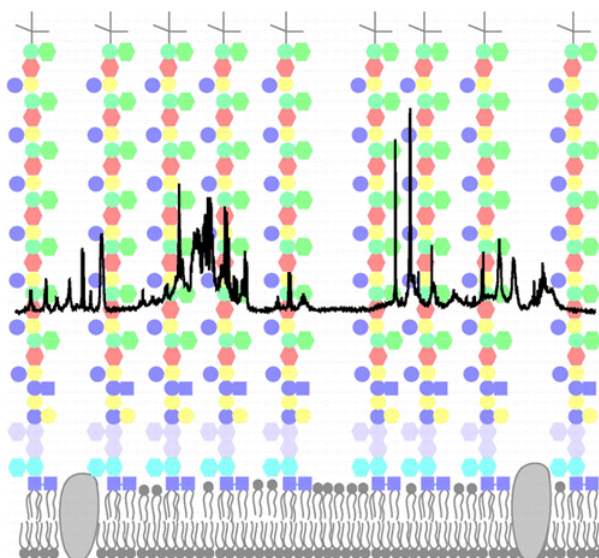
A major challenge for diagnosing and monitoring the progression of amyloid-based diseases is the capability to distinguish between amyloid deposits that are associated with related, but distinctly different, diseases. Here, we demonstrate that aminonaphthalenyl 2-cyanoacrylate-based probes can fluorescently discriminate between different types of amyloid deposits in brain. The discriminating capability of these molecular rotors is due to the stabilization of the ground versus excited states of these probes as a function of the polarity of their microenvironment (i.e., within the binding pocket on the amyloid). This property makes it possible, for the first time, to estimate the inherent static relative permittivity ( $\epsilon_0$ ) of the binding pocket of each amyloid within tissue. The capability to

selectively follow the deposition of specific amyloids in tissue may provide important information for therapeutic development that is not readily accessible from currently available technology.

- On-Cell MAS NMR: Physiological Clues from Living Cells

Zandomeneghi, G.; Ilg, K.; Aebi, M.; Meier, B. H. *J. Am. Chem. Soc.* **2012**, *134*, 17513–17519.

Abstract:

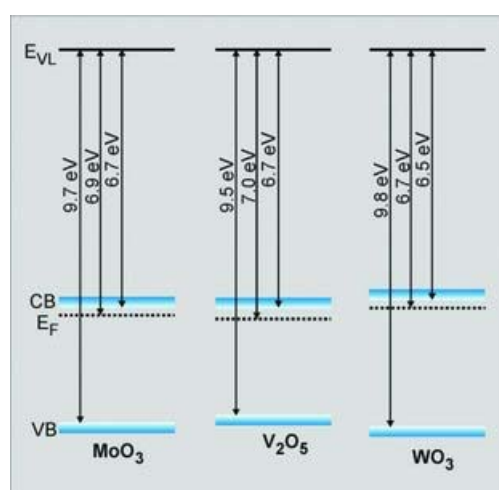


While structural information on biomolecules is mainly obtained from purified in vitro samples, NMR can also be applied in the context of entire cells or organisms. The present study describes maturation processes in living *Salmonella enterica* serovar Typhimurium, a prevalent cause for human gastroenteritis. In our physiological study, we follow the composition of the O-antigen on the outer bacterial membrane with high-resolution MAS NMR spectroscopy. We detect and characterize an evolution of the O-antigen composition, in particular of the O-acetylation state of the O-antigen, a factor that can play an important role in vaccine development.

- Transition Metal Oxides for Organic Electronics: Energetics, Device Physics and Applications

Meyer, J.; Hamwi, S.; Kröger, M.; Kowalsky, W.; Riedl, T.; Kahn, A. *Adv. Mater.* **2012**, *24*, 5408–5427.

Abstract:



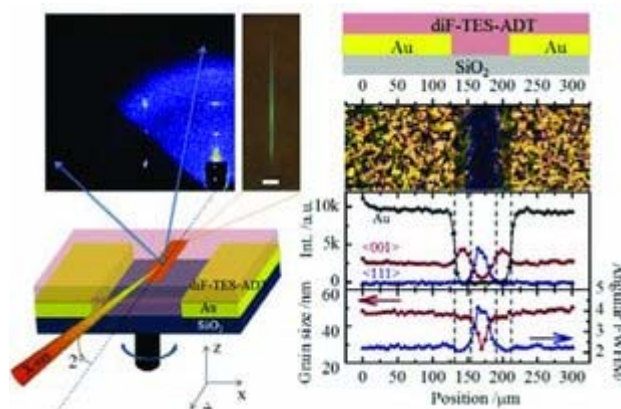


During the last few years, transition metal oxides (TMO) such as molybdenum tri-oxide ( $\text{MoO}_3$ ), vanadium pent-oxide ( $\text{V}_2\text{O}_5$ ) or tungsten tri-oxide ( $\text{WO}_3$ ) have been extensively studied because of their exceptional electronic properties for charge injection and extraction in organic electronic devices. These unique properties have led to the performance enhancement of several types of devices and to a variety of novel applications. TMOs have been used to realize efficient and long-term stable p-type doping of wide band gap organic materials, charge-generation junctions for stacked organic light emitting diodes (OLED), sputtering buffer layers for semi-transparent devices, and organic photovoltaic (OPV) cells with improved charge extraction, enhanced power conversion efficiency and substantially improved long term stability. Energetics in general play a key role in advancing device structure and performance in organic electronics; however, the literature provides a very inconsistent picture of the electronic structure of TMOs and the resulting interpretation of their role as functional constituents in organic electronics. With this review we intend to clarify some of the existing misconceptions. An overview of TMO-based device architectures ranging from transparent OLEDs to tandem OPV cells is also given. Various TMO film deposition methods are reviewed, addressing vacuum evaporation and recent approaches for solution-based processing. The specific properties of the resulting materials and their role as functional layers in organic devices are discussed.

- Direct Structural Mapping of Organic Field-Effect Transistors Reveals Bottlenecks to Carrier Transport

Li, R.; Ward, J. W.; Smilgies, D.-M.; Payne, M. M.; Anthony, J. E.; Jurchescu, O. D.; Amassian, A. *Adv. Mater.* **2012**, *24*, 5553–5558.

Abstract:

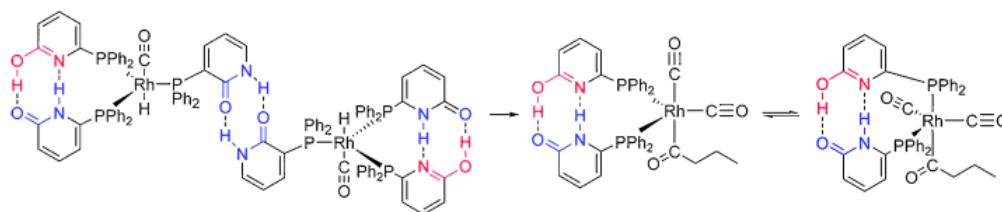


**X-ray microbeam scattering** is used to map the microstructure of the organic semiconductor along the channel length of solution-processed bottom-contact OFET devices. Contact-induced nucleation is known to influence the crystallization behavior within the channel. We find that microstructural inhomogeneities in the center of the channel act as a bottleneck to charge transport. This problem can be overcome by controlling crystallization of the preferable texture, thus favoring more efficient charge transport throughout the channel.

- Mechanistic Insights into a Supramolecular Self-Assembling Catalyst System: Evidence for Hydrogen Bonding during Rhodium-Catalyzed Hydroformylation

Gellrich, U.; Seiche, W.; Keller, M.; Breit, B. *Angew. Chem. Int. Ed.* **2012**, *51*, 11033–11038.

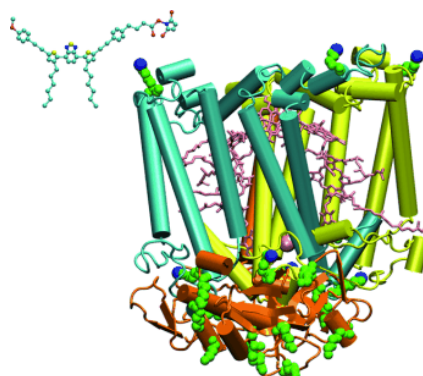
Abstract:



**The structural integrity and flexibility** provided by intermolecular hydrogen bonds leads to the outstanding properties of the 6-diphenylphosphinopyridin-(2H)-1-one ligand (see scheme) in the rhodium-catalyzed hydroformylation of terminal alkenes, as demonstrated by the combination of spectroscopic methods and DFT computations. Hydrogen bonds were also detected in a competent intermediate of the catalytic cycle.

- Enhancing the Light Harvesting Capability of a Photosynthetic Reaction Center by a Tailored Molecular Fluorophore  
Milano, F.; Tangorra, R. R.; Hassan Omar, O.; Ragni, R.; Operamolla, A.; Agostiano, A.; Farinola, G. M.; Trotta, M. *Angew. Chem. Int. Ed.* **2012**, 51, 11019–11023.

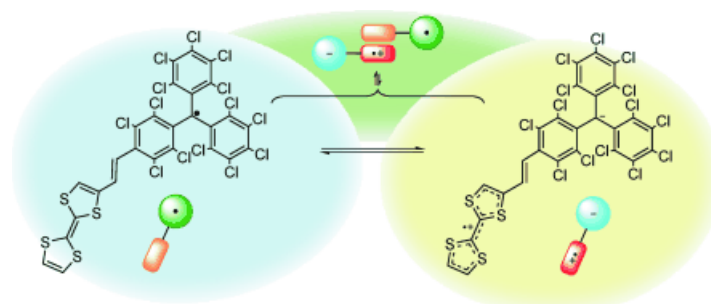
Abstract:



**Light machine:** The simplest photosynthetic protein able to convert sunlight into other energy forms is covalently functionalized with a tailored organic dye to obtain a fully functional hybrid complex that outperforms the natural system in light harvesting and conversion ability.

- Induced Self-Assembly of a Tetrathiafulvalene-Based Open-Shell Dyad through Intramolecular Electron Transfer  
Guasch, J.; Grisanti, L.; Lloveras, V.; Vidal-Gancedo, J.; Souto, M.; Morales, D. C.; Vilaseca, M.; Sissa, C.; Painelli, A.; Ratera, I.; Rovira, C.; Veciana, J. *Angew. Chem. Int. Ed.* **2012**, 51, 11024–11028.

Abstract:



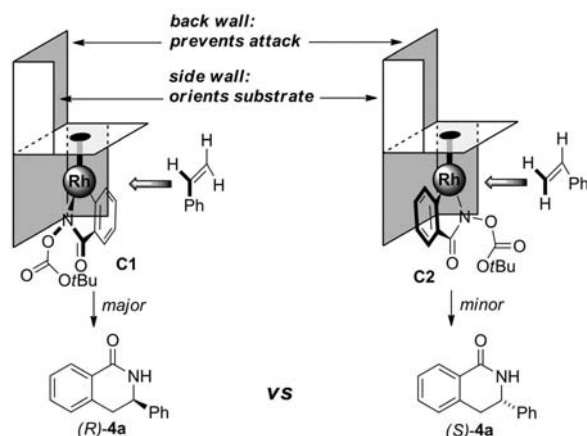
**An organic switch:** An open-shell dyad, consisting of an electron acceptor perchlorotriphenylmethyl radical unit linked to an electron  $\pi$ -donor tetrathiafulvalene unit through a vinylene  $\pi$ -bridge, was

synthesized (see picture). The self-assembly of the dyad in solution induced by its intramolecular electron transfer was studied.

- Chiral Cyclopentadienyl Ligands as Stereocontrolling Element in Asymmetric C-H Functionalization

Ye, B.; Cramer, N. *Science* **2012**, 338, 504-506.

Abstract:

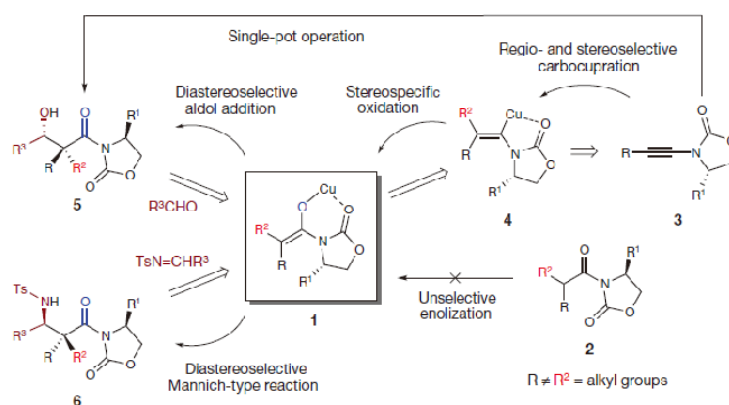


Metal complexes coordinated by a single cyclopentadienyl (Cp) ligand are widely used, versatile catalysts, but their application to asymmetric reactions has been hindered by the difficulty of designing Cp substituents that effectively bias the coordination sphere. Here, we report on a class of simple C<sub>2</sub>-symmetric Cp derivatives that finely control the spatial arrangement of the transiently coordinated reactants around the central metal atom. Rhodium (III) complexes bearing these ligands proved to be highly enantioselective catalysts for directed carbon-hydrogen (C-H) bond functionalizations of hydroxamic acid derivatives.

- Forming all-carbon quaternary stereogenic centres in acyclic systems from alkynes

Minko, Y.; Pasco, M.; Lercher, L.; Botoshansky, M.; Marek, I. *Nature* **2012**, 490, 522-526.

Abstract:



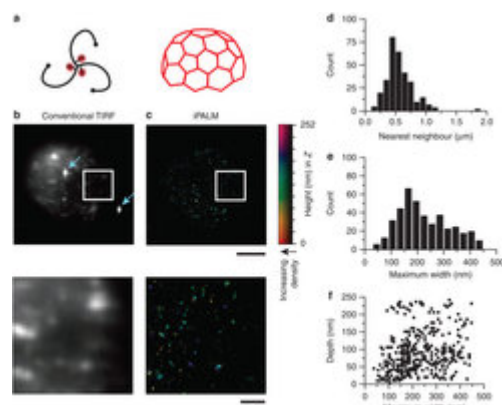
The formation of all-carbon quaternary stereocentres in acyclic systems is one of the most difficult contemporary challenges in modern synthetic organic chemistry. Particularly challenging is the preparation of all-carbon quaternary stereocentres in aldol adducts; this difficulty is problematic because the aldol reaction represents one of the most valuable chemical transformations in organic synthesis. The main problem that limits the formation of these stereocentres is the absence of an efficient method of preparing stereodefined trisubstituted enolates in acyclic systems. Here we



describe a different approach that involves the formation of two new stereogenic centres-including the all-carbon quaternary One-via a combined carbometalation-oxidation reaction of an organocuprate to give a stereodefined trisubstituted enolate. We use this method to generate a series of aldol and Mannich products from ynamides with excellent diastereomeric and enantiomeric ratios and moderate yields.

- Imaging the post-fusion release and capture of a vesicle membrane protein  
Sochacki, K. A.; Larson, B. T.; Sengupta, D. C.; Daniels, M. P.; Shtengel, G.; Hess, H. F.; Taraska, J. W. *Nature Communications* **2012**, 3, 1154.

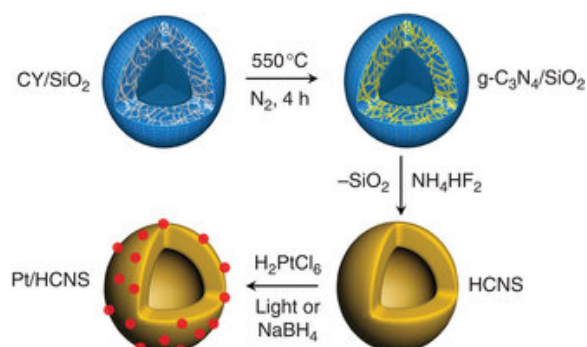
Abstract:



The molecular mechanism responsible for capturing, sorting and retrieving vesicle membrane proteins following triggered exocytosis is not understood. Here we image the post-fusion release and then capture of a vesicle membrane protein, the vesicular acetylcholine transporter, from single vesicles in living neuroendocrine cells. We combine these measurements with super-resolution interferometric photo-activation localization microscopy and electron microscopy, and modelling to map the nanometer-scale topography and architecture of the structures responsible for the transporter's capture following exocytosis. We show that after exocytosis, the transporter rapidly diffuses into the plasma membrane, but most travels only a short distance before it is locally captured over a dense network of membrane-resident clathrin-coated structures. We propose that the extreme density of these structures acts as a short-range diffusion trap. They quickly sequester diffusing vesicle material and limit its spread across the membrane. This system could provide a means for clathrin-mediated endocytosis to quickly recycle vesicle proteins in highly excitable cells.

- Bioinspired hollow semiconductor nanospheres as photosynthetic nanoparticles  
Sun, J.; Zhang, J.; Zhang, M.; Antonietti, M.; Fu, X.; Wang, X. *Nature Communications* **2012**, 3, 1139.

Abstract:

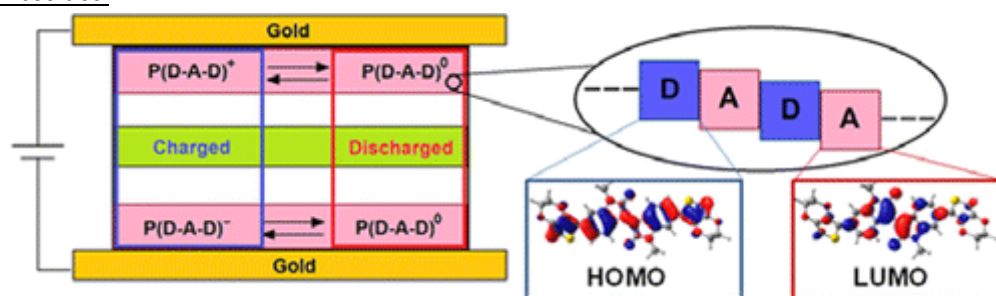


Natural photosynthesis occurs in the thylakoid membrane where functional proteins and electron carriers are precisely arranged to efficiently convert sunlight into a chemical potential between the two membrane sides, via charge separation and electron transport chains, for use in oxygen generation and CO<sub>2</sub> fixation. These light-harvesting complexes and cofactors have been actively mimicked using dyes, semiconductors and catalytic nanoparticles. However, the photosynthetic scaffold that optimizes both the capture and distribution of light and separates both the oxidative and reductive species has been mimicked much less often, especially using polymer substances. Here we report the synthesis of hollow nanospheres sized in the optical range and made of a robust semiconductor, melon or carbon-nitride polymer. These hollow nanospheres are shown to function as both light-harvesting antennae and nanostructured scaffolds that improve photoredox catalysis, which was determined to have a 7.5% apparent quantum yield via a hydrogen-generation assay.

- Poly[Bis-EDOT-Isoindigo]: An Electroactive Polymer Applied to Electrochemical Supercapacitors

Estrada, L. A.; Liu, D. Y.; Salazar, D. H.; Dyer, A. L.; Reynolds, J. R. *Macromolecules* **2012**, *45*, 8211–8220.

Abstract:

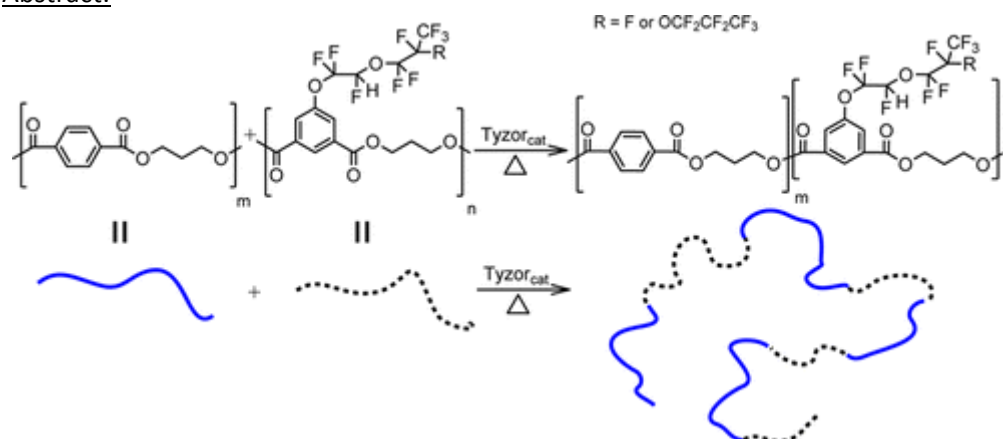


Poly[6,6'-bis(ethylene-3,4-dioxythien-2-yl)]-*N,N'*-dialkylisoindigo (PBEDOT-il) was synthesized and incorporated as an electroactive material into electrochemical supercapacitors (ESCs) in type I and type III configurations. In type I ESCs, PBEDOT-il provides a specific power of ~360 W/kg and specific energy of ~0.5 Wh/kg, while retaining about 80% of its electroactivity over 10 000 cycles. In addition, we report on the use of PBEDOT-il in type III supercapacitors where operating voltages as high as 2.5 V were achieved with specific energies of ca. 15 Wh/kg, albeit with limited stability.

- Melt Derived Blocky Copolyesters: New Design Features for Polycondensation

Drysdale, N. E.; Brun, Y.; McCord, E. F.; Nederberg, F. *Macromolecules* **2012**, *45*, 8245–8256.

Abstract:

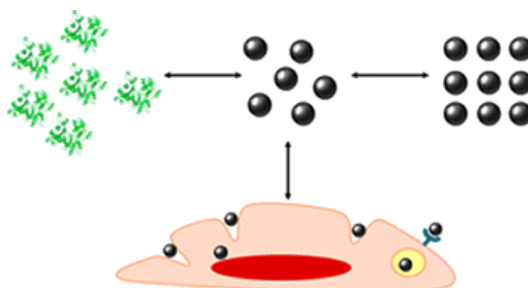


Melt polycondensation was utilized to chain extend polytrimethylene terephthalate with 1,3-propanediol based fluorinated isophthalic oligomers, resulting in copolymers with retained microstructure. Our findings point toward the formation of a blocky type copolymer. In general, formation of block or segmented copolymers from melt derived polycondensation is a very challenging task due to the propensity for adverse randomization reactions. Supported by size exclusion chromatography, our copolymers are fully chain extended, with no presence of the initial components. Furthermore, thermal differential scanning calorimetry has confirmed that the melt characteristics of the starting components are retained. In addition, interaction polymer chromatography and sequence distribution analysis using  $^{13}\text{C}$  NMR supports a blocky backbone microstructure. Seemingly, intermolecular chain end condensation occurs, whereas transesterification is dormant. While these findings open up new doors for polymer/materials development, we are particularly interested in these structures as melt additives to address oil repellency of polyester blends. When used in blends these blocky additives show an improvement in oil repellency compared with random additives of identical molar composition, i.e., they are more fluorine efficient.

- The State of Nanoparticle-Based Nanoscience and Biotechnology: Progress, Promises, and Challenges

Pelaz, B.; Jaber, S.; Jimenez de Aberasturi, D.; Wulf, V.; Aida, T.; de la Fuente, J. M.; Feldmann, J.; Gaub, H. E.; Josephson, L.; Kagan, C. R.; Kotov, N. A.; Liz-Marzán, L. M.; Mattoussi, H.; Mulvaney, P.; Murray, C. B.; Rogach, A. L.; Weiss, P. S.; Willner, I.; Parak, W. J. *ACS Nano* **2012**, 6, 8468-8483.

Abstract:

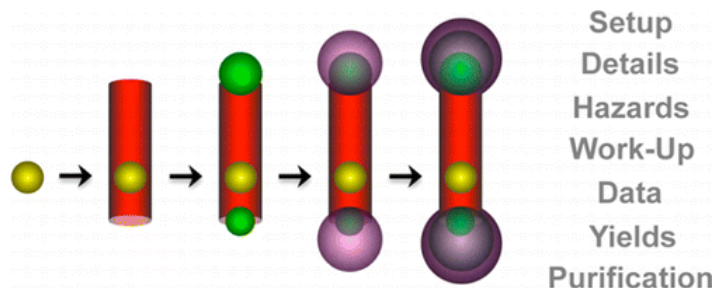


Colloidal nanoparticles (NPs) have become versatile building blocks in a wide variety of fields. Here, we discuss the state-of-the-art, current hot topics, and future directions based on the following aspects: narrow size-distribution NPs can exhibit protein-like properties; monodispersity of NPs is not always required; assembled NPs can exhibit collective behavior; NPs can be assembled one by one; there is more to be connected with NPs; NPs can be designed to be smart; surface-modified NPs can directly reach the cytosols of living cells.

- Full Disclosure: The Practical Side of Nanoscale Total Synthesis

Schaak, R. E.; Williams, M. E. *ACS Nano* **2012**, 6, 8492-8497.

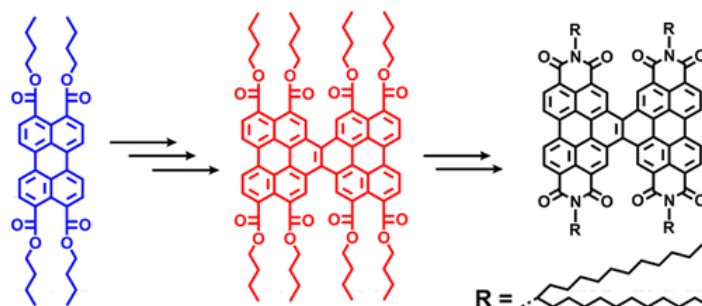
Abstract:



Colloidal hybrid nanoparticles merge multiple distinct materials into single particles, producing nanostructures that often exhibit synergistic properties and multifunctionality. As the complexity of such nanostructures continues to expand and the design criteria become increasingly stringent, the synthetic pathways required to access such materials are growing in sophistication. Multistep pathways are typically needed to generate complex hybrid nanoparticles, and these synthetic protocols have important conceptual analogies to the total synthesis framework used by chemists to construct complex organic molecules. This issue of *ACS Nano* includes a new nanoscale total synthesis: a five-step route to  $\text{Co}_x\text{O}_y\text{-Pt-(CdSe@CdS)-Pt-Co}_x\text{O}_y$  nanorods, a material which consists of CdSe@CdS nanorods that have Pt and cobalt oxide ( $\text{Co}_x\text{O}_y$ ) at the tips. In addition to the conceptual analogies between molecular and nanoparticle total syntheses, there are practical analogies, as well, which are important for ensuring the reproducible and high-yield production of multicomponent nanostructured products with the highest possible purities. This Perspective highlights some of the practical considerations that are important for all nanoparticle syntheses but that become magnified significantly when multiple sequential reactions are required to generate a target product. These considerations include detailed reporting of reaction setups, experimental and workup procedures, hazards, yields of all intermediates and final products, complete data analysis, and separation techniques for ensuring high purity.

- Synthesis and Properties of Ethylene-Annulated Di(perylene diimides)  
Li, Y.; Wang, C.; Li, C.; Di Motta, S.; Negri, F.; Wang, Z. *Org. Lett.* **2012**, 14, 5278–5281.

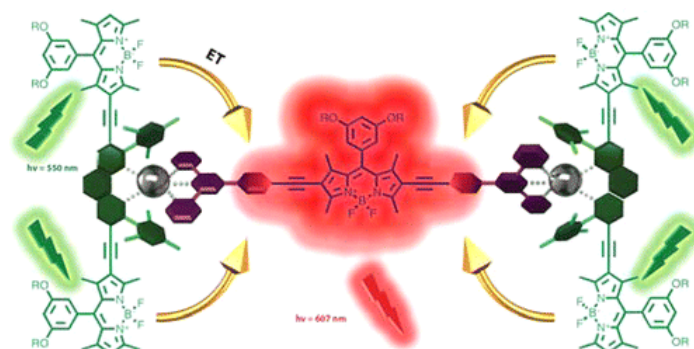
Abstract:



A new synthetic method toward ethylene-annulated di(perylene diimides) from easily available ethylene-annulated di(perylene esters), which is conducted by ICl-induced cyclization and Mizoroki–Heck coupling of ethynylene-linked di(perylene esters), is reported.

- Heteroleptic Metallosupramolecular Complexes of Bodipy Dyes as Energy Transfer Cassettes  
Sozmen, F.; Oksal, B. S.; Bozdemir, O. A.; Buyukcakil, O.; Akkaya, E. U. *Org. Lett.* **2012**, 14, 5286–5289.

Abstract:

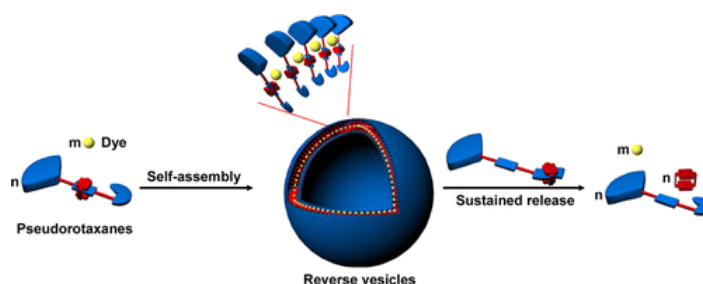


Bodipy dyes with integral phenanthroline and terpyridine units heteroleptically assemble in the presence of zinc(II) ions to form energy transfer cassettes. These discrete complexes exhibit an approach to modularly designed efficient energy transfer and light harvesting systems through metal ion coordination.

- Redox-Responsive Reverse Vesicles Self-Assembled by Pseudo[2]rotaxanes for Tunable Dye Release

Zhang, K.-D.; Zhou, T.-Y.; Zhao, X.; Jiang, X.-K.; Li, Z.-T. *Langmuir* **2012**, 28, 14839–14844.

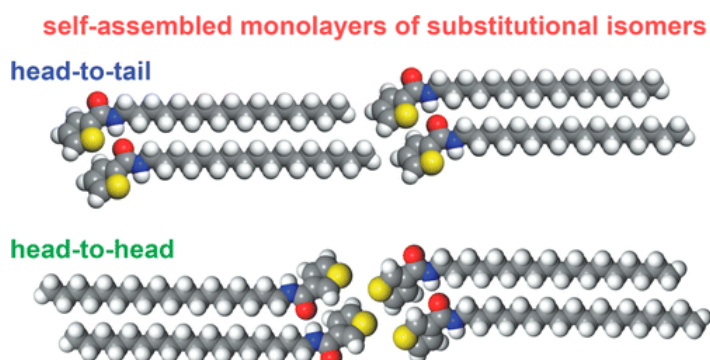
Abstract:



Reverse vesicles exhibiting functions similar to those of normal vesicles have been constructed through the self-assembly of TTF/CBPQT4+-based pseudo[2]rotaxanes in a nonpolar solvent. The ends of the threads of the pseudo[2]rotaxanes are attached with a Fréchet-type G-3 dendron and a hydrogen-bonded arylamide foldamer. These vesicles exhibit a response to redox. By exploiting the dynamic feature—spontaneously slow disassociation of the pseudorotaxanes—the sustained release of dyes embedded in the reverse vesicles has been demonstrated, which can be further tuned by changing the solvent polarity.

- Self-Assembly of Isomeric Monofunctionalized Thiophenes
- Heller, L. E.; Whitleigh, J.; Roth, D. F.; Oherlein, E. M.; Lucci, F. R.; Kolonko, K. J.; Plass, K. E. *Langmuir* **2012**, 28, 14855–14859.

Abstract:

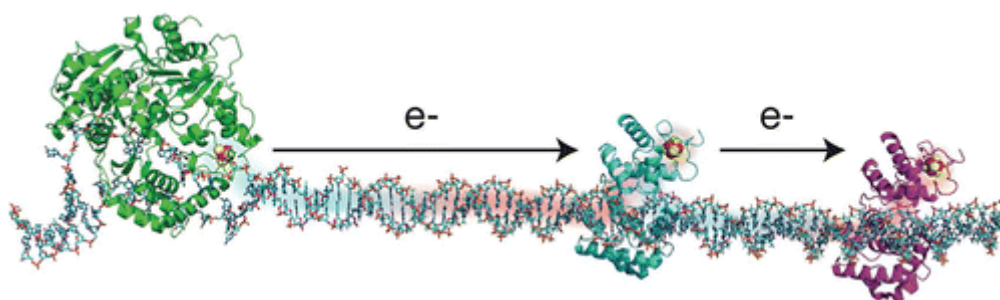


Controlling the self-assembly of thiophene-containing molecules and polymers requires a strong fundamental understanding of the relationship between molecular features and structure-directing forces. Here, the effects of ring-substitution position on the two-dimensional self-assembly of monosubstituted thiophenes at the phenyloctane/HOPG interface are studied using scanning tunneling microscopy (STM). The influence of  $\pi\cdots\pi$ -stacking, hydrogen-bonding, and alkyl-chain interactions are explored computationally. Alteration of the amide attachment point from the 2- to the 3-position induces transformation from head-to-tail packing to head-to-head packing. This may be attributed to canceling of lateral dipoles.

- DNA Charge Transport for Sensing and Signaling

Sontz, P. A.; Muren, N. B.; Barton, J. K. *Acc. Chem. Res.* **2012**, *45*, 1792-1800.

Abstract:



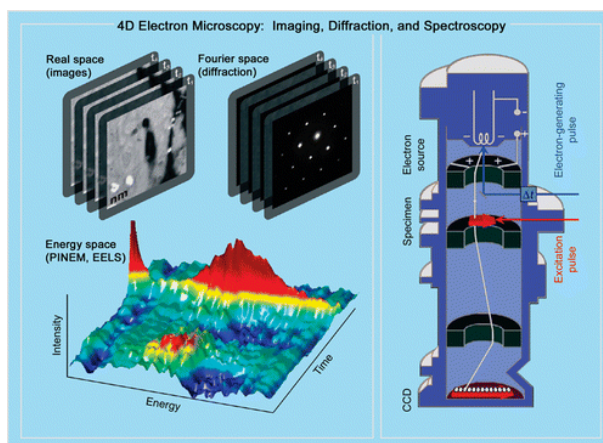
The DNA duplex is an exquisite macromolecular array that stores genetic information to encode proteins and regulate pathways. Its unique structure also imparts chemical function that allows it also to mediate charge transport (CT). We have utilized diverse platforms to probe DNA CT, using spectroscopic, electrochemical, and even genetic methods. These studies have established powerful features of DNA CT chemistry. DNA CT can occur over long molecular distances as long as the bases are well stacked. The perturbations in base stacking that arise with single base mismatches, DNA lesions, and the binding of some proteins that kink the DNA all inhibit DNA CT. Significantly, single molecule studies of DNA CT show that ground state CT can occur over 34 nm if the duplex is well stacked; one single base mismatch inhibits CT. The DNA duplex is an effective sensor for the integrity of the base pair stack. Moreover, the efficiency of DNA CT is what one would expect for a stack of graphite sheets: equivalent to the stack of DNA base pairs and independent of the sugar-phosphate backbone.

- 4D Electron Microscopy: Principles and Applications

Flannigan, D. J.; Zewail, A. H. *Acc. Chem. Res.* **2012**, *45*, 1828-1839.

Abstract:





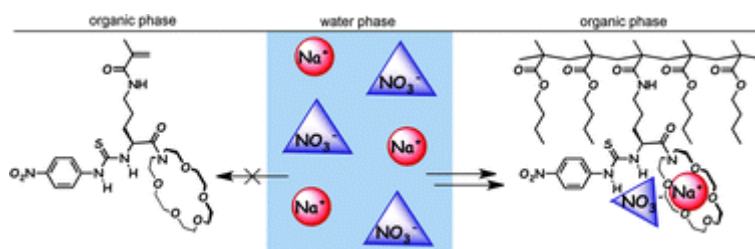
The transmission electron microscope (TEM) is a powerful tool enabling the visualization of atoms with length scales smaller than the Bohr radius at a factor of only 20 larger than the relativistic electron wavelength of 2.5 pm at 200 keV. The ability to visualize matter at these scales in a TEM is largely due to the efforts made in correcting for the imperfections in the lens systems which introduce aberrations and ultimately limit the achievable spatial resolution. In addition to the progress made in increasing the spatial resolution, the TEM has become an all-in-one characterization tool. Indeed, most of the properties of a material can be directly mapped in the TEM, including the composition, structure, bonding, morphology, and defects. The scope of applications spans essentially all of the physical sciences and includes biology.

In this Account, we discuss the development of four-dimensional ultrafast electron microscopy (4D UEM) and summarize techniques and applications that illustrate the power of the approach. In UEM, images are obtained either stroboscopically with coherent single-electron packets or with a single electron bunch. Coulomb repulsion is absent under the single-electron condition, thus permitting imaging, diffraction, and spectroscopy, all with high spatiotemporal resolution, the atomic scale (sub-nanometer and femtosecond). The time resolution is limited only by the laser pulse duration and energy carried by the electron packets; the CCD camera has no bearing on the temporal resolution. In the regime of single pulses of electrons, the temporal resolution of picoseconds can be attained when hundreds of electrons are in the bunch.

- Tuning the binding properties of a new heteroditopic salt receptor through embedding in a polymeric system

Romanski, J.; Piątek, P. *Chem. Commun.* **2012**, 48, 11346–11348.

Abstract:

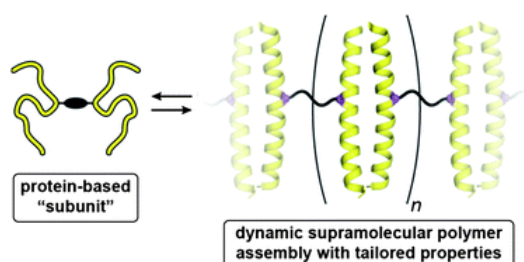


In this communication, we describe a polymerizable, heteroditopic salt receptor, based on an amino acid scaffold, which is able to bind sodium salts of chloride, acetate and nitrate. A poly(butyl methacrylate) derivative 2 containing receptor 1 was then prepared. In contrast to receptor 1 copolymer 2 is capable of extracting sodium nitrate from aqueous media.

- A modular synthetic platform for the construction of protein-based supramolecular polymers *via* coiled-coil self-assembly

Staples, J. K.; Oshaben, K. M.; Horne, W. S. *Chem. Sci.* **2012**, 3, 3387–3392.

Abstract:

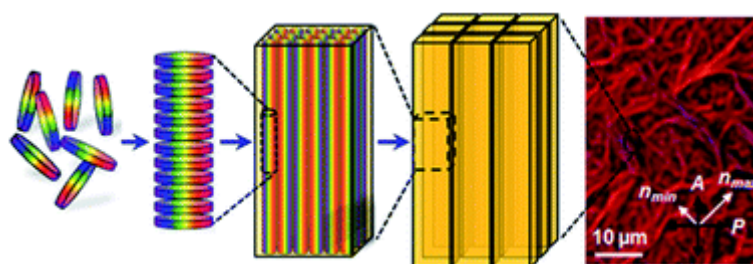


Programmed biomolecular self-assembly is a powerful method for the construction of designed supramolecular materials. Here, we show that branched  $\sim 8$  kDa subunits composed of  $\alpha$ -helical coiled-coil protein domains cross-linked at their midpoints by an organic bridging group can form defined supramolecular polymer assemblies in aqueous solution. The subunits are accessible by a modular and convergent synthetic route based on the chemoselective ligation of unprotected peptide building blocks. Systematic characterization of solution folding and self-assembly demonstrate that the properties of the assemblies (*e.g.*, chain length, hydrodynamic radius) are sensitive to both the structure of the organic bridge and the sequence of the protein domain. These findings raise the possibility of the rational design of a family of supramolecular materials with tunable properties based on well-established sequence–folding relationships in coiled-coil proteins.

- Macroscopically oriented hierarchical structure of the amphiphilic tetrathiafulvalene molecule

Kim, N.; Wang, L.; Kim, D.-Y.; Hwang, S.-H.; Kuo, S.-W.; Lee, M.-H.; Jeong, K.-U. *Soft Matter* **2012**, 8, 9183-9192.

Abstract:

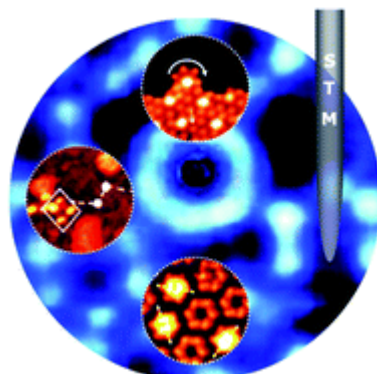


Since the physical properties of electronic and biological molecules strongly depend on the nature of molecular self-assembly and organization, it is essential to control their molecular packing structure and morphology on the different length scales. In this aspect, a programmed amphiphilic tetrathiafulvalene (TTF) molecule (abbreviated as amph-7TTF14) was newly designed and synthesized. Differential scanning calorimetry (DSC) combined with one-dimensional (1D) wide angle X-ray diffraction (WAXD) techniques revealed that a highly ordered crystalline phase emerged below the isotropic phase. From the 2D WAXD pattern of the macroscopically oriented amph-7TTF14 film, the crystal structure was identified to be a monoclinic unit cell. The face-to-face  $\pi$ – $\pi$  interaction between TTF groups and the nanophase separation between rigid TTF groups and flexible hydrophobic alkyl and hydrophilic tri(ethylene oxide) tails were the main driving forces for the self-assembly of amph-7TTF14. The morphological observations using transmission electron microscopy (TEM), atomic force microscopy (AFM), and polarized optical microscopy (POM) indicated that the

amph-7TTF14 formed not only flat ribbons but also scrolls and helices, in which the ribbons further aggregated to create the fibrous hierarchical structures. Based on the experimental results and careful analyses, it was realized that the scrolls and helices were induced by the unbalanced surface stresses generated during the crystallization process. When the macroscopically oriented fibrous hierarchical structure is properly applied to the electrooptical and bio-mimetic devices, the targeted physical properties may be significantly improved and tuned for the specific practical applications.

- Artificial molecular rotors and motors on surfaces: STM reveals and triggers  
Lensen, D.; Elemans, J. A. A. W. *Soft Matter* **2012**, 8, 9053-9063.

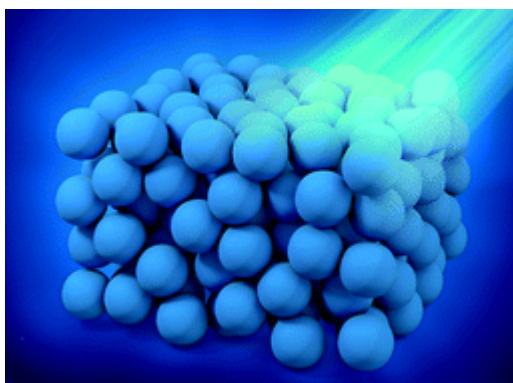
Abstract:



Inspired by the biomolecular motors that can be found everywhere in nature and are essential to numerous processes of life, nanoscientists have been developing artificial molecular rotors and motors with the ultimate aim to include them into bottom-up constructed working devices. Once mounted onto a surface, scanning tunnelling microscopy (STM) is a powerful technique to characterise these rotor and motor molecules, since it allows their direct visualisation at submolecular resolution. It can furthermore track translational motion in real-time, and rotational motion even at the millisecond level by performing tunnelling current-time spectroscopy. Finally, the STM can be a useful tool to power molecular rotors and motors, by injecting tunnelling electrons of sufficient energy into the molecules *via* the STM tip. This review addresses recent advances in revealing the structure, motion, and manipulation of molecular rotors and motors on a surface by STM.

- Angle-independent structural coloured amorphous arrays  
Takeoka, Y. *J. Mater. Chem.* **2012**, 22, 23299–23309.

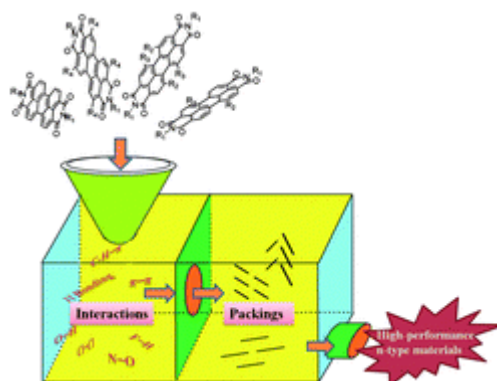
Abstract:



We are able to observe a colour due to the interference of light from microstructures composed of different refractive index materials that is comparable to the visible wavelength of light; such a colour is called a structural colour. Because structural colour is fadeless and no energy is lost from the colour mechanism, structurally coloured materials are expected to be used for energy-saving reflective displays and sensors. Previously, however, the word “iridescence” rather than “structural colour” was used to describe the property of a surface that appears to change colour as the viewing angle or the angle of light illumination changes. Thus, people who are aware of the concept of interference colour have a strong impression that all structurally coloured materials change hue when viewed from different angles, as indicated by the term “iridescence.” In fact, most artificial structurally coloured materials that we and other groups have studied so far change their hue depending on the viewing and light illumination angles because these structural colours are derived from Bragg reflection. Such angle dependence presents a barrier for developing displays and sensors using structurally coloured materials. Therefore, my group has been working to develop angle-independent structural coloured materials. The latest most notable ones are amorphous array systems. In this review, I first introduce the microstructures and optical properties of low-angle-dependent structurally coloured amorphous arrays in biological systems, then describe the fabrication and the optical nature of the artificially prepared imitations of such biological systems, and finally, present the related theoretical studies.

- The interplay of intermolecular interactions, packing motifs and electron transport properties in perylene diimide related materials: a theoretical perspective  
Geng, Y.; Li, H.-B.; Wu, S.-X.; Su, Z.-M. *J. Mater. Chem.* **2012**, 22, 20840–20851.

Abstract:



Perylene diimide (PDI) and its derivatives hold great promise, since they are undeniably considered as an important family of organic n-type semiconductors with both high carrier mobilities and air stabilities comparable to p-type ones, although they traditionally stand out as a class of high-performance dyes and pigments. In this feature article, we summarize the influences of substituents on different positions (imide, ortho, bay) of PDI on their electronic and morphological (packing) properties, which are in close connection with the ability for carrier transport. Then representative molecular packing motifs for PDIs are also classified, with an emphasis on the intricate interplay of intermolecular interactions, packing motifs and electron transport properties of perylene imide related carrier transport materials from a theoretical point of view, towards paving the way for boosting and improving the electron transport mobilities and air stabilities of PDIs-based materials.