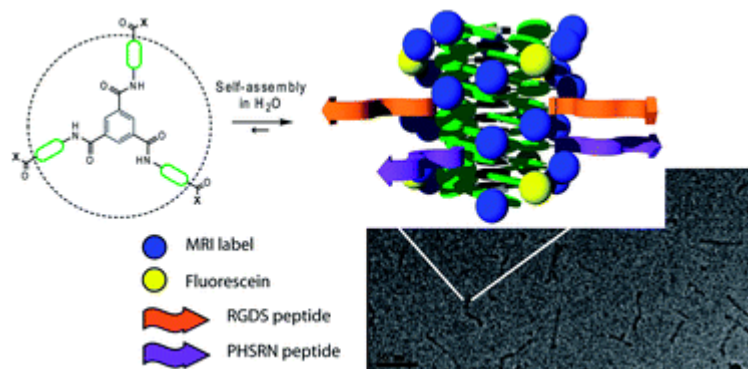


- Peptide functionalised discotic amphiphiles and their self-assembly into supramolecular nanofibres

Besenius, P.; Goedegebure, Y.; Driesse, M.; Koay, M.; Bomans, P. H. H.; Palmans, A. R. A.; Dankers, P. Y. W.; Meijer, E. W. *Soft Matter* **2011**, *7*, 7980-7983.

Abstract:

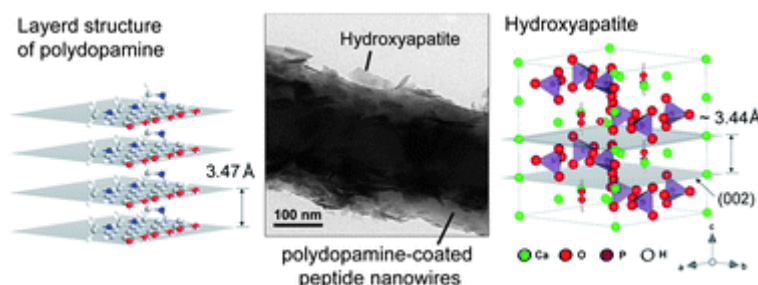


The multicomponent co-assembly of discotic amphiphiles provides a modular and versatile approach to prepare RGDS- and PHSRN-peptide functionalised supramolecular nanofibres, bearing pendant paramagnetic Gd(III)-chelates.

- Bone-like peptide/hydroxyapatite nanocomposites assembled with multi-level hierarchical structures

Ryu, J.; Ku, S. H.; Lee, M.; Park, C. B. *Soft Matter* **2011**, *7*, 7201-7206.

Abstract:

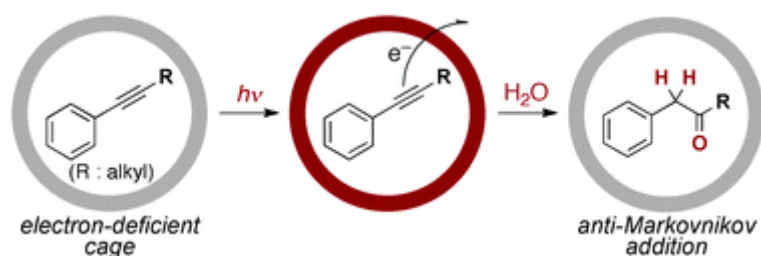


Inspired by nature's strategy for creating organic/inorganic hybrid composite materials, we developed a simple but powerful method to synthesize bone-like peptide/hydroxyapatite nanocomposites using a mussel-mimetic adhesive, polydopamine. We found that polydopamine was uniformly coated in a graphite-like layered structure on the surface of self-assembled diphenylalanine (Phe-Phe, FF) nanowires and enabled the epitaxial growth of *c*-axis-oriented hydroxyapatite nanocrystals along the nanowires, which is similar to mineralized collagen nanofibers of natural bone. The mineralized peptide nanowires were further organized in relation to each other and then readily hybridized with osteoblastic cells, resulting in the formation of multi-level hierarchical structures. They were found to be nontoxic and enabled efficient adhesion and proliferation of osteoblastic cells by guiding filopodial extension.

- Photo-driven anti-Markovnikov alkyne hydration in self-assembled hollow complexes

Murase, T.; Takezawa, H.; Fujita, M. *Chem. Commun.* **2011**, *47*, 10960-10962.

Abstract:

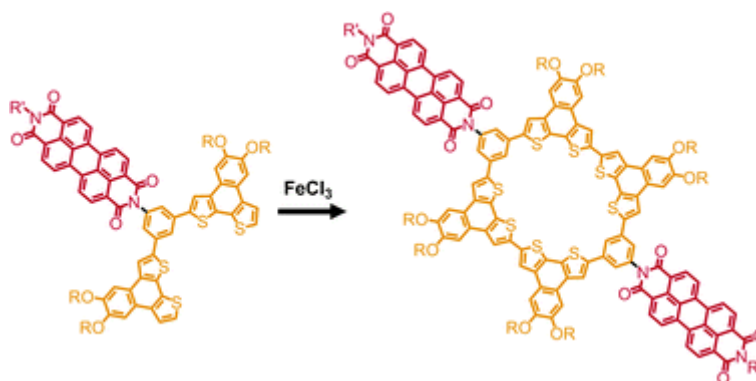


Under UV-light irradiation, the anti-Markovnikov hydration of internal arylalkynes proceeds in the cavity of an electron-deficient coordination cage to give benzyl ketones; the reaction is triggered by cage-mediated, photo-induced electron transfer from the alkynes to the cage.

- An oxidative coupling route to macrocyclic thiophenes and its application in the synthesis of a donor/acceptor hybrid molecule

Maier, S. K.; Jester, S.-S.; Müller, U.; Müller, W. M.; Höger, S. *Chem. Commun.* **2011**, 47, 11023-11025.

Abstract:

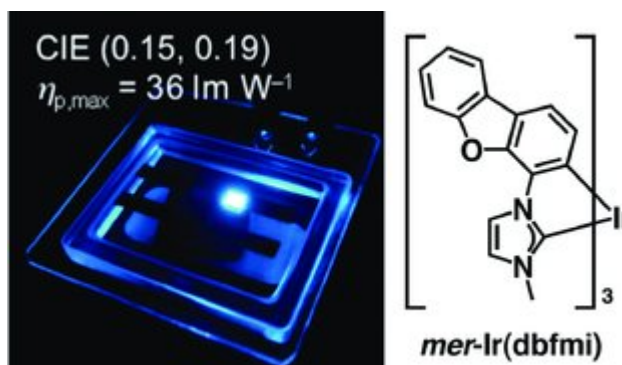


A route towards phenylene-bithiophene macrocycles *via* oxidative thiophene coupling under pseudo-high dilution conditions is reported. This method is applied to the synthesis of a shape-persistent thiophene macrocycle with extraannularly attached perylenebisimide moieties that forms supramolecular aggregates at the solid/liquid interface.

- High-Efficiency Blue and White Organic Light-Emitting Devices Incorporating a Blue Iridium Carbene Complex

Sasabe, H.; Takamatsu, J.; Motoyama, T.; Watanabe, S.; Wagenblast, G.; Langer, N.; Molt, O.; Fuchs, E.; Lennartz, C.; Kido, J. *Adv. Mater.* **2010**, 22, 5003–5007.

Abstract:

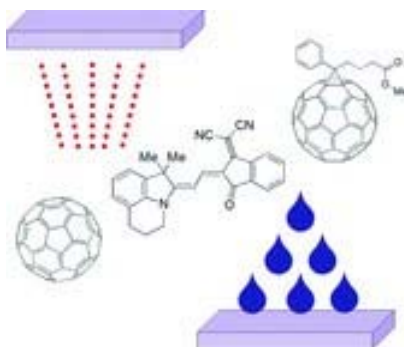


In this communication, we report on the development of high-efficiency blue and white OLEDs incorporating a blue iridium carbene complex. The blue OLED showed a maximum power efficiency

($\eta_{p,max}$) of 35.9 lm W^{-1} and a power efficiency at 100 cd m^{-2} ($\eta_{p,100}$) of 19.6 lm W^{-1} . Furthermore, we also realize a white OLED with a $\eta_{p,max}$ of 59.9 lm W^{-1} and $\eta_{p,1000}$ of 43.3 lm W^{-1} without any light-outcoupling enhancement. This extremely efficient white OLED also shows an illumination-acceptable CRI over 80.

- Direct Comparison of Highly Efficient Solution and Vacuum-Processed Organic Solar Cells Based on Merocyanine Dyes
Kronenberg, N. M.; Steinmann, V.; Bürckstümmer, H.; Hwang, J.; Hertel, D.; Würthner, F.; Meerholz, K. *Adv. Mater.* **2010**, *22*, 4193–4197.

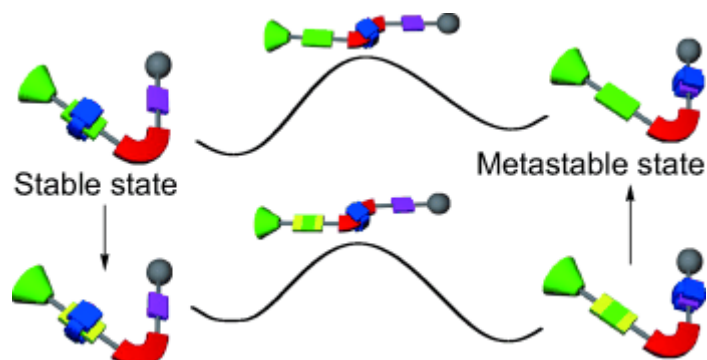
Abstract:



Identically configured bulk heterojunction organic solar cells based on merocyanine dye donor and fullerene acceptor compounds (see figure) are manufactured either from solution or by vacuum deposition, to enable a direct comparison. Whereas the former approach is more suitable for screening purposes, the latter approach affords higher short-circuit current density and power conversion efficiency.

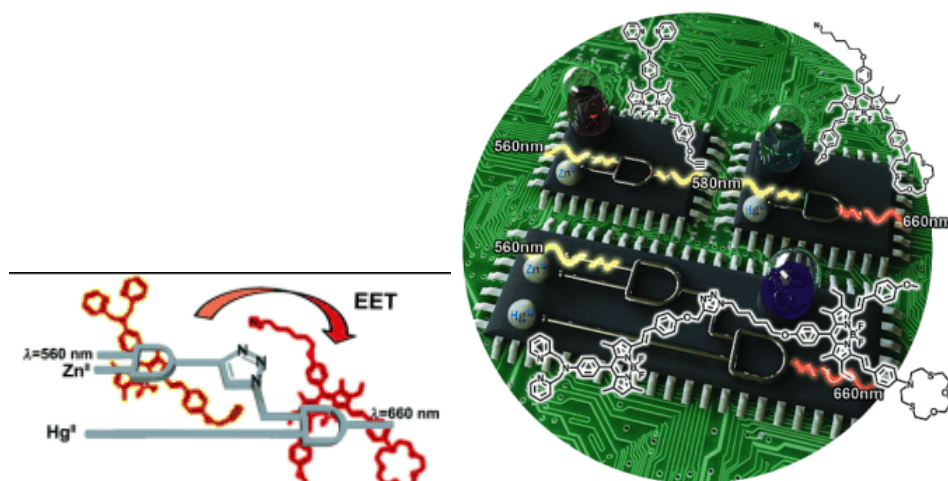
- Foldamer-Tuned Switching Kinetics and Metastability of [2]Rotaxanes
Zhang, K.; Zhao, X.; Wang, G.; Liu, Y.; Zhang, Y.; Lu, H.; Jiang, X.; Li, Z. *Angew. Chem. Int. Ed.* **2011**, *50*, 9866–9870.

Abstract:



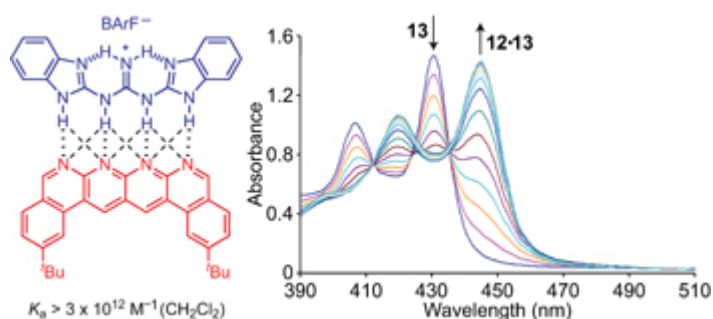
Slip sliding away: Foldamers (see picture, red) can function as modular stoppers to regulate the slippage and de-slippage of pseudorotaxanes and the switching kinetics and metastability of bistable rotaxanes. By simply changing the solvent or the length of the hydrogen-bonded foldamer, the lifetime of the metastable co-conformation state can be increased dramatically, from several minutes to as long as several days.

- From Virtual to Physical: Integration of Chemical Logic Gates
Guliyev, R.; Ozturk, S.; Kostereli, Z.; Akkaya, E. *Angew. Chem. Int. Ed.* **2011**, *50*, 9826–9831.

Abstract:

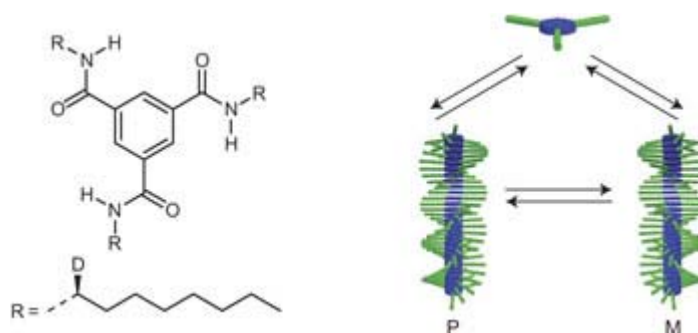
Integration by parts: Advanced information processing at the molecular level requires integrated logic gates, which has to date been possible only virtually. Now, two independently working AND and molecular logic gates are brought together by “click” chemistry to form integrated logic gates which respond exactly as predicted from such an integration scheme (see picture, EET=excitation energy transfer).

- An AAAA–DDDD quadruple hydrogen-bond array
Blight, B. A.; Hunter, C. A.; Leigh, D. A.; McNab, H.; Thomson, P. I. T. *Nature Chem.* **2011**, *3*, 244-248.

Abstract:

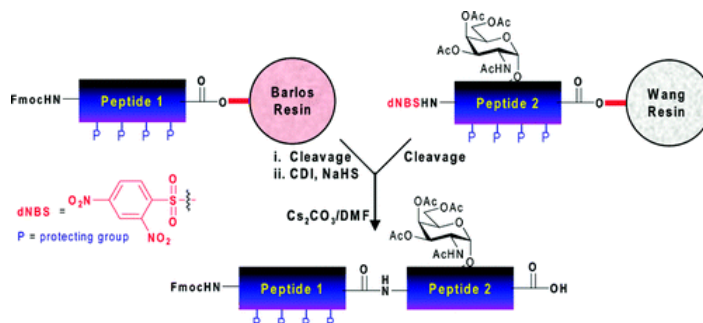
Secondary electrostatic interactions between adjacent hydrogen bonds can have a significant effect on the stability of a supramolecular complex. In theory, the binding strength should be maximized if all the hydrogen-bond donors (D) are on one component and all the hydrogen-bond acceptors (A) are on the other. Here, we describe a readily accessible AAAA–DDDD quadruple hydrogen-bonding array that exhibits exceptionally strong binding for a small-molecule hydrogen-bonded complex in a range of different solvents ($K_a > 3 \times 10^{12} \text{ M}^{-1}$ in CH_2Cl_2 , $1.5 \times 10^6 \text{ M}^{-1}$ in CH_3CN and $3.4 \times 10^5 \text{ M}^{-1}$ in 10% v/v DMSO/ CHCl_3). The association constant in CH_2Cl_2 corresponds to a binding free energy (ΔG) in excess of -71 kJ mol^{-1} (more than 20% of the thermodynamic stability of a carbon–carbon covalent bond), which is remarkable for a supramolecular complex held together by just four intercomponent hydrogen bonds.

- The effect of isotopic substitution on the chirality of a self-assembled helix
Cantekin, S.; Balkenende, D. W. R.; Smulders, M. M. J.; Palmans, A. R. A.; Meijer, E. W. *Nature Chem.* **2011**, *3*, 42-46.

Abstract:

N,N,N'-trialkylbenzene-1,3,5-tricarboxamides (BTAs) self-assemble by means of strong, threefold α -helix-type intermolecular hydrogen bonding into well-defined, helical, one-dimensional columnar aggregates. When a stereogenic centre is introduced into the alkyl side chains of these BTAs, strong Cotton effects are observed in dilute apolar solutions, indicating the preference for one helical conformation over the other. Here, we report the creation of a helical sense preference in self-assembled BTAs by introducing deuterium/hydrogen isotope chirality into the alkyl side chains. We determine the relative stabilities of the left- and right-handed helical conformations of these deuterated supramolecular polymers by performing a conformational analysis. Our findings show that the results of deuterium/hydrogen substitution in BTA-based supramolecular polymers and helical polyisocyanates are very similar, although the formation mechanisms differ. The selectively deuterated BTAs discussed here represent the first example of supramolecular chirality resulting from isotope substitution.

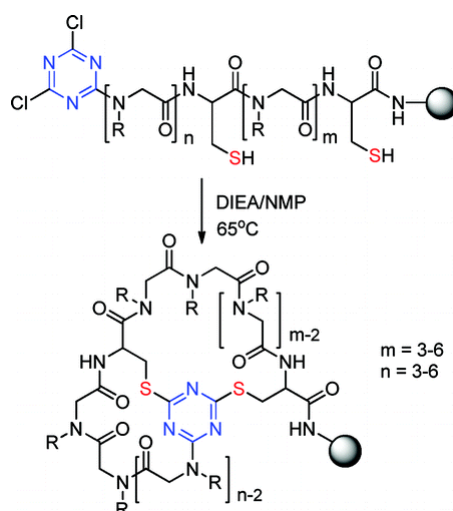
- Mixed-Phase Synthesis of Glycopeptides Using a *N*-Peptidyl-2,4-dinitrobenzenesulfonamide – Thioacid Ligation Strategy
Karmakar, P.; Talan, R. S.; Sucheck, S. J. *Org. Lett.* **2011**, *13*, 5298–5301.

Abstract:

A strategy for the solid phase peptide synthesis (SPPS) and coupling of *N*-peptidyl and *N*-glycopeptidyl 2,4-dinitrobenzenesulfonamides (dNBS) with C-terminal peptidyl thioacids has been developed. The resulting *N*-dNBS peptides were coupled to generate longer peptides. Ligation reactions were complete within 15 to 20 min.

- Design and Facile Solid-Phase Synthesis of Conformationally Constrained Bicyclic Peptoids
Lee, J. H.; Kim, H.-S.; Lim, H.-S. *Org. Lett.* **2011**, *13*, 5012–5015.

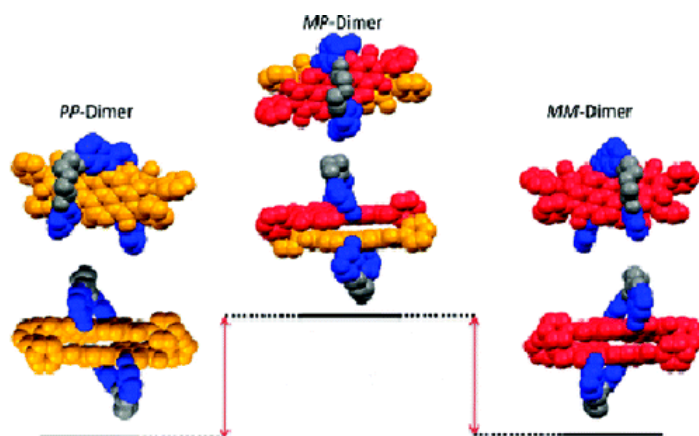
Abstract:



Triazine-bridged bicyclic peptoids as conformationally constrained peptidomimetics are described. Bicyclic peptoids composed of 6–12 peptoid residues (m , $n = 3-6$) were synthesized in excellent yields using a highly efficient solid-phase synthetic route.

- Impact of Molecular Flexibility on Binding Strength and Self-Sorting of Chiral π -Surfaces
Safont-Sempere, M. M.; Osswald, P.; Stolte, M.; Grüne, M.; Renz, M.; Kaupp, M.; Radacki, K.; Braunschweig, H.; Würthner, F. *J. Am. Chem. Soc.* **2011**, *133*, 9580–9591.

Abstract:



In this work, we have explored for the first time the influence of conformational flexibility of π -core on chiral self-sorting properties of perylene bisimides (PBIs) that are currently one of the most prominent classes of functional dyes. For this purpose, two series of chiral macrocyclic PBIs **3a–c** and **4a–c** comprising oligoethylene glycol bridges of different lengths at the 1,7 bay positions were synthesized and their atropo-enantiomers (P and M enantiomers) were resolved. Single crystal analysis of atropo-enantiomerically pure (P)-**3a** not only confirmed the structural integrity of the ethylene glycol bridged macrocycle but also illustrated the formation of π -stacked dimers with left-handed supramolecular helicity. Our detailed studies with the series of highly soluble chiral PBIs **4a–c** by 1- and 2-D ^1H NMR techniques, and temperature- and concentration-dependent UV/vis absorption and circular dichroism (CD) spectroscopy revealed that in π - π -stacking dimerization of these PBIs chiral self-recognition (i.e., PP and MM homodimer formation) prevails over self-discrimination (i.e., PM heterodimer formation). Our studies clearly showed that with increasing conformational flexibility of PBI cores imparted by longer bridging units, the binding strength for the dimerization process increases, however, the efficiency for chiral self-recognition decreases. These

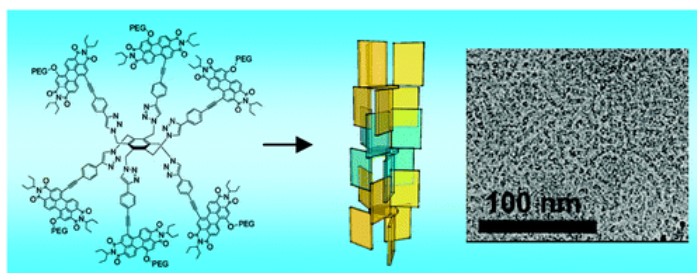
results are rationalized in terms of an induced-fit mechanism facilitating more planarized π -scaffolds of PBIs containing longer bridging units upon π - π -stacking.

7

- Supramolecular Polymers in Aqueous Medium: Rational Design Based on Directional Hydrophobic Interactions

Ustinov, A.; Weissman, H.; Shirman, E.; Pinkas, I.; Zuo, X.; Rybtchinski, B. *J. Am. Chem. Soc.* **2011**, *133*, 16201–16211.

Abstract:

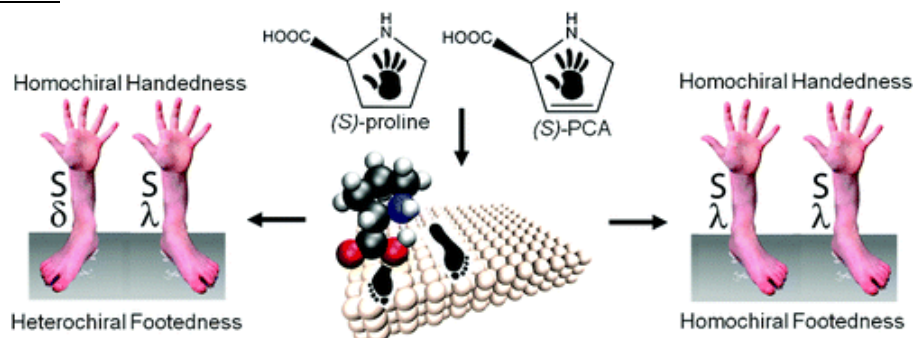


Self-assembly in aqueous medium is of primary importance and widely employs hydrophobic interactions. Yet, unlike directional hydrogen bonds, hydrophobic interactions lack directionality, making difficult rational self-assembly design. Directional hydrophobic motif would significantly enhance rational design in aqueous self-assembly, yet general approaches to such interactions are currently lacking. Here, we show that pairwise directional hydrophobic/ π -stacking interactions can be designed using well-defined sterics and supramolecular multivalency. Our system utilizes a hexasubstituted benzene scaffold decorated with 3 (compound **1**) or 6 (compound **2**) amphiphilic perylene diimides. It imposes a pairwise self-assembly mode, leading to well-defined supramolecular polymers in aqueous medium. The assemblies were characterized using cryogenic electron microscopy, small-angle X-ray scattering, optical spectroscopy, and EPR. Supramolecular polymerization studies in the case of **2** revealed association constants in 10^8 M^{-1} range, and significant enthalpic contribution to the polymerization free energy. The pairwise PDI motif enables exciton confinement and localized emission in the polymers based on **1** and **2**'s unique photonic behavior, untypical of the extended π -stacked systems. Directional pairwise hydrophobic interactions introduce a novel strategy for rational design of noncovalent assemblies in aqueous medium, and bring about a unique photofunction.

- Tailoring Homochirality at Surfaces: Going Beyond Molecular Handedness

Forster, M.; Dyer, M. S.; Persson, M.; Raval, R. *J. Am. Chem. Soc.* **2011**, *133*, 15992-16000.

Abstract:



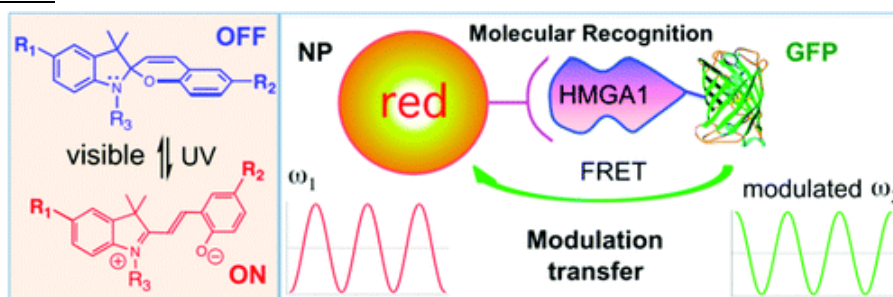
Chirality can be bestowed upon a surface by the adsorption of molecules and is usually discussed in terms of the molecular handedness. However, the adsorption process often leads to a new

manifestation of chirality in the form of the adsorption footprint, which can also be chiral and generate mirror-images in 2-D. Therefore, in describing the chirality of the interface, one must consider both the *handedness* and the adsorption '*footedness*' of the system. Specifically, the creation of a truly homochiral surface must ensure that a single chirality is expressed for each aspect, and requires not only the control of molecule handedness but also direct control over footedness. Here, we demonstrate the ability to engineer homochiral footedness by a structural modification of enantiopure (*S*)-proline, which normally creates a (4 × 2) organization on a Cu(110) surface with heterochiral footedness. This modification of proline via the addition of a double bond within the pyrrolidine ring, yielding 3-pyrroline-2-carboxylic acid (PCA), is sufficient to drive the footprints of the entire (4 × 2) assembly from heterochiral to homochiral, leading to the creation of a truly homochiral interface. The effects of modifications upon the footprint arrangements were characterized at the single-molecule level by scanning tunnelling microscopy, reflection absorption infrared spectroscopy and periodic density functional theory calculations. The control of adsorption footprints is not only pivotal to tailoring chirality at surfaces but also plays a key role in dictating the organization, the outward facing functionalities and the response of the organic–inorganic interface.

- Photoswitching-Induced Frequency-Locked Donor–Acceptor Fluorescence Double Modulations Identify the Target Analyte in Complex Environments

Tian, Z.; Wu, W.; Wan, W.; Li, A. D. Q. *J. Am. Chem. Soc.* **2011**, *133*, 16092-16100.

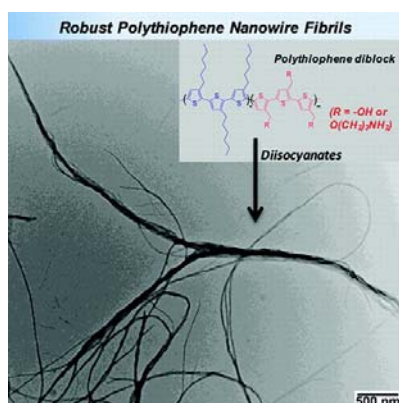
Abstract:



Precisely identifying biological targets and accurately extracting their relatively weak signals from complicated physiological environments represent daunting challenges in biological detection and biomedical diagnosis. Fluorescence techniques have become the method of choice and offer minimally invasive and ultrasensitive detections, thus, providing a wealth of information regarding the biological mechanisms in living systems. Despite fluorescence analysis has advanced remarkably, conventional detections still encounter considerable limitations. This stems from the fact that the fluorescence intensity signal (I) is sensitive and liable to numerous external factors including temperature, light source, medium characteristics, and dye concentration. The interferences exasperatingly undermine the precision of measurements, and frequently render the signal undetectable. For example, fluorescence from single-molecule emitters can be measured on glass substrates under optimum conditions, but single-molecule events in complicated physiological environments such as live cells can hardly be detected because of autofluorescence interference and other factors. Furthermore, traditional intensity (I) and wavelength (λ) measurements do not reveal the interactive nature between the donor and the acceptor. Thus, innovative detection strategies to circumvent these aforementioned limitations of the conventional techniques are critically needed. With the use of photoswitching-induced donor–acceptor-fluorescence double modulations, we present a novel strategy that introduces three additional physical parameters: modulation amplitude (A), phase shift ($\Delta\Phi$), and lock-in frequency (ω), and demonstrate that such a strategy can circumvent

the limitation of the conventional fluorescence detection techniques. Together, these five physical quantities (I , λ , A , $\Delta\Phi$, ω) reveal insightful information regarding molecular interactive strength between the probe and the analyte and enable extracting weak-fluorescence spectra from large interfering noises in complex environments.

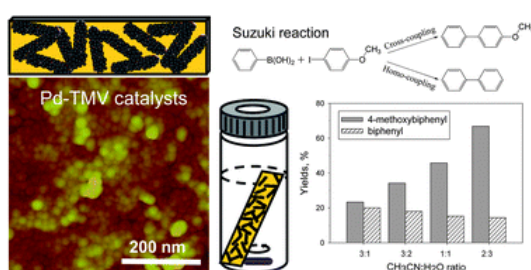
- Cross-Linked Conjugated Polymer Fibrils: Robust Nanowires from Functional Polythiophene Diblock Copolymers
Hammer, B. A. G.; Bokel, F. A.; Hayward., R. C.; Emrick, T. *Chem. Mater.* **2011**, *23*, 4250–4256.
Abstract:



A series of poly(3-hexyl thiophene) (P3HT)-based diblock copolymers were prepared and examined in solution for their assembly into fibrils, and post-assembly cross-linking into robust nanowire structures. P3HT-b-poly(3-methanol thiophene) (P3MT), and P3HT-b-poly(3-aminopropylmethyl thiophene) (P3AmT) diblock copolymers were synthesized using Grignard metathesis (GRIM) polymerization. Fibrils formed from solution assembly of these copolymers are thus decorated with hydroxyl and amine functionality, and cross-linking is achieved by reaction of diisocyanates with the hydroxyl and amine groups. A variety of cross-linked structures, characterized by transmission electron microscopy (TEM), were produced by this method, including dense fibrillar sheets, fibril bundles, or predominately individual fibrils, depending on the chosen reaction conditions. In solution, the cross-linked fibrils maintained their characteristic vibronic structure in solvents that would normally disrupt (dissolve) the structures.

- Viral-templated palladium nanocatalysts for Suzuki coupling reaction
Yang, C.; Manocchi, A. K.; Lee, B.; Yi, H. *J. Mater. Chem.* **2011**, *21*, 187-194.

Abstract:



We demonstrate and thoroughly examine tobacco mosaic virus (TMV)-templated palladium (Pd) nanocatalysts for the ligand-free Suzuki coupling reaction under mild conditions. The surface-assembled TMV templates allow for facile catalyst synthesis under mild aqueous conditions that leads to high Pd surface loading and stability. Further, the chip-based format enables simple catalyst separation and reuse as well as facile product recovery. Reaction condition studies demonstrated

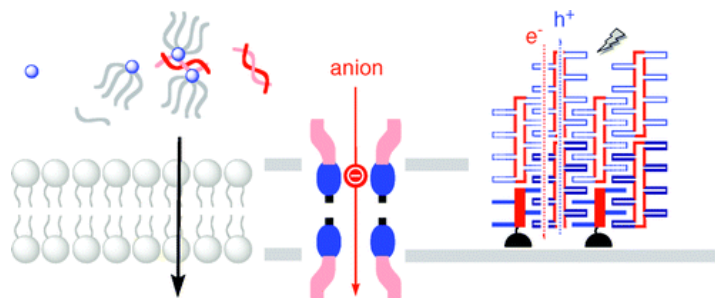
that the solvent ratio played an important role in the selectivity of the Suzuki reaction, and that a higher water/acetonitrile ratio significantly facilitated the cross-coupling pathway. We envision that our viral template-based bottom-up assembly approach can be readily extended to other biotemplates, metal catalysts and organic reaction systems.

10

- Recent Progress with Functional Biosupramolecular Systems

Alonso Doval, D.; Areephong, J.; Bang, E.-K.; Bertone, L.; Charbonnaz, P.; Fin, A.; Lin, N.-T.; Lista, M.; Matile, S.; Montenegro, J.; Orentas, E.; Sakai, N.; Tran, D.-H.; Vargas Jentzsch, A. *Langmuir* **2011**, *27*, 9696-9705.

Abstract:

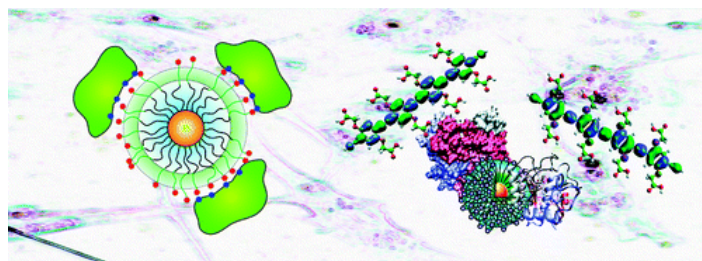


The objective of this account is to summarize our recent progress with functional biosupramolecular systems concisely. The functions covered are artificial photosynthesis, anion transport, and sensing in lipid bilayer membranes. With artificial photosynthesis, the current emphasis is on the construction of ordered and oriented architectures on solid surfaces. Recent examples include the zipper assembly of photosystems with supramolecular n/p-heterojunctions and oriented antiparallel redox gradients. Current transport systems in lipid bilayers reveal new interactions at work. Examples include anion-macrodipole or anion- π interactions. Current attention with membrane-based sensing systems shifts from biosensor approaches with enzymatic signal generation to aptamers (i.e., the DNA version of immunosensing) and differential sensing with dynamic polyion-counterion transporters. The functional diversity accessible with biosupramolecular systems is highlighted, as is the critical importance of cross-fertilization at intertopical convergence zones.

- Nano Meets Biology: Structure and Function at the Nanoparticle Interface

Moyano, D. F.; Rotello, V. M. *Langmuir* **2011**, *27*, 10376-10385.

Abstract:



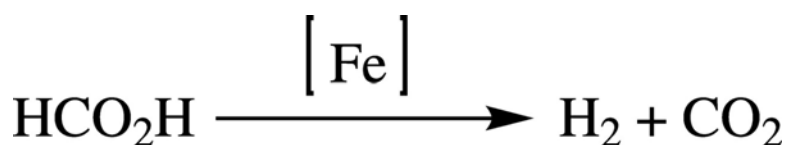
Understanding the interactions of nanomaterials with biosystems is a critical goal in both biomedicine and environmental science. Engineered nanoparticles provide excellent tools for probing this interface. In this feature article, we will summarize one of the themes presented in our recent Langmuir lecture discussing the use of monolayer design to understand and control the interactions of nanoparticles with biomolecules and cells.

- Efficient Dehydrogenation of Formic Acid Using an Iron Catalyst

Boddien, A.; Mellmann, D.; Gärtner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, 333, 1733-1736.

11

Abstract:

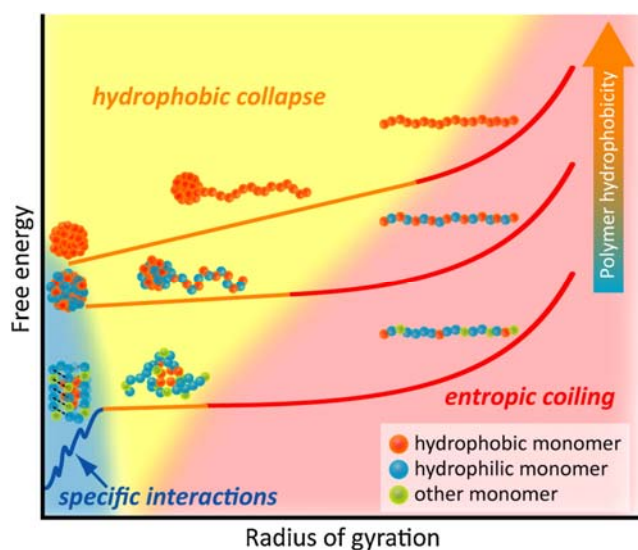


Hydrogen is one of the essential reactants in the chemical industry, though its generation from renewable sources and storage in a safe and reversible manner remain challenging. Formic acid (HCO₂H or FA) is a promising source and storage material in this respect. Here, we present a highly active iron catalyst system for the liberation of H₂ from FA. Applying 0.005 mole percent of Fe(BF₄)₂·6H₂O and tris[(2-diphenylphosphino)ethyl]phosphine [P(CH₂CH₂PPh₂)₃, PP₃] to a solution of FA in environmentally benign propylene carbonate, with no further additives or base, affords turnover frequencies up to 9425 per hour and a turnover number of more than 92,000 at 80°C. We used in situ nuclear magnetic resonance spectroscopy, kinetic studies, and density functional theory calculations to explain possible reaction mechanisms.

- Signature of hydrophobic hydration in a single polymer

Li, I. T. S.; Walker, G. C. *Proc. Nat. Acad. Sci.* **2011**, 108, 16527-16532.

Abstract:



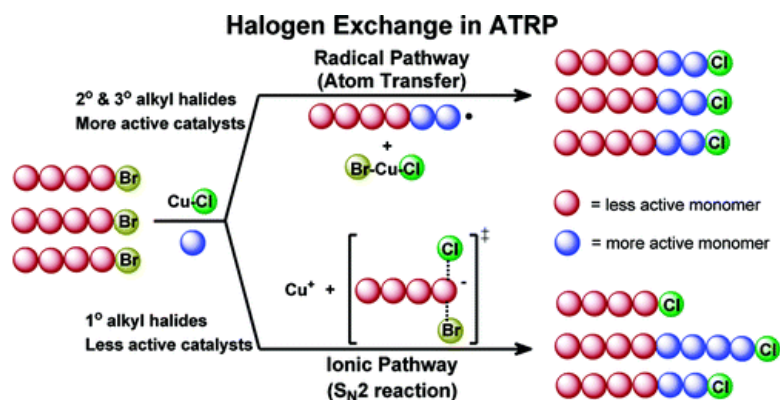
Hydrophobicity underpins self-assembly in many natural and synthetic molecular and nanoscale systems. A signature of hydrophobicity is its temperature dependence. The first experimental evaluation of the temperature and size dependence of hydration free energy in a single hydrophobic polymer is reported, which tests key assumptions in models of hydrophobic interactions in protein folding. Herein, the hydration free energy required to extend three hydrophobic polymers with differently sized aromatic side chains was directly measured by single molecule force spectroscopy. The results are threefold. First, the hydration free energy per monomer is found to be strongly dependent on temperature and does not follow interfacial thermodynamics. Second, the temperature dependence profiles are distinct among the three hydrophobic polymers as a result of a hydrophobic size effect at the subnanometer scale. Third, the hydration free energy of a monomer

on a macromolecule is different from a free monomer; corrections for the reduced hydration free energy due to hydrophobic interaction from neighboring units are required.

- Mechanism of Halogen Exchange in ATRP

Peng, C.; Kong, J.; Seeliger, F.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 7546–7557.

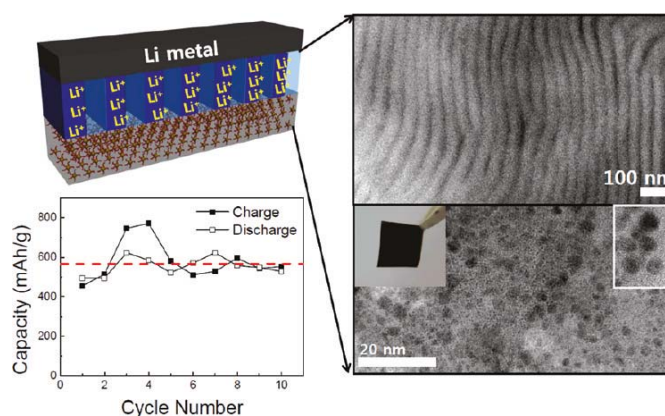
Abstract:



Detailed mechanistic studies reveal that halogen exchange (HE) in ATRP can occur not only by a radical pathway (atom transfer) but also by an ionic pathway (S_N2 reaction) because $Cu(I)(L)X$ and $Cu(II)(L)X_2$ complexes contain weakly associated halide anion that can participate in the S_N2 reaction with alkyl halide (ATRP initiator). Both pathways were kinetically studied, and their contributions to the HE process were quantitatively evaluated for seven alkyl halides and three $Cu(I)(L)Cl$ complexes. Radical pathway dominates the HE process for 3° and 2° alkyl bromides with more active complexes such as $Cu(I)(TPMA)Cl$. Interestingly, ionic pathway dominates for 1° alkyl bromides and less active ATRP catalysts. These studies also revealed that degree of association of alkyl halide anion depends on the structure of copper complexes. In addition, radical pathway is accompanied by the reverse reactions such as deactivation of radicals to alkyl bromides and also activation of alkyl chlorides, reducing the efficiency of halogen exchange.

- Enhanced Performance in Lithium-Polymer Batteries Using Surface-Functionalized Si Nanoparticle Anodes and Self-Assembled Block Copolymer Electrolytes
- Choi, I.; Ahn, H.; Park, P. M. *Macromolecules* **2011**, *44*, 7327–7334.

Abstract:

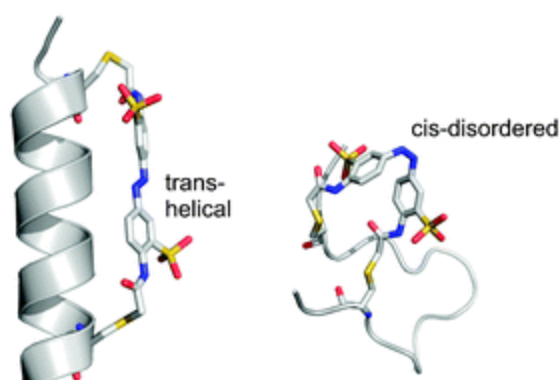


We have explored new Li-polymer batteries composed of surface functionalized Si nanoparticles (SiNPs) as anode active materials and nanostructured block copolymers as solid electrolytes. Surface protection of SiNPs with poly(ethylene oxide) chains successfully prevents aggregation of SiNPs during cycling and also helps fast Li^+ transport to the active centers in the anodes. The self-assembly

nature of block copolymer electrolytes in ca. 50 nm periodicity is aimed to restrain the formation of macroscopic ionic clusters during Li-insertion/desertion. To decouple the electrical and mechanical properties of polymer electrolytes, two different nonvolatile additives (ionic liquid and non ionic plasticizer) were incorporated and remarkably different cycle performances have been observed. The incorporation of ionic liquid yields the utmost ionic conductivity and distinctly large first lithium insertion capacity of 2380 mA h/g was seen. However, the formation of solid electrolyte interphase (SEI) was responsible for highly irreversible lithium desertion capacity and the system indicate fast capacity fading during cycling. With the use of non ionic plasticizer, in contrast, the SiNPs anode can store lithium up to a reversible capacity of 1850 mA h/g under aggressive test profiles of 80 °C and voltage window between 0–4.5 V. The focused ion beam technique was successfully used to obtain ex-situ transmission electron microscopy images of cycled polymer electrolytes and anode materials to underpin the origin of capacity retention or fading upon cycling. The results suggest that the structural retention of both polymer electrolytes and SiNPs during cycling attributes to the improved battery performance.

- Azobenzene photoswitches for biomolecules
Beharry, A. A.; Woolley, A. G. A. *Chem. Soc. Rev.*, **2011**, *40*, 4422-4437.

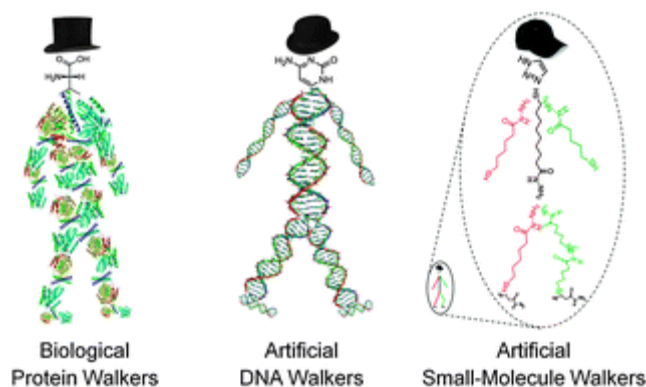
Abstract:



The photoisomerization of azobenzene has been known for almost 75 years but only recently has this process been widely applied to biological systems. The central challenge of how to productively couple the isomerization process to a large functional change in a biomolecule has been met in a number of instances and it appears that effective photocontrol of a large variety of biomolecules may be possible. This *critical review* summarizes key properties of azobenzene that enable its use as a photoswitch in biological systems and describes strategies for using azobenzene photoswitches to drive functional changes in peptides, proteins, nucleic acids, lipids, and carbohydrates (192 references).

- Walking molecules
Delius, M.; Leigh, D. A. *Chem. Soc. Rev.*, **2011**, *40*, 3656-3676.

Abstract:



Movement is intrinsic to life. Biologists have established that most forms of directed nanoscopic, microscopic and, ultimately, macroscopic movements are powered by molecular motors from the dynein, myosin and kinesin superfamilies. These motor proteins literally walk, step by step, along polymeric filaments, carrying out essential tasks such as organelle transport. In the last few years biological molecular walkers have inspired the development of artificial systems that mimic aspects of their dynamics. Several DNA-based molecular walkers have been synthesised and shown to walk directionally along a track upon sequential addition of appropriate chemical fuels. In other studies, autonomous operation—*i.e.* DNA-walker migration that continues as long as a complex DNA fuel is present—has been demonstrated and sophisticated tasks performed, such as moving gold nanoparticles from place-to-place and assistance in sequential chemical synthesis. Small-molecule systems, an order of magnitude smaller in each dimension and 1000× smaller in molecular weight than biological motor proteins or the walker systems constructed from DNA, have also been designed and operated such that molecular fragments can be progressively transported directionally along short molecular tracks. The small-molecule systems can be powered by light or chemical fuels. In this *critical review* the biological motor proteins from the kinesin, myosin and dynein families are analysed as systems from which the designers of synthetic systems can learn, ratchet concepts for transporting Brownian substrates are discussed as the mechanisms by which molecular motors need to operate, and the progress made with synthetic DNA and small-molecule walker systems reviewed (142 references).