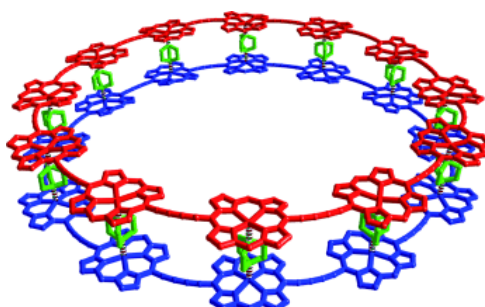


- All-or-Nothing Cooperative Self-Assembly of an Annulene Sandwich

Sprafke, J. K.; Odell, B.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 5572–5575.

Abstract:

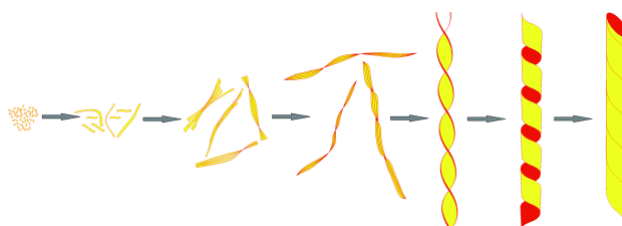


**Ring-fenced:** A 14-component assembly is formed by coordinating 1,4-diazabicyclo[2.2.2]octane (DABCO) to a [12]porphyrin nanoring. The 24 zinc–nitrogen interactions in this sandwich complex lock each conjugated macrocycle into a planar conformation, dramatically sharpening the near-IR absorption band. This result highlights the scope of double-strand formation as a way of creating nano-objects with well-defined shapes.

- Direct Observation of Time-Resolved Polymorphic States in the Self-Assembly of End-Capped Heptapeptides

Adamcik, J.; Castelletto, V.; Bolisetty, S.; Hamley, I. W.; Mezzenga, R. *Angew. Chem. Int. Ed.* **2011**, *50*, 5495–5498.

Abstract:

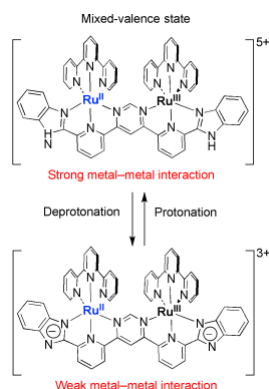


**Fibrillation processes in peptides:** Structural states in the time-dependent self-assembly of an amyloid heptapeptide were resolved by single-molecule atomic force microscopy. Statistical analysis of the structures and their topological details revealed a continuous evolution of the polymorphs over time from the initial small spherical micelles into protofilaments, helical ribbons, and finally nanotube-like structures (see picture).

- Proton-Induced Tuning of Metal–Metal Communication in Rack-Type Dinuclear Ru Complexes Containing Benzimidazolyl Moieties

Kobayashi, K.; Ishikubo, M.; Kanaizuka, K.; Kosuge, K.; Masaoka, S.; Sakai, K.; Nozaki, K.; Haga, M. *Chem. Eur. J.* **2011**, *17*, 6954–6963.

Abstract:

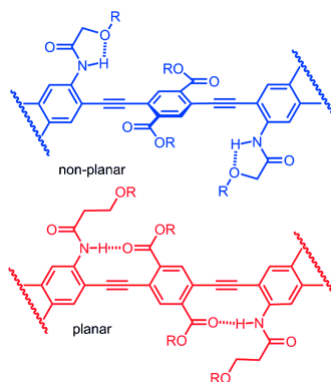


Ru complexes bearing a bis-tridentate benzimidazolyl ligand have been synthesized. The dinuclear ones act as a dibasic acid with  $pK_{a1}=4.36$  and  $pK_{a2}=5.90$ . The protonated form of the dinuclear complex exhibited two one-electron oxidations at +0.91 and +1.02 V versus the ferrocenium/ferrocene (Fc/Fc<sup>+</sup>) couple (the potential difference ( $\Delta E$ )=0.11 V), but the deprotonated form showed two waves at +0.50 and +0.58 V versus Fc/Fc<sup>+</sup> ( $\Delta E=0.08$  V). Since the potential difference between two waves reflects the strength of the metal–metal interaction, the deprotonation of the benzimidazole moieties in the complexes weakened the Ru–Ru communication. The degree of electronic coupling between two metal centers, estimated from the intervalence charge transfer (IVCT) band, was greater for the protonated form. DFT calculations for the protonated and deprotonated forms of the dinuclear complex suggest that the Ru<sup>II</sup>–L(H<sub>2</sub>)  $\pi^*$  interaction plays a key role in the Ru–Ru interaction.

- Oligo(*p*-phenylene-ethynylene)s with Backbone Conformation Controlled by Competitive Intramolecular Hydrogen Bonds

Hu, W.; Yan, Q.; Zhao, D. *Chem. Eur. J.* **2011**, *17*, 7087–7094.

Abstract:

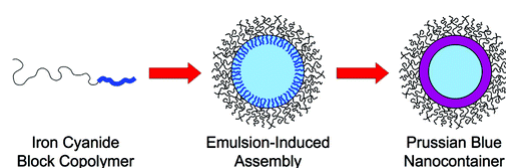


A series of conjugated oligo(*p*-phenylene-ethynylene) (OPE) molecules with backbone conformations (that is, the relative orientations of the contained phenylene units) controlled by competitive intramolecular hydrogen bonds to be either co-planar or random were synthesised and studied. In these oligomers, carboxylate and amido substituents were attached to alternate phenylene units in the OPE backbone. These functional groups were able to form intramolecular hydrogen bonds between neighbouring phenylene units. Thereby, all phenylene units in the backbone were confined in a co-planar conformation. This planarised structure featured a more extended effective conjugation length than that of regular OPEs with phenylene units adopting random orientation due to a low rotational-energy barrier. However, if a tri(ethylene glycol) (Tg) side chain was appended to the amido group, it enabled another type of intramolecular hydrogen bond, formed by the Tg chain

folding back and the contained ether oxygen atom competing with the ester carbonyl group as the hydrogen-bond acceptor. The outcome of this competition was proven to depend on the length of the alkylene linker joining the ether oxygen atom to the amido group. Specifically, if the Tg chain folded back to form a five-membered cyclic structure, this hydrogen-bonding motif was sufficiently robust to overrule the hydrogen bonds between adjacent phenylene units. Consequently, the oligomers assumed non-planar conformations. However, if the side chain formed a six-membered ring by hydrogen bonding with the amido NH group, such a motif was much less stable and yielded in the competition with the ester carbonyl group from the adjacent phenylene unit. Thus, the hydrogen bonds between the phenylene units remained, and the co-planar conformation was manifested. In our system, the hydrogen bonds formed by the back-folded Tg chain and amido NH group relied on a single oxygen atom as the hydrogen-bond acceptor. The additional oxygen atoms in the Tg chain made a negligible contribution. A bifurcated hydrogen-bond motif was unimportant. From our results, in combination with the results from an independent study by Meijer et al.,<sup>13</sup> it is evident that intramolecular hydrogen bonds involving back-folded oligo(ethylene glycol) moieties may differ in their structural details. Absorption spectroscopy served as a convenient yet sensitive technique for analysing hydrogen-bonding motifs in our study.

- Prussian Blue Nanocontainers: Selectively Permeable Hollow Metal–Organic Capsules from Block Ionomer Emulsion-Induced Assembly  
Roy, X.; Hui, J. K.-H.; Rabnawaz, M.; Liu, G.; MacLachlan, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 8420–8423.

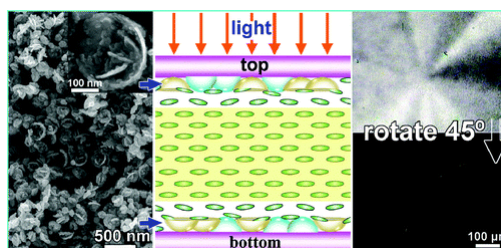
Abstract:



Hollow polymer-based particles are useful for the encapsulation, protection, and release of active compounds. Adding a metal–organic coordination framework shell to nanocontainers is an attractive goal because it should help control their stability and permeability while yielding new properties and functions. We have discovered that polymer capsules with a Prussian blue analogue inner shell can be synthesized by emulsion-induced assembly of a metal-containing amphiphilic block ionomer. The capsules are selectively permeable and were used as nanocontainers to encapsulate and release a model compound. Further, these nanomaterials are tunable in size and organize into 2-D close-packed arrays in the solid state. Potential applications for these materials include the encapsulation and nanopatterning of pharmaceutical, biological, and catalytic compounds.

- Synthesis of Nickel Bowl-like Nanoparticles and Their Doping for Inducing Planar Alignment of a Nematic Liquid Crystal  
Zhou, W.; Lin, L.; Zhao, D.; Guo, L. *J. Am. Chem. Soc.* **2011**, *133*, 8389–8391.

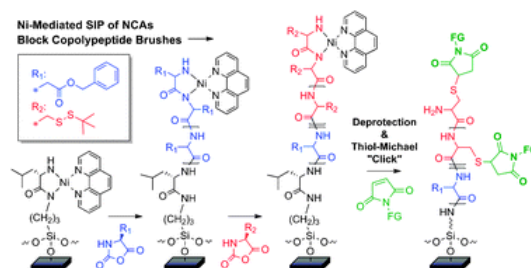
Abstract:



Nickel bowl-like nanoparticles have first been synthesized by a magnetic self-assembly process stabilized by polyvinyl pyrrolidone (PVP) without any sphere-like materials as templates. A trace of doped bowls can induce liquid crystal (LC) molecules into a perfect planar alignment, attributable to their bowl-like shape and magnetic self-assembly into a 1D structure. It would provide a novel method of establishing LCs alignment by doping special nanostructured materials.

- Synthesis of thiol-clickable and block copolypeptide brushes *via* nickel-mediated surface initiated polymerization of  $\alpha$ -amino acid *N*-carboxyanhydrides (NCAs)  
Sparks, B. J.; Ray, J. G.; Savin, D. A.; Stafford, C. M.; Patton, D. L. *Chem. Commun.* **2011**, 47, 6245-6247.

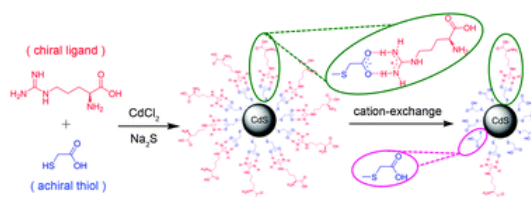
Abstract:



Homo-, block, and clickable copolypeptide brushes were synthesized using nickel-mediated surface-initiated polymerization of  $\alpha$ -amino *N*-carboxyanhydrides from low surface area substrates.

- Alternative chiral thiols for preparation of chiral CdS quantum dots covered immediately by achiral thiols  
Zhou, R.; Wei, K.-Y.; Zhao, J.-S.; Jiang, Y.-B. *Chem. Commun.* **2011**, 47, 6362-6364.

Abstract:



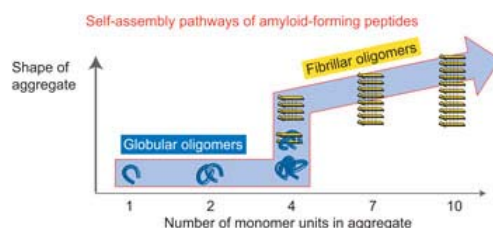
Developing of alternative chiral thiol stabilizers was proposed and successfully applied to an efficient preparation of chiral CdS quantum dots (QDs).

- Ion mobility–mass spectrometry reveals a conformational conversion from random assembly to  $\beta$ -sheet in amyloid fibril formation

Bleiholder, C.; Dupuis, N. F.; Wyttenbach, T.; Bowers, M. T. *Nature Chem.* **2011**, *3*, 172-177.

Abstract:

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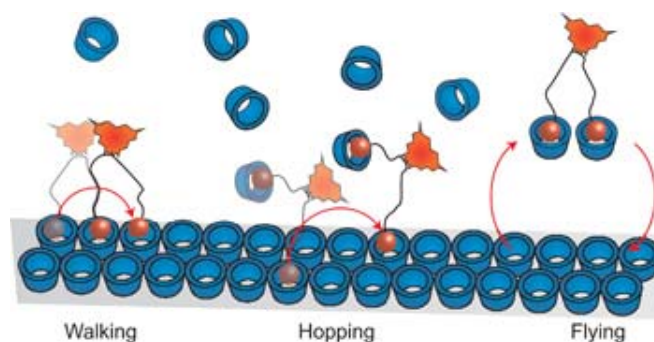


Amyloid cascades that lead to peptide  $\beta$ -sheet fibrils and plaques are central to many important diseases. Recently, intermediate assemblies of these cascades were identified as the toxic agents that interact with cellular machinery. The location and cause of the transformation from a natively unstructured assembly to the  $\beta$ -sheet oligomers found in all fibrils is important in understanding disease onset and the development of therapeutic agents. Largely, research on this early oligomeric region was unsuccessful because all the traditional techniques measure only the average oligomer properties of the ensemble. We utilized ion-mobility methods to deduce the peptide self-assembly mechanism and examined a series of amyloid-forming peptides clipped from larger peptides or proteins associated with disease. We provide unambiguous evidence for structural transitions in each of these fibril-forming peptide systems and establish the potential of this method for the development of therapeutic agents and drug evaluation.

- Gradient-driven motion of multivalent ligand molecules along a surface functionalized with multiple receptors

Perl, A.; Gomez-Casado, A.; Thompson, D.; Dam, H. H.; Jonkheijm, P.; Reinhoudt, D. N.; Huskens, J. *Nature Chem.* **2011**, *3*, 317-322.

Abstract:

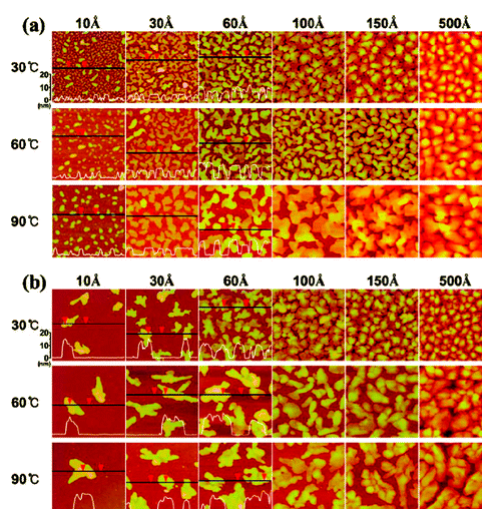


The kinetics of multivalent (multisite) interactions at interfaces is poorly understood, despite its fundamental importance for molecular or biomolecular motion and molecular recognition events at biological interfaces. Here, we use fluorescence microscopy to monitor the spreading of mono-, di- and trivalent ligand molecules on a receptor-functionalized surface, and perform multiscale computer simulations to understand the surface diffusion mechanisms. Analogous to chemotaxis, we found that the spreading is directional (along a developing gradient of vacant receptor sites) and is strongly dependent on ligand valency and concentration of a competing monovalent receptor in solution. We identify multiple surface diffusion mechanisms, which we call walking, hopping and flying. The study shows that the interfacial behaviour of multivalent systems is much more complex than that of monovalent ones.

- Experimental Techniques for the Fabrication and Characterization of Organic Thin Films for Field-Effect Transistors

Wen, Y.; Liu, Y.; Guo, Y.; Yu, G.; Hu, W. *Chem. Rev.* **2011**, *111*, 3358–3406.

Abstract:



As a result of the continuous drive to fabricate electronic devices on lightweight, large-area plastic substrates by low-cost processing techniques, organic electronics is currently running in the fast lane. Following this trend, organic thin-film transistors (OTFTs) have developed rapidly over the past decade due to their promise as components in cheap and flexible electronic circuits. Many potential applications have been demonstrated, ranging from flexible displays and sensor systems to radio frequency identification (RF-ID) tags, and some of these systems are now getting excitingly close to the commercial world. There have been two motivations for the surge in OTFT research and development in the past 5–10 years. The first is the need to manufacture products at very low cost. The manufacture of commercial liquid crystal displays (LCDs) has moved through a series of technology generations, defined by the increasing size of the substrate, which gives rise to considerable challenges. On the one hand, conventional integrated circuits for large-area LCDs are currently patterned by photolithographic processes, and the manufacturing costs associated with this technique increase rapidly with this increase in size. On the other hand, amorphous silicon (a-Si) thin-film transistors (TFTs) are now capturing a large fraction of the market as backplane circuits for active matrix liquid crystal displays. Fabrication of films of this material becomes both very challenging technically and also costly for such large size displays. The unique properties of organic materials have opened the door to a suite of fabrication techniques that can simplify the equipment and reduce the processing complexity required to meet the demands of large-scale LCDs. Another motivation is flexible or stretchable electronics. Organic electronic devices or circuits fabricated on lightweight, bendable plastic substrates have great potential for applications in electronic displays, electronic smart cards, or biomedical systems that are not easily achieved by conventional inorganic electronics. Organic TFTs and electronic circuits deposited by printing-like techniques can be expected to meet the new needs of the next generation of large area flexible backplanes.

Progress in OTFTs has been driven by advances in experimental techniques, material synthesis, and theoretical calculations, and new improved experimental techniques are playing an increasingly important role in this expansion. We believe that the next rapid advance will come if low-cost, large-area printing-like manufacturing techniques become sufficiently mature for successful commercial-scale production. Many innovative techniques have been developed for fabrication of OTFTs, but no

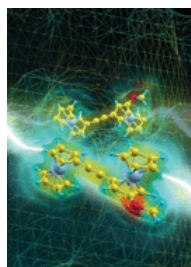


one technique has been found to be clearly superior in a manufacturing environment. In fact, every technique has its advantages and disadvantages, and therefore it is necessary to have a comprehensive understanding of these experimental techniques in order to be able to exploit the various strengths of the different techniques. This review begins by describing the use of characterization techniques in OTFTs, including high-resolution microscopy techniques, various spectroscopic techniques, and other characterization methods. Next, we describe fabrication or processing techniques—ranging from patterning and printing techniques to deposition techniques—that have been successfully employed in the fabrication of the key components of organic devices. Finally, we conclude with some discussion of likely future trends and advances in such sophisticated experimental techniques for the fabrication and characterization of OTFTs.

- Molecular spintronics

Sanvito, S. *Chem. Soc. Rev.* **2011**, *40*, 3336–3355.

Abstract:

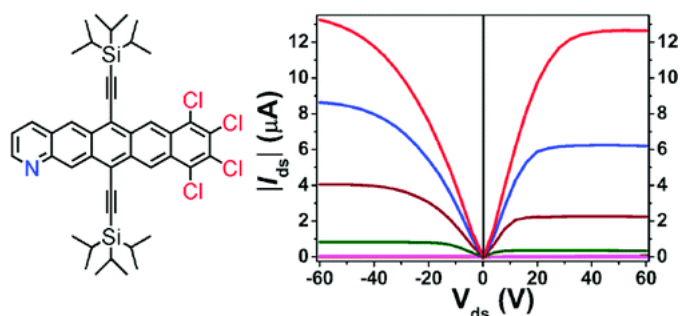


The electron spin made its debut in the device world only two decades ago but today our ability of detecting the spin state of a moving electron underpins the entire magnetic data storage industry. This technological revolution has been driven by a constant improvement in our understanding on how spins can be injected, manipulated and detected in the solid state, a field which is collectively named *Spintronics*. Recently a number of pioneering experiments and theoretical works suggest that organic materials can offer similar and perhaps superior performances in making spin-devices than the more conventional inorganic metals and semiconductors. Furthermore they can pave the way for radically new device concepts. This is *Molecular Spintronics*, a blossoming research area aimed at exploring how the unique properties of the organic world can marry the requirements of spin-devices. Importantly, after a first phase, where most of the research was focussed on exporting the concepts of inorganic spintronics to organic materials, the field has moved to a more mature age, where the exploitation of the unique properties of molecules has begun to emerge. Molecular spintronics now collects a diverse and interdisciplinary community ranging from device physicists to synthetic chemists to surface scientists. In this *critical review*, I will survey this fascinating, rapidly evolving, field with a particular eye on new directions and opportunities. The main differences and challenges with respect to standard spintronics will be discussed and so will be the potential cross-fertilization with other fields (177 references).

- Synthesis of Tetrachloro-azapentacene as an Ambipolar Organic Semiconductor with High and Balanced Carrier Mobilities

Song, C. L.; Ma, C.-B.; Yang, F.; Zeng, W.-J.; Zhang, H.-L.; Gong, X. *Org. Lett.* **2011**, *13*, 2880–2883.

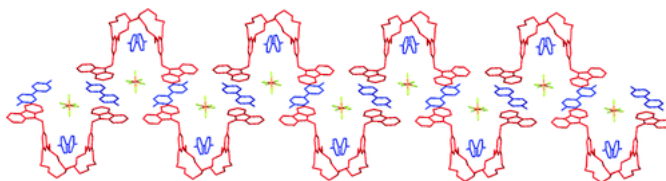
Abstract:



Two new azapentacene derivatives 9,10-dibromo-6,13-bis(triisopropylsilylethynyl)-1-azapentacene (**a**) and 8,9,10,11-tetrachloro-6,13-bis(triisopropylsilylethynyl)-1-azapentacene (**b**) were synthesized, and their FET properties were investigated. Compound **b** exhibits high and balanced ambipolar transport properties, with the hole and electron mobilities reaching up to  $0.12$  and  $0.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. This work suggests that chlorination to the *N*-heteropentacene framework is an efficient way for producing high performance ambipolar organic semiconductors.

- The First [2]Pseudorotaxane and the First Pseudocryptand-Type Poly[2]pseudorotaxane Based on Bis(*meta*-phenylene)-32-Crown-10 and Paraquat Derivatives  
Niu, Z.; Slobodnick, C.; Bonrad, K.; Huang, F.; Gibson, H. W. *Org. Lett.* **2011**, *13*, 2872–2875.

Abstract:



By the self-assembly of a bis(*meta*-phenylene)-32-crown-10 bearing two electron-donating groups (carbazoles) with electron-accepting paraquat derivatives, the first [2]pseudorotaxane and the first pseudocryptand-type poly[2]pseudorotaxane based on bis(*meta*-phenylene)-32-crown-10 were isolated as crystalline solids as shown by X-ray analyses.

- Nanoscale Assembly in Biological Systems: From Neuronal Cytoskeletal Proteins to Curvature Stabilizing Lipids  
Safinya, C. R.; Raviv, U.; Needleman, D. J.; Zidovska, A.; Choi, M. C.; Ojeda-Lopez, M. A.; Ewert, K. K.; Li, Y.; Miller, H. P.; Quispe, J.; Carragher, B.; Potter, C. S.; Kim, M. W.; Feinstein, S. C.; Wilson, L. *Adv. Mater.* **2011**, *23*, 2260-2270.

Abstract:



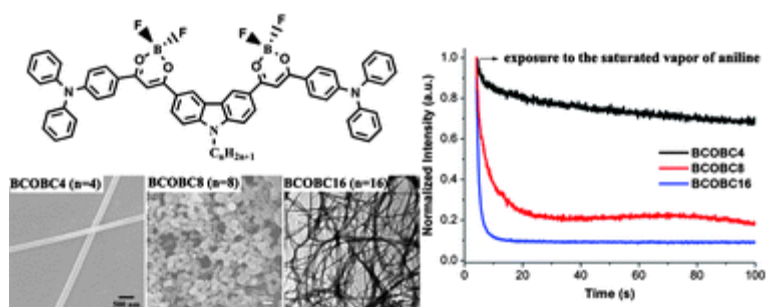


The review will describe experiments inspired by the rich variety of bundles and networks of interacting microtubules (MT), neurofilaments, and filamentous-actin in neurons where the nature of the interactions, structures, and structure-function correlations remain poorly understood. We describe how three-dimensional (3D) MT bundles and 2D MT bundles may assemble, in cell free systems in the presence of counter-ions, revealing structures not predicted by polyelectrolyte theories. Interestingly, experiments reveal that the neuronal protein tau, an abundant MT-associated-protein in axons, modulates the MT diameter providing insight for the control of geometric parameters in bio- nanotechnology. In another set of experiments we describe lipid-protein-nanotubes, and lipid nano- tubes and rods, resulting from membrane shape evolution processes involving protein templates and curvature stabilizing lipids. Similar membrane shape changes, occurring in cells for the purpose of specific functions, are induced by interactions between membranes and proteins. The biological materials systems described have applications in bio-nanotechnology.

- Low-dimensional nanostructures fabricated from bis(dioxaborine)carbazole derivatives as fluorescent chemosensors for detecting organic amine vapors

Liu, X.; Zhang, X.; Lu, R.; Xue, P.; Xu, D.; Zhou, H. *J. Mater. Chem.* **2011**, *21*, 8756-8765.

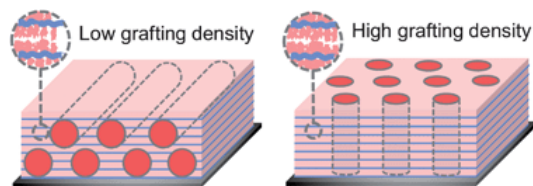
Abstract:



New triphenylamine functionalized bis(dioxaborine)carbazole derivatives (BDOBC<sub>n</sub>,  $n = 4, 8, 16$ ) have been synthesized, and low-dimensional nanostructures with different morphologies have been fabricated from BDOBC<sub>n</sub> with carbon chains of different lengths. For example, 1D single-crystalline nanowires are generated from BDOBC<sub>4</sub> via a reprecipitation approach, 1D nanofibers based on BDOBC<sub>16</sub> are prepared through an organogelation process, and amorphous nanoparticles are obtained from BDOBC<sub>8</sub>. It is interesting that the films formed from the obtained nanostructures can give strong fluorescence emission under irradiation and can act as fluorescent chemosensors for probing aniline vapors, with different response rates and different sensitivity controlled by their morphologies. The mesh-like film obtained from the BDOBC<sub>16</sub>-based gel exhibits faster fluorescent response in milliseconds and higher sensitivity than the nanoparticle- and nanowire-based films, because the supramolecular objects primarily formed in the gelling process percolate and fill the entire volume at a low-over all-volume fraction, and the entangled piling of the fibers leads to increased porosity. Thus, it not only provides a large surface for enhanced adsorption and accumulation of gaseous molecules but also enables expedient cross-film diffusion of gaseous species. Notably, the organogel fibers of BDOBC<sub>16</sub> allow high selectivity for probing aniline vapor, and the detection limit reaches 8.6 ppm.

- Microdomain control in block copolymer-based supramolecular thin films through varying the grafting density of additives

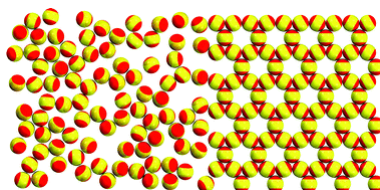
Lee, C.; Tung, S. *Soft Matter*, **2011**, *7*, 5660-5668.

Abstract:

It is well known that the supramolecular assembly of block copolymers with associated low-molecular-weight additives leads to rich phase behaviors in both bulk and thin films. In this study, we demonstrate that the supramolecular assembly is also an efficient approach to control the microdomain orientation in block copolymer thin films. We investigated the effect of the content of low-molecular-weight additives on the microdomain orientation in supramolecular thin films formed by poly(styrene)-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) with hydrogen-bonded 3-pentadecylphenol (PDP) and found that at low grafting density of PDP onto P4VP chains, the PS microdomains are parallel to the surface, while above a critical grafting density, the orientation is switched to be perpendicular. Such orientation transitions are observed for both cylindrical and lamellar structures, as confirmed by AFM, TEM and GISAXS. We propose that the microdomain orientation is governed by the combining effect of interfacial energy and the spatial distribution of additive molecules that varies with grafting density.

- Two dimensional assembly of triblock Janus particles into crystal phases in the two bond per patch limit

Romano, F.; Sciortino, F. *Soft Matter*, **2011**, *7*, 5799-5804.

Abstract:

In recent experimental work on spherical colloidal particles decorated with two hydrophobic poles separated by an electrically charged middle band (triblock Janus particles)—when particles are confined by gravity at the bottom of the sample holder—self-assembly into a Kagome two dimensional lattice has been documented [Qian Chen, Sung Chul Bae and Steve Granick, *Nature*, 2011, 469, 381]. Here, we assess the ability of a simple two-patch effective potential to reproduce the experimental findings. The model parameters are selected to match the experimental values, with a short-range attraction mimicking hydrophobic interactions and a patch width that allows for a maximum of two contacts per patch. We show that the effective potential is able to reproduce the observed crystallisation pathway in the Kagome structure. On the basis of free energy calculations, we also show that the Kagome lattice is stable at low temperature and low pressure, but that it transforms into a hexagonal lattice with alternating attractive and repulsive bands on increasing pressure.