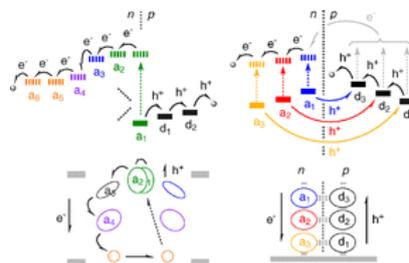


- Supramolecular n/p-heterojunction photosystems with oriented multicolored antiparallel redox gradients (OMARG-SHJs)

1

Bhosale, R.; Mířek, J.; Sakai, N.; Matile, S. *Chem. Soc. Rev.* **2010**, *39*, 138 – 149.

Abstract:

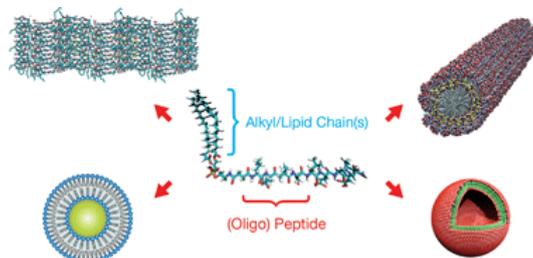


Directional electron and hole transport is essential in photosynthesis. Applied to molecular optoelectronics such as organic solar cells, these lessons from nature call for oriented supramolecular n/p-heterojunctions (SHJs) that contain various chromophores and antiparallel redox gradients (OMARGs). In this *tutorial review*, we summarize recent progress made toward the construction of OMARG-SHJs. This conceptually innovative twist added to a timely topic should appeal to the synthetic organic, supramolecular, biological, physical, analytical and materials chemist as well as to the expert in energy and environmental sciences.

- Amphiphilic peptides and their cross-disciplinary role as building blocks for nanoscience

Cavalli, S.; Albericio, F.; Kros, A. *Chem. Soc. Rev.* **2010**, *39*, 241 – 263.

Abstract:

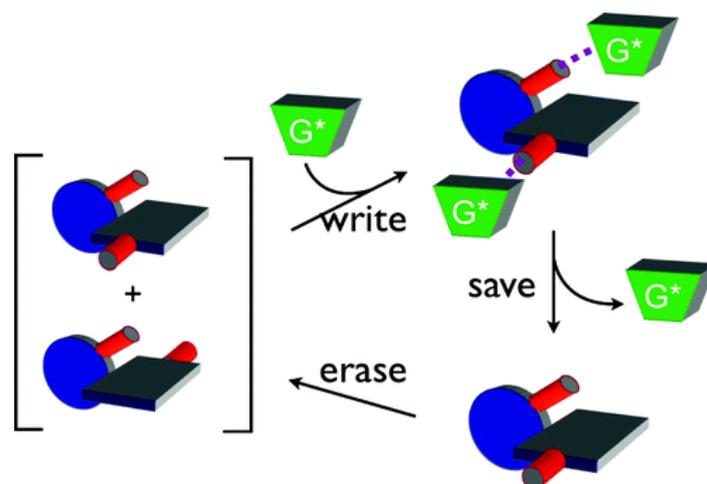


Peptides are particularly attractive as molecular building blocks in the bottom-up fabrication of supramolecular structures based on self-assembly and have potential in many important applications in the fields of biotechnology and bioengineering. In the first part of this *critical review* the main categories of peptide-based amphiphiles will be discussed by showing some relevant examples, which demonstrate the importance of amphiphilic peptides as molecular building blocks for nanostructures. In the second part of this review we will review the cross-disciplinary role of peptide-based supramolecular nanoarchitectures ranging from chemistry to biology, medicine, materials science, and engineering through discussing several examples of applied nanomaterials (216 references).

- A Small Molecule Diacid with Long-Term Chiral Memory

Raspberry, R. D.; Wu, X.; Bullock, B. N.; Smith, M. D.; Shimizu, K. D. *Org. Lett.* **2009**, *11*, 2599–2602.

Abstract :

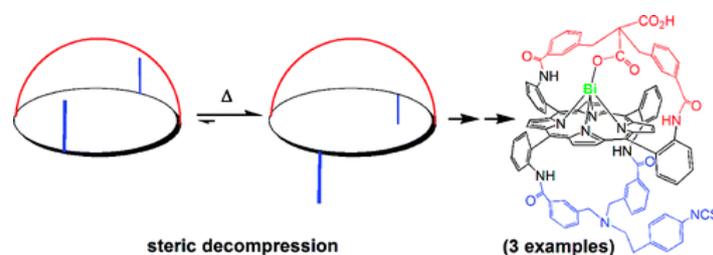


A small, axially chiral diacid was designed with chiral memory based on restricted rotation. Heating a racemic sample with a chiral alkaloid led to an enantiomeric excess of up to 40% ee. The guest-induced chirality was preserved on cooling to rt, which was maintained even in the absence of guest ($t_{1/2} = 14\text{y}$). The chiral enrichment process was also reversible, allowing the diacid to be used as a chiral switch.

- Steric Decompression of Picket-Strapped Porphyrins for the Synthesis of Side-Differentiated Chelates

Balieu, S.; Hijazi, I.; Motreff, N.; Lachaud, F.; Even-Hernandez, P.; Boitrel, B. *Org. Lett.* **2010**, *12*, 8–11.

Abstract:

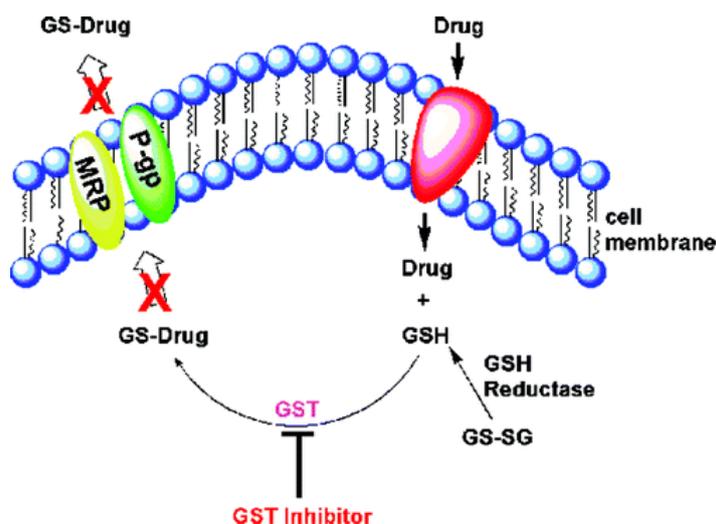


A general method to synthesize various $\alpha\beta\alpha\beta$ bis-strapped porphyrins, with a different functionalization on each side of the macrocycle, is described. The resulting new chelates may find applications as analogues of heme protein active sites, bifunctional chelates, or specific bis-chelating molecules with potential medical utility.

- Overcoming the Drug Resistance in Breast Cancer Cells by Rational Design of Efficient Glutathione S-Transferase Inhibitors

Li, W.-S.; Lam, W. S.; Liu, K.-C.; Wang, C.-H.; Chang, H. C.; Jen, Y. C.; Hsu, Y.-T.; Shivatare, S. S.; Jao, S.-C. *Org. Lett.* **2010**, *12*, 20–23.

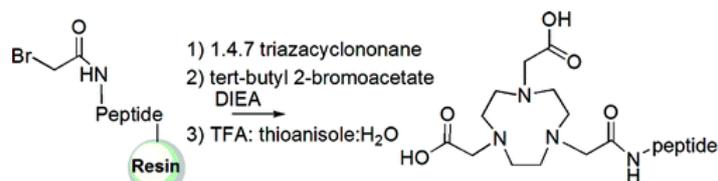
Abstract:



A new type of competitive human GST inhibitors has been developed via the bioisostere and structure activity profile strategies; we report their discovery, preparation, inhibitory activity, and synergetic effect in combination with chemotherapy drugs against breast cancer cells.

- Total Solid-Phase Synthesis of NOTA-Functionalized Peptides for PET Imaging
Guérin, B.; Ait-Mohand, S.; Tremblay, M.-C.; Dumulon-Perreault, V.; Fournier, P.; Bénéard, F.
Org. Lett. **2010**, *12*, 280–283.

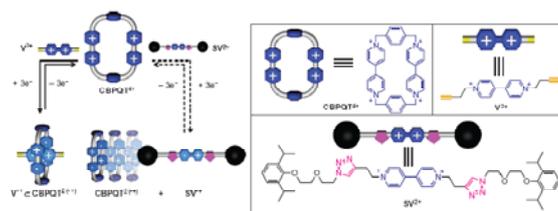
Abstract:



A convenient approach to functionalize peptides either at the N-terminal or on a lysine side chain with 1,4,7-triazacyclononane-*N,N',N''*-triacetic acid (NOTA) chelating unit has been developed on solid support. The chelate was assembled in a two-step process starting with bromo-acetylated peptides. Deprotection and cleavage of the resin-bound NOTA peptides were performed with use of trifluoroacetic acid (TFA) in the presence of thioanisole and water to give free NOTA peptides.

- Radically enhanced molecular recognition
Trabolsi, A.; Khashab, N.; Fahrenbach, A. C.; Friedman, D. C.; Colvin, M. T.; Cotí, K. K.; Benítez, D.; Tkatchouk, E.; Olsen, J.-C.; Belowich, M. E.; Carmielli, R.; Khatib, H. A.; Goddard, III, W. A.; Wasielewski, M. R.; Stoddart, J. F. *Nature Chemistry* **2009**, *2*, 42 – 49.

Abstract:



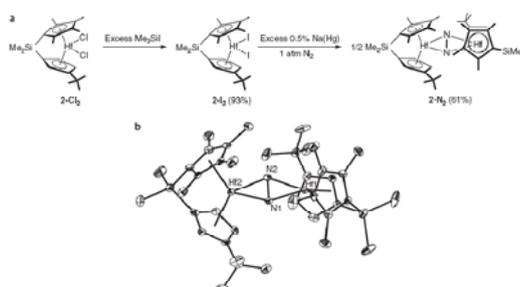
The tendency for viologen radical cations to dimerize has been harnessed to establish a recognition motif based on their ability to form extremely strong inclusion complexes with cyclobis(paraquat-p-phenylene) in its diradical dicationic redox state. This previously unreported complex involving three

bipyridinium cation radicals increases the versatility of host– guest chemistry, extending its practice beyond the traditional reliance on neutral and charged guests and hosts. In particular, transporting the concept of radical dimerization into the field of mechanically interlocked molecules introduces a higher level of control within molecular switches and machines. Herein, we report that bistable and tristable [2]rotaxanes can be switched by altering electrochemical potentials. In a tristable [2]rotaxane composed of a cyclobis(paraquat-p-phenylene) ring and a dumbbell with tetrathiafulvalene, dioxynaphthalene and bipyridinium recognition sites, the position of the ring can be switched. On oxidation, it moves from the tetrathiafulvalene to the dioxynaphthalene, and on reduction, to the bipyridinium radical cation, provided the ring is also reduced simultaneously to the diradical dication.

- Dinitrogen cleavage and functionalization by carbon monoxide promoted by a hafnium complex

Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. *Nature Chemistry* **2009**, 2, 30 – 35.

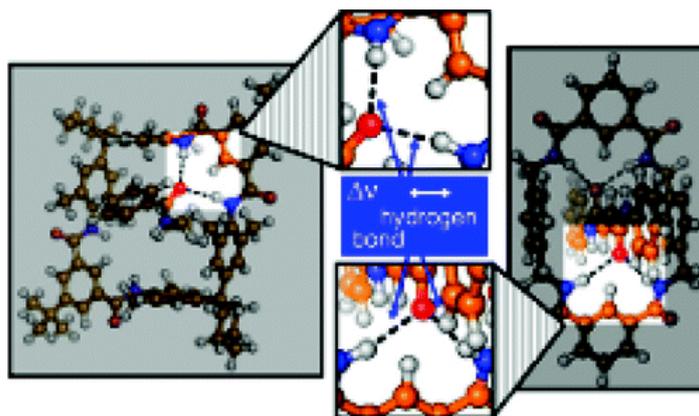
Abstract:



Molecular nitrogen (N_2) and carbon monoxide (CO) have the two strongest bonds in chemistry and present significant challenges in developing new transformations that exploit these two abundant feedstocks. At the core of this objective is the discovery of transition-metal compounds that promote the six-electron reductive cleavage of N_2 at ambient temperature and pressure and also promote new nitrogen–element bond formation. Here we show that an organometallic hafnium compound induces N_2 cleavage on the addition of CO, with a simultaneous assembly of new nitrogen–carbon and carbon–carbon bonds. Subsequent addition of a weak acid liberates oxamide, which demonstrates that an important agrochemical can be synthesized directly from N_2 and CO. These studies introduce an alternative paradigm for N_2 cleavage and functionalization in which the six-electron reductive cleavage is promoted by both the transition metal and the incoming ligand, CO, used for the new bond formations.

- Uncovering Individual Hydrogen Bonds in Rotaxanes by Frequency Shifts
Kirchner, B.; Spickermann, C.; Reckien, W.; Schalley, C. A.; *J. Am. Chem. Soc.* **2010**, 132, 484–494.

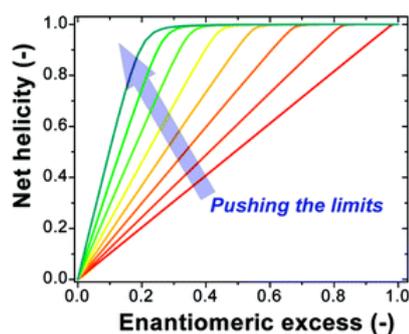
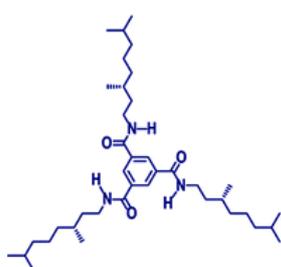
Abstract:



We present a theoretical investigation of amide pseudorotaxane IR spectra in the harmonic approximation. In particular, we focus on the effect of axle substitution on the hydrogen bonds that are formed between axle and wheel. Two types of pseudorotaxanes are studied: one with the substituent affecting mostly the axle's carbonyl group and one with the effect influencing primarily the amide NH group. Sizeable red shifts are predicted for the carbonyl stretching frequencies, and large red shifts for the NH stretching frequencies. For the wheel amide groups involved in hydrogen bonding merely with their NH hydrogens, a small shift is observed for the carbonyl stretch mode. A clear relation is observed between the NH stretch shifts and individual hydrogen bond energies. This is confirmed by correlations of the shared electron number with the NH stretch shift showing that this quantity can be taken as an indicator for individual hydrogen bond energies. Axle substitution influences the strengths of the individual hydrogen bonds which is again reflected in the NH stretch frequency shifts. A linear relationship of Hammett's substituent parameters with the NH frequency shifts can be established.

- Probing the Limits of the Majority-Rules Principle in a Dynamic Supramolecular Polymer
Smulders, M. M. J.; Stals, P. J. M.; Mes, T.; Paffen, T. F. E.; Schenning, A. P. H. J.; Palmans, A. R. A.; Meijer, E. W. *J. Am. Chem. Soc.* **2010**, *132*, 620-626.

Abstract:



By systematic variation of the chemical structure of benzene-1,3,5-tricarboxamide (BTA) derivatives, the effect of chemical structure on the amplification of chirality was studied and quantified. In combination with temperature-dependent amplification experiments, the limits of the majority-rules principle were also investigated. For all BTA derivatives a high, constant helix reversal penalty was determined, which is related to the intermolecular hydrogen bonds that are present in all studied derivatives. For asymmetrically substituted BTA derivatives an odd-even effect was found in the degree of chiral amplification when changing the position of the stereogenic center with respect to the amide functionality. It was found that the mismatch penalty could be directly related to the number of stereocenters present in the molecules. Increasing this number from one to three resulted

in an increase in this energy penalty while leaving the helix reversal penalty unaffected. For the majority-rules principle this implies that a single stereocenter present in the molecule contains sufficient chiral information at the molecular level to result in a chirally amplified state at the supramolecular level. Further evidence that the mismatch penalty is directly related to the number of stereocenters was obtained from mixed majority-rules experiments where two BTA derivatives with different numbers of stereocenters with opposite stereoconfiguration were studied in a majority-rules experiment. Finally, the ultimate limits of chiral amplification for the majority-rules principle were investigated, revealing that, given a certain helix reversal penalty, there is an optimum to which the mismatch penalty can be reduced while also enhancing the degree of chiral amplification. Temperature-dependent majority-rules experiments could indeed confirm these simulations. These findings show the relevance of both energy penalties when trying to enhance the degree of chiral amplification for the majority-rules principle in a one-dimensional helical supramolecular polymer.

- Dynamic Supramolecular Polymers Based on Benzene-1,3,5-tricarboxamides: The Influence of Amide Connectivity on Aggregate Stability and Amplification of Chirality
Stals, P. J. M.; Everts, J. C.; de Bruijn, R.; Filot, I. A. W.; Smulders, M. M. J.; Martín-Rapún, R.; Pidko, E. A.; De Greef, T. F. A.; Palmans, A. R. A.; Meijer, E. W. *Chem. Eur. J.* **2009**, *16*, 810-821.

Abstract:



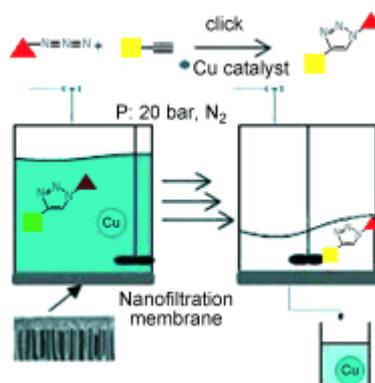
N-Centred benzene-1,3,5-tricarboxamides (N-BTAs) composed of chiral and achiral alkyl substituents were synthesised and their solid-state behaviour and self-assembly in dilute alkane solutions were investigated. A combination of differential scanning calorimetry (DSC), polarisation optical microscopy (POM) and X-ray diffraction revealed that the chiral N-BTA derivatives with branched 3,7-dimethyloctanoyl chains were liquid crystalline and the mesophase was assigned as Col_{ho} . In contrast, N-BTA derivatives with linear tetradecanoyl or octanoyl chains lacked a mesophase and were obtained as crystalline compounds. Variable-temperature infrared spectroscopy showed the presence of threefold, intermolecular hydrogen bonding between neighbouring molecules in the mesophase of the chiral N-BTAs. In the crystalline state at room temperature a more complicated packing between the molecules was observed. Ultraviolet and circular dichroism spectroscopy on dilute solutions of N-BTAs revealed a cooperative self-assembly behaviour of the N-BTA molecules

into supramolecular polymers with preferred helicity when chiral alkyl chains were present. Both the sergeants-and-soldiers as well as the majority-rules principles were operative in stacks of N-BTAs. In fact, the self-assembly of N-BTAs resembles closely that of their carbonyl (C=O)-centred counterparts, with the exception that aggregation is weaker and amplification of chirality is less pronounced. The differences in the self-assembly of N- and C=O-BTAs were analysed by density functional theory (DFT) calculations. These reveal a substantially lower interaction energy between the monomeric units in the supramolecular polymers of N-BTAs. The lower interaction energy is due to the higher energy penalty for rotation around the Ph-NH bond compared to the Ph-CO bond and the diminished magnitude of dipole-dipole interactions. Finally, we observed that mixed stacks are formed in dilute solution when mixing N-BTAs and C=O BTAs.

- Solvent-Resistant Nanofiltration for Product Purification and Catalyst Recovery in Click Chemistry Reactions

Cano-Odena, A.; Vandezande, P.; Fournier, D.; Van Camp, W.; Du Prez, F. E.; Vankelecom, I. F. *J. Chem. Eur. J.* **2009**, *16*, 1061-1067.

Abstract:

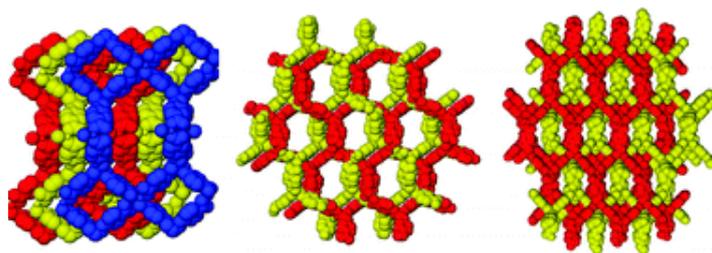


The quickly developing field of “click” chemistry would undoubtedly benefit from the availability of an easy and efficient technology for product purification to reduce the potential health risks associated with the presence of copper in the final product. Therefore, solvent-resistant nanofiltration (SRNF) membranes have been developed to selectively separate “clicked” polymers from the copper catalyst and solvent. By using these solvent-stable cross-linked polyimide membranes in diafiltration, up to 98% of the initially present copper could be removed through the membrane together with the DMF solvent, the polymer product being almost completely retained. This paper also presents the first SRNF application in which the catalyst permeates through the membrane and the reaction product is retained.

- Flexible metal–organic supramolecular isomers for gas séparation.

Kishan, M. R.; Tian, J.; Thallapally, P. K.; Fernandez, C. A.; Dalgarno, S. J.; Warren, J. E.; McGrail, B. P.; Atwood, J. L. *Chem. Commun.* **2010**, *46*, 538 – 540.

Abstract:

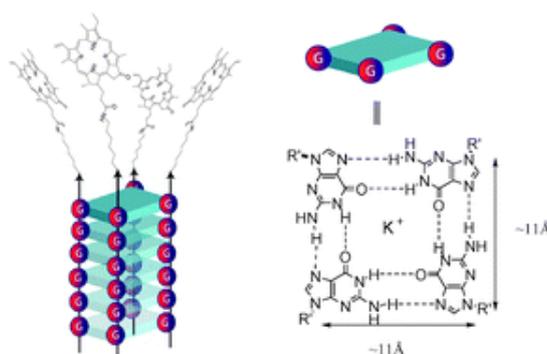


Three interpenetrated metal–organic supramolecular isomers were synthesised using a flexible tetrahedral organic linker and Zn_2 clusters that sorb CO_2 preferably over N_2 , H_2 and methane at room temperature.

- Ultrafast energy transfer within pyropheophorbide-a tethered to self-assembling DNA quadruplex

Cai, J.; Niedzwiedzki, D. M.; Frank, H. A.; Hamilton, A. D. *Chem. Commun.* **2010**, 46, 544 – 546.

Abstract:

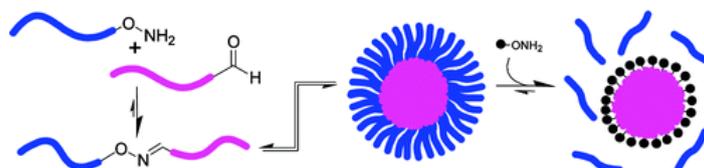


A DNA quadruplex system that exhibits ultrafast intramolecular energy transfer is discussed.

- Dynamic Covalent Diblock Copolymers Prepared from RAFT Generated Aldehyde and Alkoxyamine End-Functionalized Polymers

Jackson, A. W.; Fulton, D. A. *Macromolecules* **2010**, 43, 1069–1075.

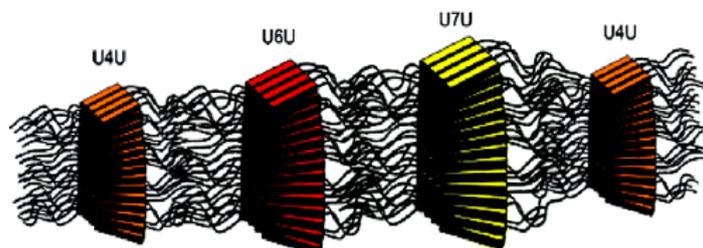
Abstract:



Aldehyde- or alkoxyamine-containing trithiocarbonate chain transfer agents were prepared and used to mediate the synthesis of a series of polymers end-functionalized with either aldehyde or alkoxyamines functions, utilizing reversible addition–fragmentation polymerization techniques. Aldehyde end-functionalized polymers were shown to link through reversible oxime bond formation with alkoxyamine end-functionalized polymers forming diblock copolymers. The dynamic nature of the oxime bond linking these polymer blocks together was demonstrated through a simple exchange reaction with a small molecule alkoxyamine. A diblock copolymer prepared from the self-assembly of an aldehyde end-functionalized polyisoprene with an alkoxyamine end-functionalized polystyrene was shown to undergo further hierarchical self-assembly into micellar aggregates in DMF. It was shown that the addition of an excess of a small molecule alkoxyamine triggered the disassembly of these micelles.

- Self-Sorting of Guests and Hard Blocks in Bisurea-Based Thermoplastic Elastomers
Botterhuis, N. E.; Karthikeyan, S.; Spiering, A. J. H.; Sijbesma, R. P. *Macromolecules* **2010**, *43*, 745–751.

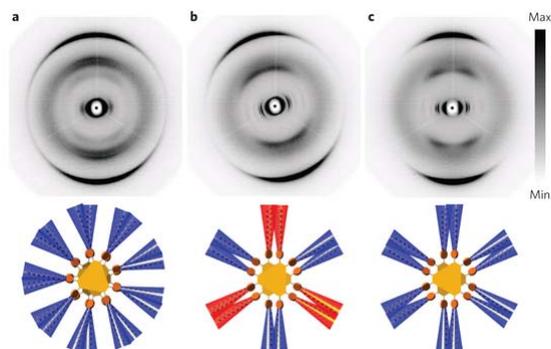
Abstract:



Self-sorting in thermoplastic elastomers was studied using bisurea-based thermoplastic elastomers (TPEs) which are known to form hard blocks via hierarchical aggregation of bisurea segments into ribbons and of ribbons into fibers. Self-sorting of different bisurea hard blocks in mixtures of polymers to give separate ribbons was established by studying exciplex formation between fluorescent pyrene and dimethylaniline (DMA) functionalized bisurea probes. If both probes had the same spacing between the bisurea units as the matrix hard segments, exciplex bands were observed in the fluorescence emission spectra, whereas exciplex intensities were strongly reduced when DMA and pyrene probes with different spacer lengths were incorporated in a mixed matrix that provided matching host segments for each guest separately. Probes with butylene spaced bisurea groups showed the highest degree of self-sorting. Self-sorting was further improved by annealing of the polymer films leading to a degree of self-sorting of more than 95%. Self-sorting at the fiber level of aggregation was studied by fluorescence resonance energy transfer (FRET) between naphthalene (donor) and pyrene (acceptor) bisurea guests. Large differences in FRET behavior for matching and nonmatching probes showed that significant self-sorting takes places between ribbons to give separate fibers.

- Towards high charge-carrier mobilities by rational design of the shape and periphery of discotics
Feng, X.; Marcon, V.; Pisula, W.; Hansen, M. R.; Kirkpatrick, J.; Grozema, F.; Andrienko, D.; Kremer, K. Müllen, K. *Nature Materials* **2009**, *8*, 421-426.

Abstract:



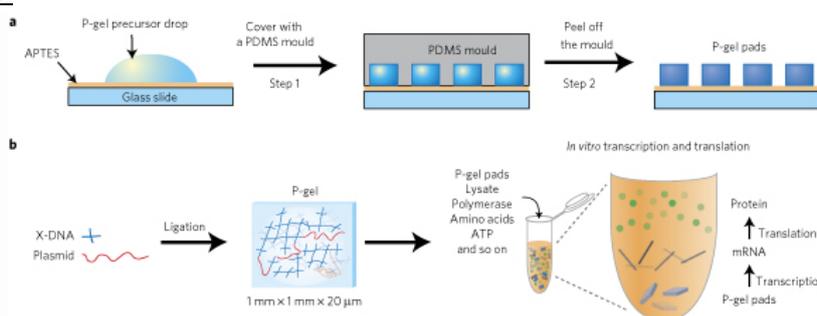
Discotic liquid crystals are a promising class of materials for molecular electronics thanks to their self-organization and charge transporting properties. The best discotics so far are built around the coronene unit and possess six-fold symmetry. In the discotic phase six-fold-symmetric molecules stack with an average twist of 30° , whereas the angle that would lead to the greatest electronic

coupling is 60° . Here, a molecule with three-fold symmetry and alternating hydrophilic/hydrophobic side chains is synthesized and X-ray scattering is used to prove the formation of the desired helical microstructure. Time-resolved microwave-conductivity measurements show that the material has indeed a very high mobility, $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The assemblies of molecules are simulated using molecular dynamics, confirming the model deduced from X-ray scattering. The simulated structures, together with quantum-chemical techniques, prove that mobility is still limited by structural defects and that a defect-free assembly could lead to mobilities in excess of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

- A cell-free protein-producing gel

Park, N.; Um, S. H.; Funabashi, H.; Xu, J.; Luo, D. *Nature Materials* **2009**, *8*, 432-437.

Abstract:



Proteins are important biomaterials and are generally produced in living cells. Here, we show a novel DNA hydrogel that is capable of producing functional proteins without any living cells. This protein-producing gel (termed 'the P-gel system' or 'P-gel') consists of genes as part of the gel scaffolding. This is the first time that a hydrogel has been used to produce proteins. The efficiency was about 300 times higher than current, solution-based systems. In terms of volumetric yield, the P-gel produced up to 5 mg ml^{-1} of functional proteins. The mechanisms behind the high efficiency and yield include improved gene stability, higher local concentration and a faster enzyme turnover rate due to a closer proximity of genes. We have tested a total of 16 different P-gels and have successfully produced all 16 proteins including membrane and toxic proteins, demonstrating that the P-gel system can serve as a general protein production technology.

- Multiresponsive Reversible Gels Based on Charge-Driven Assembly

Lemmers, M.; Sprakel, J.; Voets, I. K.; van der Gucht, J.; Cohen Stuart, M. A. *Angew. Chem. Int. Ed.* **2010**, *49*, 708–711.

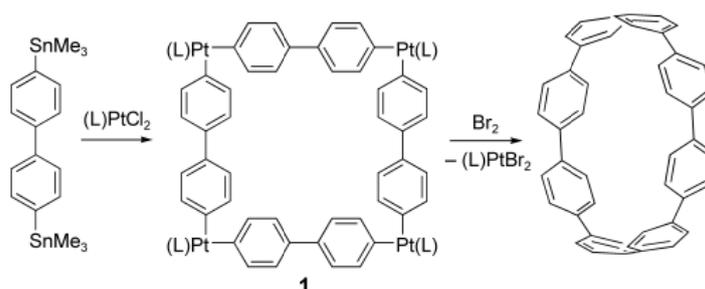
Abstract:



Linked in? Coassembly of an ABA triblock copolymer with charged end blocks and an oppositely charged polyelectrolyte yields gels that respond to changes in concentration, temperature, ionic strength, pH value, and charge composition. Above the critical gel concentration, the triblock copolymers bridge micelles, forming a sample-spanning transient network of interconnected micelles.

- Synthesis of [8]Cycloparaphenylene from a Square-Shaped Tetranuclear Platinum Complex Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 757–759.

Abstract:



Square goes to loop: A selective synthesis of [8]cycloparaphenylene under mild and neutral reaction conditions was achieved in a small number of steps and in a high yield through the square-shaped platinum biphenyl intermediate **1**. Compound **1** is the smallest cycloparaphenylene derivative synthesized to date.