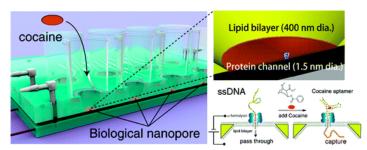
Rapid Detection of a Cocaine-Binding Aptamer Using Biological Nanopores on a Chip Kawano, R.; Osaki, T.; Sasaki, H.; Takinoue, M.; Yoshizawa, S.; Takeuchi, S. *J. Am. Chem. Soc.* 2011, 133, 8474-8477.

Abstract:

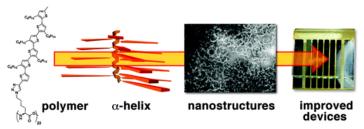


This paper describes a methodology for the rapid and highly selective detection of cocaine using a membrane protein channel combined with a DNA aptamer. The DNA aptamer recognizes the cocaine molecule with high selectivity. We successfully detected a low concentration of cocaine (300 ng/mL, the drug test cutoff limit) within 60 s using a biological nanopore embedded in a microchip.

ullet Hierarchical Self-Assembly of Semiconductor Functionalized Peptide lpha-Helices and Optoelectronic Properties

Kumar, R. J.; MacDonald, J. M.; Singh, T. B.; Waddington, L. J.; Holmes, A. B. *J. Am. Chem. Soc.* **2011**, *133*, 8564-8573.

Abstract:

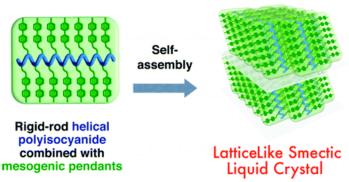


To determine the ability of semiconductors templated by α -helical polypeptides to form higher order structures and the charge carrier properties of the supramolecular assemblies, I-lysine was functionalized with a sexithiophene organic semiconductor unit via iterative Suzuki coupling and the click reaction. The resultant amino acid was incorporated into a homopolypeptide by ring-opening polymerization of an amino acid N-carboxyanhydride. Spectroscopic investigation of the polypeptide revealed that it adopted an α -helical secondary structure in organic solvents that underwent hierarchical self-assembly to form higher order structures. In cyclohexane, the polymer formed organogels at 2% (w/v). Organic photovoltaic and organic field effect transistor devices were fabricated by deposition of the PCBM blended active layer from chlorobenzene at concentrations shown to induce self-assembly of the polymer. Compared with control compounds, these devices showed significantly greater hole mobility, short circuit current, and efficiency. This work establishes the potential of this previously unreported bioinspired motif to increase device performance.

 Lattice like Smectic Liquid Crystal Phase in a Rigid-Rod Helical Polyisocyanide with Mesogenic Pendants

Kajitani, T.; Onouchi, H.; Sakurai, S.; Nagai, K.; Okoshi, K.; Onitsuka, K.; Yashima, E. *J. Am. Chem. Soc.* **2011**, *133*, 9156–9159.

Abstract:

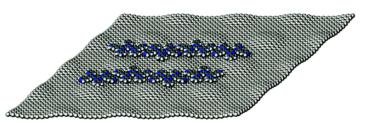


We report a unique macromolecule consisting of a rodlike helical polyisocyanide backbone with a narrow molecular weight distribution and rigid mesogenic chiral pendants linked via a flexible spacer that exhibits lyotropic nematic and latticelike new smectic (*lat-Sm*) liquid crystal phases at different concentrations. The unprecedented *lat-Sm* phase is associated with the smectic ordering of both the stiff polymer backbone and the rigid-rod side groups. A detailed investigation of the films using X-ray scattering and atomic force microscopy revealed a novel tilted smectic layer structure of the polymer backbone aligned perpendicular to the smectic layer of the mesogenic pendants, which arrange in an antiparallel overlapping interdigitated manner.

 Hierarchical Interactions and Their Influence upon the Adsorption of Organic Molecules on a Graphene Film

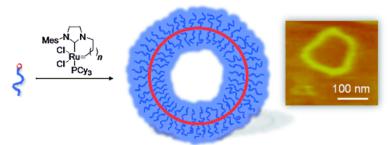
Roos, M.; Kùnzel, D.; Uhl, B.; Huang, H.; Alves, O. B.; Hoster, H. E.; Gross, A.; Jùrgen Behm; R. *J. Am. Chem. Soc.* **2011**, *133*, 9208–9211.

Abstract:



The competition between intermolecular interactions and lateral variations in the molecule—substrate interactions has been studied by scanning tunneling microscopy (STM), comparing the phase formation of (sub)monolayers of the organic molecule 2,4½-BTP on buckled graphene/Ru(0001) and Ag(111) oriented thin films on Ru(0001). On the Ag films, the molecules form a densely packed 2D structure, while on graphene/Ru(0001), only the areas between the maxima are populated. The findings are rationalized by a high corrugation in the adsorption potential for 2,4½-BTP molecules on graphene/Ru(0001). These findings are supported by temperature programmed desorption (TPD) experiments and theoretical results.

 Synthesis and Direct Imaging of Ultrahigh Molecular Weight Cyclic Brush Polymers Xia, Y.; Boydston, A. J.; Grubbs, R. H. Angew. Chem. Int. Ed. 2011, 50, 5882–5885.
 Abstract:



Convenient route to cyclic polymers: Ultrahigh molecular weight cyclic brush polymers were synthesized through ring-expansion metathesis polymerization of various macromonomers. Atomic force microscopy was used to visualize toroidal shapes and large opening pores, along with linear chains, which may result from high sensitivity of brush polymers to mechanical degradation.

A Triple Anion Helicate Assembled from a Bis(biurea) Ligand and Phosphate Ions
 Li, S.; Jia, C.; Wu, B.; Luo, Q.; Huang, X.; Yang, Z.; Li, Q.-S.; Yang, X.-J. Angew. Chem. Int. Ed.
 2011, 50, 5721–5724.

Abstract:



A word in urea: A strategy of mimicking the scaffold and metal coordination behavior of oligo-2,2′-bipyridine ligands was used to obtain a triple anion helicate from a bis(biurea) receptor and phosphate ions. The successful assembly of the triple helical structure provides guidelines for the design of new anion ligands by taking advantage of the similarities of metal and anion coordination.

Triphenylene-Fused Porphyrins
 Jiang, L.; Engle, J. T.; Sirk, L.; Hartley, C. S.; Ziegler, C. J.; Wang, H. Org. Lett. 2011, 13, 3020–3023.

Abstract:

Triphenylene has been successfully fused to the porphyrin periphery through a convenient oxidative ring-closure reaction. Bistriphenylene-fused porphyrins and a dibenzo[fg,op]tetracene-fused porphyrin have also been obtained using a similar approach. These π -extended porphyrins exhibited broadened and bathochromic shifted UV–vis absorptions.

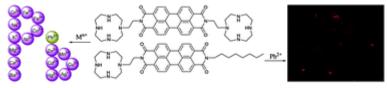
 Water-Soluble Phosphonate-Substituted BODIPY Derivatives with Tunable Emission Channels Bura, T.; Ziessel, R. Org. Lett. 2011, 13, 3072–3075.
 Abstract:



Water-soluble BODIPY dyes have been readily obtained by introduction of phosphonate fragments either on the boron for the green and yellow emitting dyes or on the side chain for the red emitting dyes. Hydrolysis of the phosphonate is realized at the end of the reaction sequence and allows isolation of the targets by precipitation. All these novel dyes are soluble and fluorescent in water with quantum yields in the 23–59% range and emission wavelength spanning from 667 to 509 nm.

• Cyclen-functionalized perylenebisimides as sensitive and selective fluorescent sensors for Pb²⁺ in aqueous solution

Zhou, R.; Li, B.; Wu, N.; Gao, G.; You, J.; Lan, J. *Chem. Commun.* **2011**, *47*, 6668-6670. Abstract:

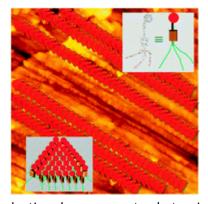


Cyclen-functionalized perylenediimides PBI-1 and PBI-2 were first synthesized as highly sensitive and selective fluorescent chemosensors for Pb²⁺ in aqueous solution. PBI-2 shows a better selectivity for Pb²⁺ in the presence of other metal ions and, importantly, it can successfully enter the cell and be applied in imaging of living cells.

 Large scale assembly of ordered donor—acceptor heterojunction molecular wires using the Langmuir—Blodgett technique

Charvet, R.; Ariga, K.; Hill, J. P.; Ji, Q.; Khan, A. H.; Acharya, S. *Chem. Commun.* **2011**, *47*, 6825-6827.

Abstract:



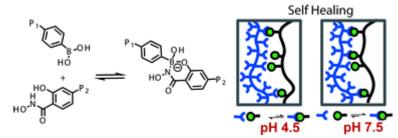
Unidirectionally aligned photoconductive donor–acceptor heterojunction molecular wires spanning over fifty square microns are fabricated using the Langmuir–Blodgett technique.

5

 Unequal stoichiometry between crosslinking moieties affects the properties of transient networks formed by dynamic covalent crosslinks

Jay, J.; Langheinrich, K.; Hanson, M.; Mahalingam, A.; Kiser, P. Soft Matter 2011, 7, 5826-5835.

Abstract:



A pH responsive system capable of forming a self-healing transient network across the pH 4.5 to 7.5 range is developed by increasing the ratio of phenylboronic acid (PBA) moieties to salicylhydroxamic acid (SHA) moieties incorporated in poly[N-2-hydroxypropyl]methacrylamide polymer backbones. We used particle tracking to assess network formation across the pH range of 4.5 to 7.5 with PBA: SHA stoichiometry of reactive groups of 1:1,5:1 and 10:1. The 10:1 ratio of PBA: SHA forms a transient network across the entire pH range, while the 1:1 PBA: SHA materials demonstrate more liquid like behavior at pH 4.5 and forms a transient network only at neutral pH. At pH 7.5 increasing the ratio of PBA to SHA from 1:1 to either 5:1 or 10:1 increases the Giplateau sixty-fold, indicating that the higher probability of crosslink formation impacts the density of crosslinks compared to a 1:1 ratio of PBA to SHA. Above pH 5.5 the 5:1 and 10:1 PBA: SHA gels behaved similarly. Over the temperature range of 10 to 55 °C, the unequal stoichiometric ratios of 10: 1 and 5 : 1 PBA: SHA transient networks behave similarly, with G' plateau dropping with a corresponding decrease in the characteristic relaxation time. Master curve analysis demonstrates superposition of the 1:1,5:1 and 10:1 PBA: SHA stoichiometry except under the weakest network conditions (low pH, high temperature) suggesting that the same crosslinking mechanism dominates the network behaviour. The simple and complex viscosity is compared as a function of pH with shear thickening behaviour observed below pH 5.5. The 10:1 PBA: SHA crosslinked-network displays self-healing properties after repeated break cycles at both pH 4.5 and pH 7.5 demonstrating that increasing the ratio of PBA to SHA provides a material that can form a self-healing transient network at low pH, where the PBA-SHA crosslink association is weak, to neutral pH where the PBA-SHA complex is stabilized.

 Reversible adhesive-free nanoscale adhesion utilizing oppositely charged polyelectrolyte brushes

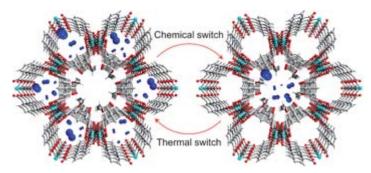
Kobayashi, M.; Terada, M.; Takahara, A. *Soft Matter* **2011**, *7*, 5717-5722. Abstract:



Reversible Nanoscale Adhesion

Two prepared silicon wafers bearing cationic and anionic polyelectrolyte brushes were joined with 2 μL of water under 0.098 MPa of pressure at room temperature. The bonded area was fixed at 5×10 mm2. A lap shear strength of 1.52 MPa was achieved through the adhesion of poly[2-(methacryloyloxy)ethyl trimethylammonium chloride] and poly(3-sulfopropyl methacrylate potassium salt) brush substrates due to electrostatic attractive interactions between the positively and negatively charged polymers. In contrast, the lap shear strength of bonded polymer brushes with like charges was only 0.027–0.072 MPa. The polyelectrolyte brushes remained on the substrates even after their separation in the lap shear test; and the brush substrates readhered in the presence of a small amount of water. Furthermore, the adhering substrates were smoothly debonded in aqueous NaCl solution due to the electrostatic interaction of the hydrated salt ions. However, the substrates did not separate in deionized water. In summary, reversible nanoscale adhesion was achieved using oppositely charged polyelectrolyte brushes combined with aqueous solution.

Protecting group and switchable pore-discriminating adsorption properties of a hydrophilic-hydrophobic metal—organic framework
 Infas M.; Mohideen, H.; Xiao, B.; Wheatley, P. S.; McKinlay, A. C.; Li, Y.; Slawin, A. M. Z.; Aldous, D. W.; Cessford, N. F.; Düren, T.; Zhao, X.; Gill, R.; Thomas, K. M.; Griffin, J. M.; Ashbrook, S. E.; Morris, R. E. *Nature Chemistry* 2011, 3, 304-310.
 Abstract:

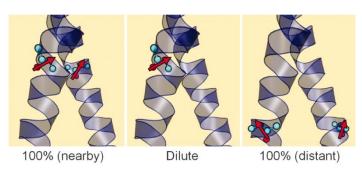


Formed by linking metals or metal clusters through organic linkers, metal—organic frameworks are a class of solids with structural and chemical properties that mark them out as candidates for many emerging gas storage, separation, catalysis and biomedical applications. Important features of these materials include their high porosity and their flexibility in response to chemical or physical stimuli. Here, a copper-based metal—organic framework has been prepared in which the starting linker (benzene-1,3,5-tricarboxylic acid) undergoes selective monoesterification during synthesis to produce a solid with two different channel systems, lined by hydrophilic and hydrophobic surfaces, respectively. The material reacts differently to gases or vapours of dissimilar chemistry, some stimulating subtle framework flexibility or showing kinetic adsorption effects. Adsorption can be

switched between the two channels by judicious choice of the conditions. The monoesterified linker is recoverable in quantitative yield, demonstrating possible uses of metal–organic frameworks in molecular synthetic chemistry as 'protecting groups' to accomplish selective transformations that are difficult using standard chemistry techniques.

Residue-Specific Vibrational Echoes Yield 3D Structures of a Transmembrane Helix Dimer
 Remorino, A.; Korendovych, I. V.; Wu, Y.; DeGrado, W. F.; Hochstrasser, R. M. Science 2011, 332, 1206-1209.

Abstract:

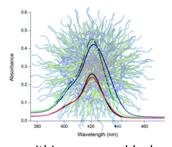


Two-dimensional (2D) vibrational echo spectroscopy has previously been applied to structural determination of small peptides. Here we extend the technique to a more complex, biologically important system: the homodimeric transmembrane dimer from the α chain of the integrin $\alpha_{\text{IIb}}\beta_3$. We prepared micelle suspensions of the pair of 30-residue chains that span the membrane in the native structure, with varying levels of heavy ($^{13}C=^{18}O$) isotopes substituted in the backbone of the central 10th through 20th positions. The constraints derived from vibrational coupling of the precisely spaced heavy residues led to determination of an optimized structure from a range of model candidates: Glycine residues at the 12th, 15th, and 16th positions form a tertiary contact in parallel right-handed helix dimers with crossing angles of $-58^{\circ} \pm 9^{\circ}$ and interhelical distances of 7.7 \pm 0.5 angstroms. The frequency correlation established the dynamical model used in the analysis, and it indicated the absence of mobile water associated with labeled residues. Delocalization of vibrational excitations between the helices was also quantitatively established.

 Porphyrin-crosslinked block copolymer assemblies as photophysically-active nanoscopic devices

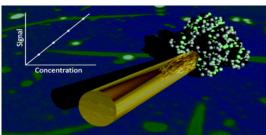
Sorrells, J. L.; Shrestha, R.; Neumann, W. L.; Wooley, K. L. *J. Mater. Chem.* **2011**, *21*, 8983-8986.

Abstract:



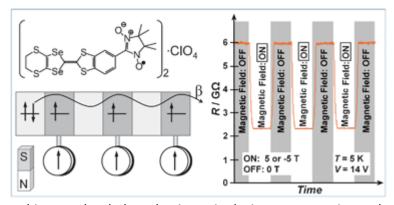
Inclusion of porphyrins as crosslinkers within aqueous block copolymer assemblies imparts water solubility to the hydrophobic macrocycle, provides critical structural information about the particle interior, gives unique pH-independent photophysical properties, and has the potential for future development of SOD mimics.

Biosensors based on one-dimensional nanostructures
 Feigel, I. M.; Vedala, H.; Star, A. J. Mater. Chem. 2011, 21, 8940-8954.
 Abstract:



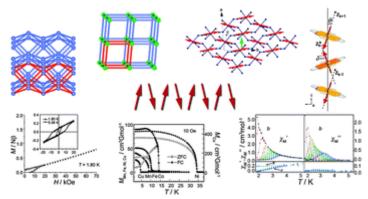
Over the past decade, one-dimensional nanostructures (1D-NS) have been studied for the detection of biological molecules. These nanometre-scale materials, with diameters comparable to the size of individual biomolecules, offer the advantage of high sensitivity. In this feature article we discuss different techniques of biosensing using 1D-NS, namely electrical, electrochemical, optical, and mechanical methods, with a focus on the advancement of these techniques. Advantages and disadvantages of various synthesis and functionalization methods of 1D-NS, as well as biosensor device fabrication procedures are discussed. The main focus of this review is to demonstrate the progress of protein and DNA sensors based on 1D-NS over the past decade, and in addition we present an outlook for the future of this technology.

 Interplay between magnetism and conductivity derived from spin-polarized donor radicals Sugawara, T.; Komatsu, H.; Suzuki, K. Chem. Soc. Rev. 2011, 40, 3105–3118.
 Abstract:



Tutorial review: to achieve molecule-based spintronic devices, an organic conducting magnet that exhibits both conductivity and magnetism in a cooperative manner must be constructed. As a building block for such new materials, a spin-polarized donor radical, which serves as a molecular "spin-filter" in its singly oxidized state, was designed and synthesized. The resistivity of ion radical salts of selenium-substituted, tetrathiafulvalene-based spin-polarized donor radicals decreased substantially in the presence of a magnetic field, thus indicating cooperative conductivity and magnetism.

Framework-structured weak ferromagnets
 Weng, D.-F.; Wang, Z.-M.; Gao, S. Chem. Soc. Rev. 2011, 40, 3157–3181.
 Abstract:



Framework-structured weak ferromagnets are new rising stars in molecule-based magnetic materials. The framework structures are powerful carriers for long-range ordering of spins. And weak ferromagnetism due to spin canting is an effective approach for magnets because of its frequent occurrence and desired spontaneous magnetization as long as the canting angle γ is large enough. In this *critical review*, we provide an overview of the various framework-structured weak ferromagnets based on different grades of ligands (from mono-atom to three-atom-like ligands). Particular emphasis is given to the relationships between structural features and the properties, rational employment of the ligands, and weak ferromagnetic strategies for molecule-based magnets with exciting properties and applications (273 references).

Zinc-Catalyzed Chemoselective Reduction of Esters to Alcohols
 Das, S.; Möller, K.; Junge, K.; Beller, M. Chem. Eur. J. 2011, 17, 7414–7417.

 Abstract:

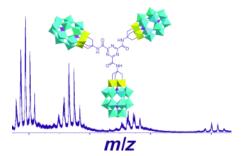
Abstract:

$$R^{1} \xrightarrow{O} R^{2} \xrightarrow{Zn(OAc)_{2}(10 \text{ mol}\%)} R^{1} \xrightarrow{OH}$$

$$R^{1}=Aryl, R^{2}=Alkyl \xrightarrow{(EtO)_{2}MeSiH, 65 °C, 24h} R^{1}$$

Economical alcohols! A general and chemoselective catalytic reduction of esters to alcohols using inexpensive zinc acetate and silanes has been developed. The operational simplicity and the high functional group tolerance, without the need for protecting and deprotecting steps, make this procedure particularly attractive for organic synthesis.

Design and Synthesis of "Dumb-bell" and "Triangular" Inorganic—Organic Hybrid Nanopolyoxometalate Clusters and Their Characterisation through ESI-MS Analyses
 Pradeep, C. P.; Li, F. Y.; Lydon, C.; Miras, H. N.; Long, D. L.; Xu, L.; Cronin, L. Chem. Eur. J. 2011, 17, 7472–7479.



A series of tris(hydroxymethyl)aminomethane (TRIS)-based linear (bis(TRIS)) and triangular (tris(TRIS)) ligands has been synthesised and were covalently attached to the Wells–Dawson type cluster [P2V3W15O62]9– to generate a series of nanometer-sized inorganic–organic hybrid polyoxometalate

clusters. These huge hybrids, with a molecular mass similar to that of small proteins in the range of ≈10−16 kDa, were unambiguously characterised by using high-resolution ESI-MS. The ESI-MS spectra of these compounds revealed, in negative ion mode, a characteristic pattern showing distinct groups of peaks corresponding to different anionic charge states ranging from 3− to 8− for the hybrids. Each peak in these individual groups could be unambiguously assigned to the corresponding hybrid cluster anion with varying combinations of tetrabutylammonium (TBA) and other cations. This study therefore highlights the prowess of the high-resolution ESI-MS for the unambiguous characterisation of large, nanoscale, inorganic—organic hybrid clusters that have huge mass, of the order of 10−16 kDa. Also, the designed synthesis of these compounds points to the fact that we were able to achieve a great deal of structural pre-design in the synthesis of these inorganic—organic hybrid polyoxometalates (POMs) by means of a ligand design route, which is often not possible in traditional "one-pot" POM synthesis.