

- Power struggles in peptide-amphiphile nanostructures

Versluis, F.; Robson Marsden, H.; Kros, A. *Chem. Soc. Rev.* **2010**, *39*, 3434-3444.

Abstract:

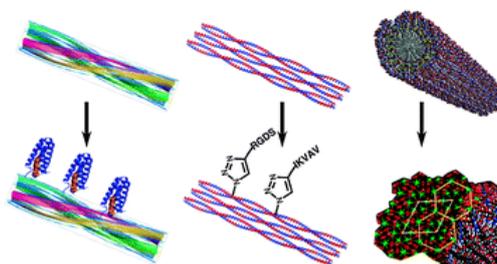


Inspired by the ubiquitous functions fulfilled by native proteins, the self-assembly of peptide amphiphiles (PAs) holds much promise for the creation of functional nanostructures. Typically, PAs are constructed by conjugating blocks of very different character: a hydrophilic peptide segment with a hydrophobic element (an alkyl chain, lipid, polymer or polypeptide). The resulting amphiphilicity governs the self-assembly process in aqueous solutions. This self-assembly process is guided by attractive forces (for example hydrophobic interactions, hydrogen bonding, electrostatic attraction) and repulsive forces (for example electrostatic repulsion, mechanical forces). The balance between these forces is responsible for the secondary structure of the peptide segment, and furthermore the size and shape of the assemblies that are formed. A result of PA self-assembly is that the properties of the peptide segment can be altered, as it is a general observation that peptides are more likely to exhibit a well-defined secondary structure at an interface (*e.g.* the corona of a micelle) than they are in solution. This characteristic of peptides can be exploited to give nanostructures with well-defined properties. The art of controlled PA self-assembly consists of carefully combining all the inter- and intramolecular forces to arrive at a material which is both structurally well-defined and has controllable functionalities. In this *tutorial review* the forces that act within PA nanostructures are discussed, that is, the effect of the hydrophobic block and peptide secondary structure on each other as well as on the aggregate as a whole. At the end of the review, a short section is devoted to the applications of these PA nanostructures.

- More than just bare scaffolds: towards multi-component and decorated fibrous biomaterials

Woolfson, D. N.; Mahmoud, Z. N. *Chem. Soc. Rev.* **2010**, *39*, 3464-3479.

Abstract:

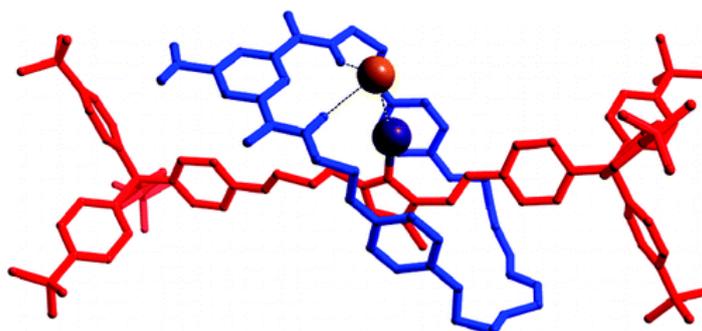


We are entering a new phase in biomaterials research in which rational design is being used to produce functionalised materials tailored to specific applications. As is evident from this Themed Issue, there are now a number of distinct types of designed, self-assembling, fibrous biomaterials. Many of these are ripe for development and application for example as scaffolds for 3D cell culture and tissue engineering, and in templating inorganic materials. Whilst a number of groups are making headway towards such applications, there is a general challenge to translate a wealth of excellent basic research into materials with a genuine future in real-life applications. Amongst other

contemporary aspects of this evolving research area, a key issue is that of decorating or functionalising what are mostly bare scaffolds. There are a number of hurdles to overcome to achieve effective and controlled labelling of the scaffolds, for instance: maintaining biocompatibility, i.e., by minimising covalent chemistry, or using milder bioconjugation methods; attaining specified levels of decoration, and, in particular, high and stoichiometric labelling; introducing orthogonality, such that two or more functions can be appended to the same scaffold; and, in relevant cases, maintaining the possibility for recombinant peptide/protein production. In this critical review, we present an overview of the different approaches to tackling these challenges largely for self-assembled, peptide-based fibrous systems. We review the field as it stands by placing work within general routes to fibre functionalisation; give worked examples on our own specific system, the SAFs; and explore the potential for future developments in the area. Our feeling is that by tackling the challenges of designing multi-component and functional biomaterials, as a community we stand to learn a great deal about self-assembling biomolecular systems more broadly, as well as, hopefully, delivering new materials that will be truly useful in biotechnology and biomedical applications (107 references).

- Enhancement of Anion Recognition Exhibited by a Halogen-Bonding Rotaxane Host System
Kilah, N. L.; Wise, M. D.; Serpell, C. J.; Thompson, A. L.; White, N. G.; Christensen, K. E.; Beer, P. D. *J. Am. Chem. Soc.* **2010**, *132*, 11893–11895.

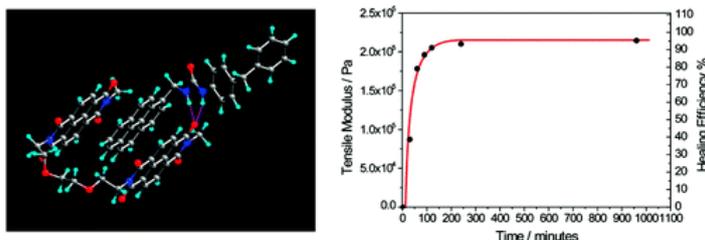
Abstract:



We report the first use of solution-phase halogen bonding to control and facilitate the assembly of an interlocked structure through the bromide anion-templated formation of a rotaxane based upon an iodotriazolium axle. The incorporation of a halogen atom into the rotaxane host cavity dramatically improves the anion-recognition capabilities of the interlocked receptor, giving unusual iodide selectivity in a competitive aqueous medium.

- A Healable Supramolecular Polymer Blend Based on Aromatic π - π Stacking and Hydrogen-Bonding Interactions
Burattini, S.; Greenland, B. W.; Hermida Merino, D.; Weng, W.; Seppala, J.; Colquhoun, H. M.; Hayes, W.; Mackay, M. E.; Hamley, I. W.; Rowan, S. J. *J. Am. Chem. Soc.* **2010**, *132*, 12051–12058.

Abstract:

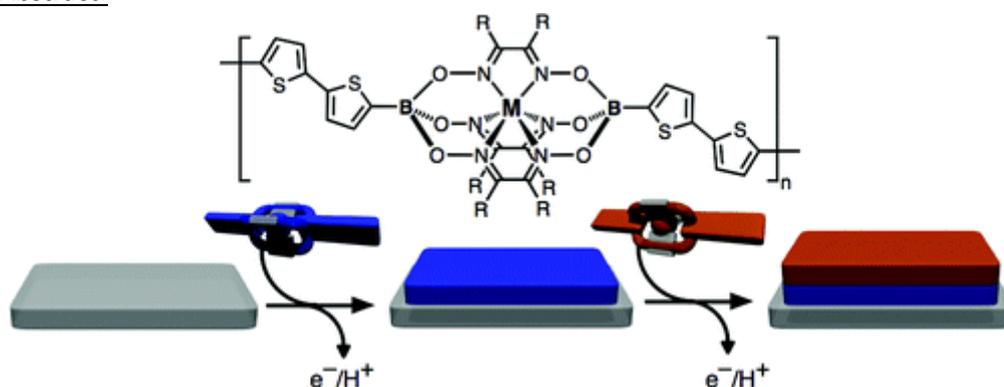


An elastomeric, healable, supramolecular polymer blend comprising a chain-folding polyimide and a telechelic polyurethane with pyrenyl end groups is compatibilized by aromatic π - π stacking between the π -electron-deficient diimide groups and the π -electron-rich pyrenyl units. This interpolymer interaction is the key to forming a tough, healable, elastomeric material. Variable-temperature FTIR analysis of the bulk material also conclusively demonstrates the presence of hydrogen bonding, which complements the π - π stacking interactions. Variable-temperature SAXS analysis shows that the healable polymeric blend has a nanophase-separated morphology and that the X-ray contrast between the two types of domain increases with increasing temperature, a feature that is repeatable over several heating and cooling cycles. A fractured sample of this material reproducibly regains more than 95% of the tensile modulus, 91% of the elongation to break, and 77% of the modulus of toughness of the pristine material.

- Layer-by-Layer Synthesis of Metal-Containing Conducting Polymers: Caged Metal Centers for Interlayer Charge Transport

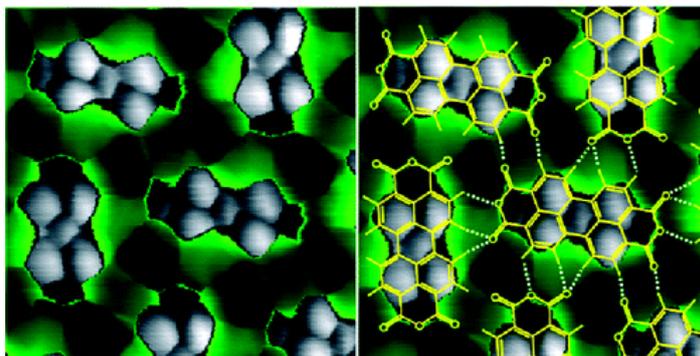
Liu, W.; Huang, W.; Pink, M.; Lee, D. *J. Am. Chem. Soc.* **2010**, *132*, 11844–11846.

Abstract:



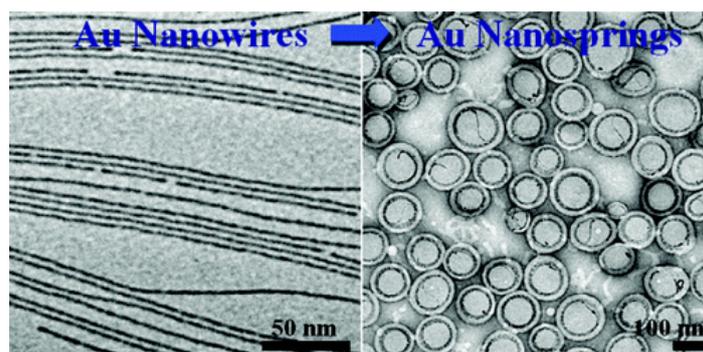
Metal-templated [2 + 3]-type cocondensation of a π -extended boronic acid and nioxime furnished a series of cage molecules, which were electropolymerized to prepare metal-containing conducting polymers (MCPs). Despite sharing essentially isostructural organic scaffolds, these materials display metal-dependent electrochemical properties as evidenced by different redox windows observed for $M = \text{Co}, \text{Fe}, \text{Ru}$. Consecutive electropolymerization using two different monomers furnished bilayer MCPs having different metals in each layer. In addition to functioning as heavy atom markers in cross-sectional analysis by FIB and EDX, redox-active metal centers participate in voltage-dependent interlayer electron transport to give rise to cyclic voltammograms that are distinctively different from those of each layer alone or random copolymers. A simple electrochemical technique can thus be used as a straightforward diagnostic tool to investigate the structural ordering of electrically conductive layered materials.

- Direct Imaging of Intermolecular Bonds in Scanning Tunneling Microscopy
Weiss, C.; Wagner, C.; Temirov, R.; Tautz, F. S. *J. Am. Chem. Soc.* **2010**, *132*, 11864–11865.

Abstract:

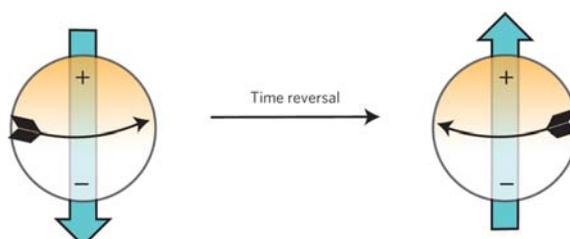
Local, noncovalent intermolecular interactions in organic monolayers have been directly imaged using scanning tunneling hydrogen microscopy (STHM). Unprecedented spatial resolution directly reveals the relation between the intermolecular interactions, the molecular chemical structure, and the ordering in the film.

- Mechanical Nanosprings: Induced Coiling and Uncoiling of Ultrathin Au Nanowires
Xu, J.; Wang, H.; Liu, C.; Yang, Y.; Chen, T.; Wang, Y.; Wang, F.; Liu, X.; Xing, B.; Chen, H. *J. Am. Chem. Soc.* **2010**, *132*, 11920–11922.

Abstract:

We report the controllable coiling of colloidal gold nanowires induced by the contraction of their polymer shells. The mechanical energy stored in this process can be released upon removal or swelling of the polymer shells.

- A multiferroic material to search for the permanent electric dipole moment of the electron
Rushchanskii, K. Z.; Kamba, S.; Goian, V.; Vaněk, P.; Savinov, M.; Prokleška, J.; Nuzhnyy, D.; Knížek, K.; Laufek, F.; Eckel, S.; Lamoreaux, S. K.; Sushkov, A. O.; Ležaić, M.; Spaldin, N. A. *Nature Materials* **2010**, *9*, 649–654.

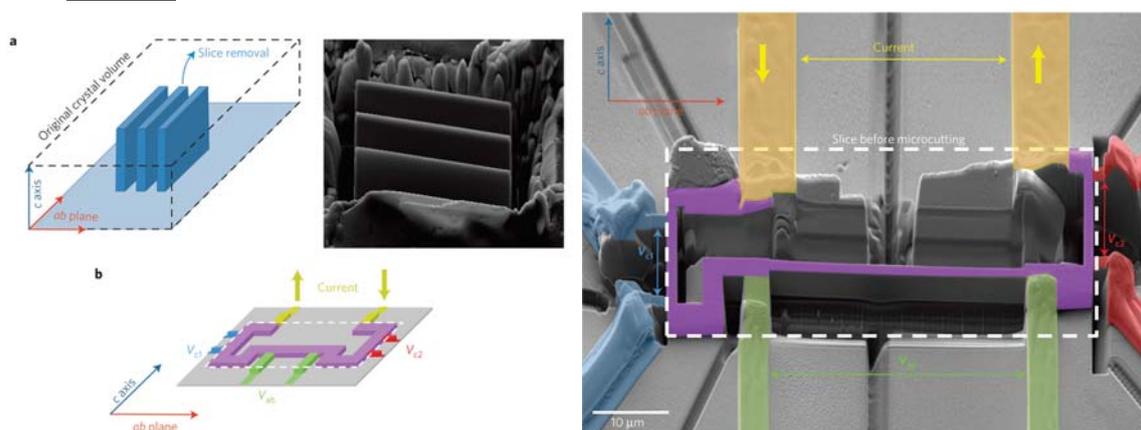
Abstract:

We describe the first-principles design and subsequent synthesis of a new material with the specific functionalities required for a solid-state-based search for the permanent electric dipole moment of the electron. We show computationally that perovskite-structure europium barium titanate should

exhibit the required large and pressure-dependent ferroelectric polarization, local magnetic moments and absence of magnetic ordering at liquid-helium temperature. Subsequent synthesis and characterization of $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ ceramics confirm the predicted desirable properties.

- High magnetic-field scales and critical currents in $\text{SmFeAs}(\text{O}, \text{F})$ crystals
Moll, P. J. W.; Puzniak, R.; Balakirev, F.; Rogacki, K.; Karpinski, J.; Zhigadlo, N. D.; Batlogg, B. *Nature Materials* **2010**, *9*, 628–633.

Abstract:

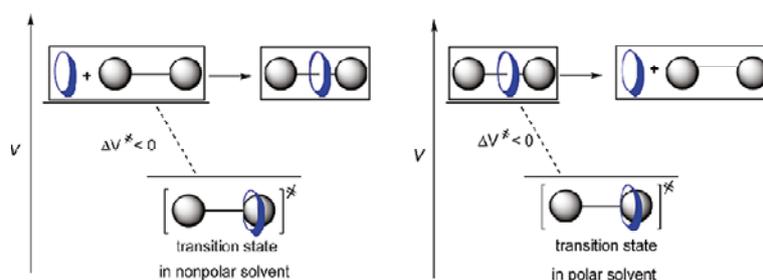


With the discovery of new superconducting materials, such as the iron pnictides¹, exploring their potential for applications is one of the foremost tasks. Even if the critical temperature T_c is high, intrinsic electronic properties might render applications difficult, particularly if extreme electronic anisotropy prevents effective pinning of vortices and thus severely limits the critical current density, a problem well known for cuprates. Although many questions concerning microscopic electronic properties of the iron pnictides have been successfully addressed⁵ and estimates point to a very high upper critical field, their application potential is less clear. Thus, we focus here on the critical currents, their anisotropy and the onset of electrical dissipation in high magnetic fields up to 65 T. Our detailed study of the transport properties of $\text{SmFeAsO}_{0.7}\text{F}_{0.25}$ single crystals reveals a promising combination of high ($>2 \times 10^6 \text{ A cm}^{-2}$) and nearly isotropic critical current densities along all crystal directions. This favourable intragrain current transport in $\text{SmFeAs}(\text{O}, \text{F})$, which shows the highest T_c of 54 K at ambient pressure, is a crucial requirement for possible applications. Essential in these experiments are four-probe measurements on focused-ion-beam-cut single crystals with a sub-square-micrometre cross-section, with current along and perpendicular to the crystallographic c axis.

- Effect of Pressure on [2]Pseudorotaxane Formation and Decomplexation and Their Corresponding Activation Volumes

Tokunaga, Y.; Wakamatsu, N.; Ohiwa, N.; Kimizuka, O.; Ohbayashi, A.; Akasaka, K.; Saeki, S.; Hisada, K.; Goda, T.; Shimomura, Y. *J. Org. Chem.* **2010**, *75*, 4950–4956.

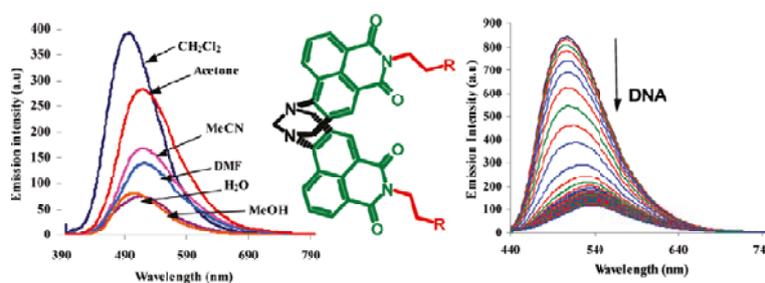
Abstract:



In this study, we investigated the effect of pressure on the formation and decomplexation of [2]pseudorotaxanes. High pressure accelerated the formation of [2]pseudorotaxanes in an aprotic nonpolar solvent ($\text{CDCl}_3/\text{CD}_3\text{CN}$) via the slipping approach when using two crown ether/secondary ammonium salt systems: dibenzo[24]crown-8/bis(cyclohexylmethyl)ammonium salt (**1a/2a**) and tetrabenzo[24]crown-8/dibenzylammonium salt (**1b/2b**). The influence of pressure on the rate constants for the formation of the [2]pseudorotaxanes **3a** and **3b** revealed activation volumes (ΔV^\ddagger) of -2.5 and $-4.6 \text{ cm}^3 \text{ mol}^{-1}$, respectively, at 303 K and zero pressure. We also investigated the effect of pressure on the decomplexation of the [2]pseudorotaxanes **3a** and **3b** in a polar solvent ($\text{DMSO-}d_6/\text{CDCl}_3$), obtaining activation volumes of -0.9 and $-0.4 \text{ cm}^3 \text{ mol}^{-1}$, respectively, at 303 K and zero pressure. Moreover, we calculated the activation parameters for the decomplexation processes on the basis of transition state theory at each pressure.

- Synthesis, Photophysical, and DNA Binding Studies of Fluorescent Tröger's Base Derived 4-Amino-1,8-naphthalimide Supramolecular Clefts
Veale, E. B.; Gunnlaugsson, T. *J. Org. Chem.* **2010**, *75*, 5513–5525.

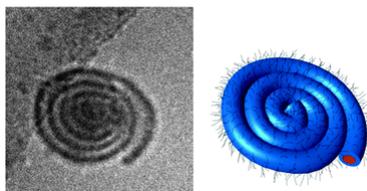
Abstract:



The synthesis and characterization of three bis-1,8-naphthalimide-containing Tröger's bases **1–3**, formed from the corresponding 4-amino-1,8-naphthalimide precursors **7–9** in a single step, is described. The photophysical investigation of **1–3** and **7–9** was carried out in various organic solvents as well as in water and as a function of pH using UV/vis and fluorescence spectroscopy. As for their 4-amino-1,8-naphthalimide precursors **7–9**, both the ground-state and excited-state characteristics of **1–3** were dependent on the polarity and the hydrogen-bonding ability of the solvent medium. The DNA-binding affinities of **1–3** were also studied in aqueous solution at pH 7.4, in the presence of *calif-thymus* DNA (*ct*-DNA), using various UV/vis absorption and fluorescence spectroscopic methods. These molecules exhibited significant DNA-binding ability, where large binding values K_b in the range of 10^6 M^{-1} were determined. Such strong binding to *ct*-DNA was maintained even in competitive media (50 and 160 mM NaCl) and was also found to be irreversible regardless of the concentration of the ionic strength. Thermal denaturation experiments also demonstrated that the interaction of **1–3** with *ct*-DNA gave rise to significant stabilization in the double-helical structure of DNA. The binding affinity of **1–3** for *ct*-DNA was also compared to that of their 4-amino-1,8-naphthalimide precursors **7–9**, determined by fitting of data using “intrinsic” methods and ethidium bromide displacement assays. The latter method gives outstanding binding constants for **1–3** in the range of 10^7 M^{-1} .

- Discovering new block terpolymer micellar morphologies
Kempe, K.; Hoogenboom, R.; Hoepfener, S.; Fustin, C.-A.; Gohy, J.-F.; Schubert, U. S. *Chem. Commun.* **2010**, *46*, 6455–6457.

Abstract:

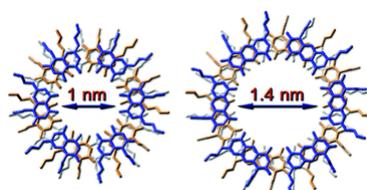


The self-assembly of a new type of triblock terpoly(2-oxazoline) was investigated in water revealing vesicular and aggregated cylindrical micellar structures.

- Rosette nanotubes with 1.4 nm inner diameter from a tricyclic variant of the Lehn–Mascal G[^]C base

Borzsonyi, G.; Johnson, R. S.; Myles, A. J.; Cho, J.-Y.; Yamazaki, T.; Beingessner, R. L.; Kovalenko, A.; Fenniri, H. *Chem. Commun.* **2010**, 46, 6527-6529.

Abstract:

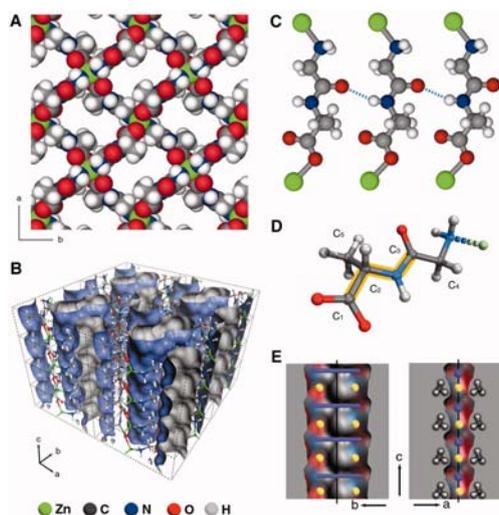


A new strategy to access rosette nanotubes with increased inner diameter is presented and demonstrated through the synthesis and self-assembly studies of a tricyclic variant of the Lehn–Mascal G[^]C base.

- An Adaptable Peptide-Based Porous Material

Rabone, J.; Yue, Y.-F.; Chong, S. Y.; Stylianou, K. C.; Bacsa, J.; Bradshaw, D.; Darling, G. R.; Berry, N. G.; Khimyak, Y. Z.; Ganin, A. Y.; Wiper, P.; Claridge, J. B.; Rosseinsky, M. J. *Science* **2010**, 329, 1053-1057.

Abstract:



Porous materials find widespread application in storage, separation, and catalytic technologies. We report a crystalline porous solid with adaptable porosity, in which a simple dipeptide linker is arranged in a regular array by coordination to metal centers. Experiments reinforced by molecular dynamics simulations showed that low-energy torsions and displacements of the peptides enabled the available pore volume to evolve smoothly from zero as the guest loading increased. The observed cooperative feedback in sorption isotherms resembled the response of proteins undergoing

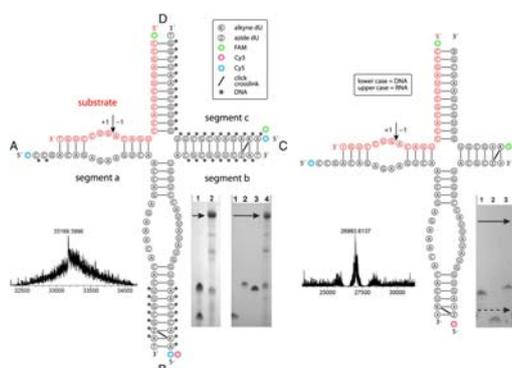
conformational selection, suggesting an energy landscape similar to that required for protein folding. The flexible peptide linker was shown to play the pivotal role in changing the pore conformation.

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- New strategy for the synthesis of chemically modified RNA constructs exemplified by hairpin and hammerhead ribozymes

El-Sagheera, A. H.; Brown, T. *Proc. Nat. Acad. Sci. USA* **2010**, *107*, 15329-15334.

Abstract:

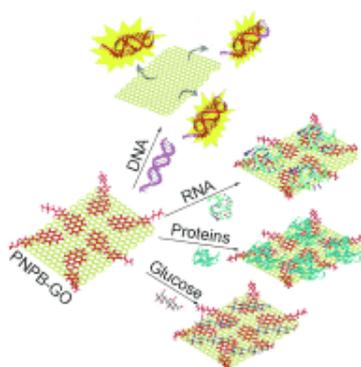


The CuAAC reaction (click chemistry) has been used in conjunction with solid-phase synthesis to produce catalytically active hairpin ribozymes around 100 nucleotides in length. Cross-strand ligation through neighboring nucleobases was successful in covalently linking presynthesized RNA strands with high efficiency (*trans*-ligation). In an alternative strategy, intrastrand click ligation was employed to produce a functional hammerhead ribozyme containing a novel nucleic acid backbone mimic at the catalytic site (*cis*-ligation). The ability to synthesize long RNA strands by a combination of solid-phase synthesis and click ligation is an important addition to RNA chemistry. It is compatible with a plethora of site-specific modifications and is applicable to the synthesis of many biologically important RNA molecules.

- A Graphene Oxide–Organic Dye Ionic Complex with DNA-Sensing and Optical-Limiting Properties

Balapanuru, A.; Yang, J. X.; Xiao, S.; Bao, Q.; Jahan, M.; Polavarapu, L.; Wei, J.; Xu, Q. H.; Loh, K. P. *Angew. Chem. Int. Ed.* **2010**, *49*, 6549–6553.

Abstract:



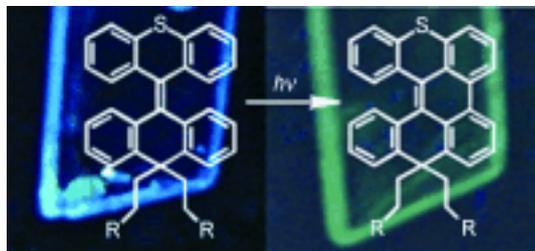
A charge-transfer complex between graphene oxide (GO) and pyrene dye PNPB has been synthesized by a simple ion-exchange process. Its highly specific interactions with DNA compared to other biomolecules (see scheme) allows selective and rapid detection of DNA in biological mixtures. It also exhibits broadband optical limiting.

- In Situ Generation of Wavelength-Shifting Donor–Acceptor Mixed-Monolayer-Modified Surfaces

9

Coleman, A. C.; Areephong, J.; Vicario, J.; Meetsma, A.; Browne, W. R.; Feringa, B. L. *Angew. Chem. Int. Ed.* **2010**, *49*, 6580–6584.

Abstract:



Given the green light: Irradiation of a monolayer of an overcrowded-alkene-based molecular switch (see picture, left) results in generation of a mixed monolayer containing its photocyclized analogue. An efficient energy-transfer process between these compounds is evident from the observed red-shifted emission of the photocyclized switch.