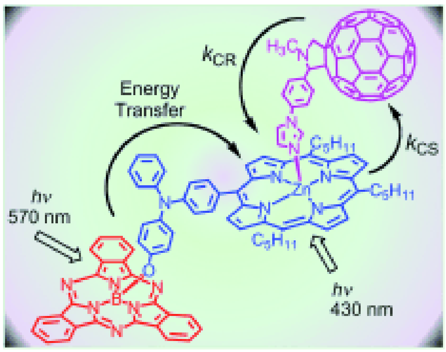
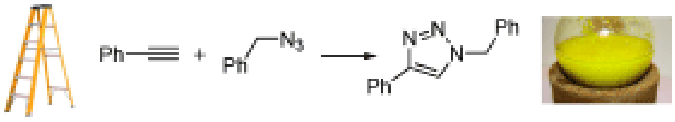
- Supramolecular Tetrad of Subphthalocyanine-Triphenylamine-Zinc Porphyrin Coordinated to Fullerene as an “Antenna-Reaction Center” Mimic: Formation of a Long-Lived Charge-Separated State in Nonpolar Solvent
  El-Khouly, M. E.; Kyu Ju, D.; Kay, K.-Y.; D'Souza, F.; Fukuzumi, S. *Chem. Eur. J.* **2010**, *16*, 6193-6202.
  Abstract:



We report here the formation of a long-lived charge-separated state of a self-assembled donor-acceptor tetrad, formed by axial coordination of a fulleropyrrolidine appended with an imidazole coordinating ligand (C_{60}Im) to the zinc center of a subphthalocyanine-triphenylamine-zinc porphyrin (SubPc-TPA-ZnP), as a charge-stabilizing antenna reaction center mimic in toluene. The subphthalocyanine and triphenylamine entities, with their high-energy singlet states, act as an energy-transferring antenna unit to produce a singlet zinc porphyrin. The formation constant for the self-assembled tetrad was determined to be 1.0×10^4 M^{-1}, suggesting a moderately stable complex formation. The geometric and electronic structures of the covalently linked SubPc-TPA-ZnP triad and self-assembled SubPc-TPA-ZnP:C_{60}Im tetrad were examined by using an ab initio B3LYP/6-31G method. The majority of the highest occupied frontier molecular orbital was found over the ZnP and TPA entities, whereas the lowest unoccupied molecular orbital was located over the fullerene entity, suggesting the formation of the radical-ion pair (SubPc-TPA-ZnP$^{\cdot +}$:C_{60}Im$^{\cdot -}$). The redox measurements revealed that the energy level of the radical-ion pair in toluene is located lower than that of the singlet and triplet states of the zinc porphyrin and fullerene entities. The femtosecond transient absorption measurements revealed fast charge separation from the singlet porphyrin to the coordinated C_{60}Im with a lifetime of 1.1 ns. Interestingly, slow charge recombination (1.6×10^5 s^{-1}) and the long lifetime of the charge-separated state (6.6 μs) were obtained in toluene by utilizing the nanosecond transient measurements.

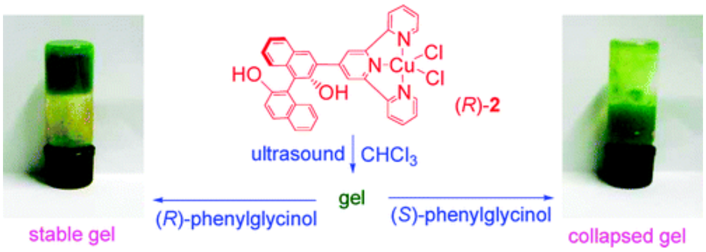
- Experimental Evidence for the Involvement of Dinuclear Alkynylcopper(I) Complexes in Alkyne-Azide Chemistry
  Buckley, B. R.; Dann, S. E.; Heaney, H. *Chem. Eur. J.* **2010,** *16*, 6278-6284.
  Abstract:



Dinuclear alkynylcopper(I) ladderane complexes are prepared by a robust and simple protocol involving the reduction of $Cu_2(OH)_3OAc$ or $Cu(OAc)_2$ by easily oxidised alcohols in the presence of terminal alkynes; they function as efficient catalysts in copper-catalysed alkyne-azide cycloaddition reactions as predicted by the Ahlquist-Fokin calculations. The same copper(I) catalysts are formed during reactions by using the Sharpless-Fokin protocol. The experimental results also provide

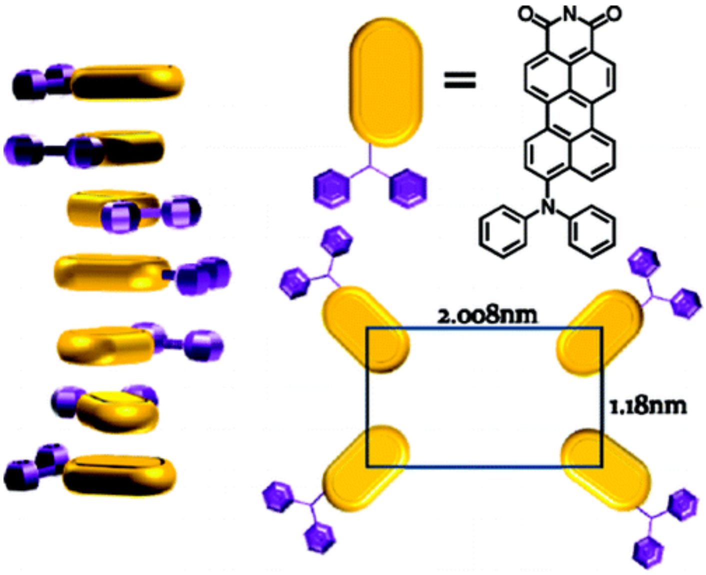
evidence that sodium ascorbate functions as a base to deprotonate terminal alkynes and additionally give a convincing alternative explanation for the fact that the Cu^I-catalysed reactions of certain 1,3-diazides with phenylacetylene give bis(triazoles) as the major products. The same dinuclear alkynylcopper(I) complexes also function as catalysts in cycloaddition reactions of azides with 1-iodoalkynes.

- Enantioselective Gel Collapsing: A New Means of Visual Chiral Sensing
  Chen, X.; Huang, Z.; Chen, S.; Li, K.; Yu, X.; Pu, L. *J. Am. Chem. Soc.* **2010**, *132*, 7297–7299.
  Abstract:



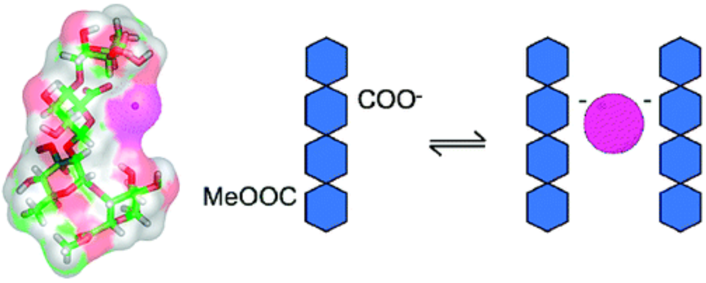
An optically active BINOL-terpyridine based Cu(II) complex (*R*)-2 was prepared. Sonication of (*R*)-2 in CHCl3 led to the formation of a stable gel. The interaction of this gel with chiral amino alcohols was studied. It was found that (*S*)-phenylglycinol (0.10 equiv) could break the gel network of (*R*)-2 (3.75% w/v, g/mL) in $CHCl_3$ to cause gel collapsing but (*R*)-phenylglycinol (0.10 equiv) could not. Similar enantioselective gel collapsing was also observed with (*R*)- and (*S*)-1-amino-2-propanol. This study demonstrates that chiral molecular gels are potentially useful for visual chiral discrimination. Complex (*R*)-2 in solution also exhibited significant enantioselective fluorescent enhancement in the presence of a variety of amino alcohols.

- Self-Assembly, Dynamics, and Phase Transformation Kinetics of Donor−Acceptor Substituted Perylene Derivatives
  Tasios, N.; Grigoriadis, C.; Hansen, M.; Wonneberger, H.; Li, C.; Spiess, H. W.; Müllen, K.; Floudas, G. *J. Am. Chem. Soc.* **2010**, *132*, 7478–7487.
  Abstract:



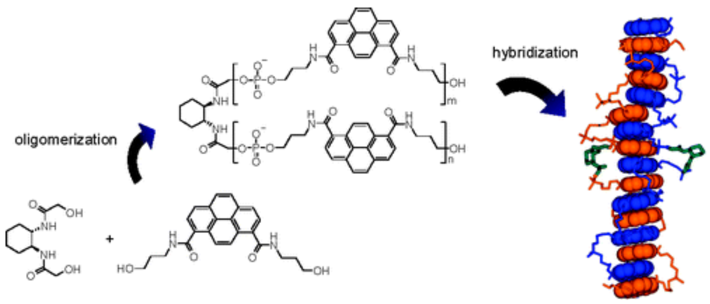
The role of alkyl chain substitution on the phase formation and core dynamics is studied in a series of diphenylamine functionalized perylenemonoimides (PMIs), by X-ray scattering, calorimetry and site-specific solid-state NMR techniques. In addition, the strong dipole associated with the donor−acceptor character of the molecules allow an investigation of the dynamics with dielectric spectroscopy. The self-assembly revealed an ordered phase only in PMIs with branched alkyl chains. This phase comprises a helical stacking of molecules with a molecular twist angle of 60°. Results from solid-state NMR further pointed out the importance of intramolecular hydrogen bonding in stabilizing the intracolumnar packing within the ordered phase. Moreover, the core dynamics are frozen as revealed by the value of the dynamic order parameters and the reduced strength of dipolar relaxation. The kinetics of phase transformation from the isotropic to the ordered phase proceeds via a nucleation and growth mechanism, and the rates are dominated by the nucleation barrier. Within the isotropic phase the core dynamics display strong temperature dependence with rates that depend on the number of methylene units in the alkyl chains.

- Synthesis and Solution-Phase Conformation of the RG-I Fragment of the Plant Polysaccharide Pectin Reveals a Modification-Modulated Assembly Mechanism
  Scanlan, E. M.; Mackeen, M. M.; Wormald, M. R.; Davis, B. G. *J. Am. Chem. Soc.* **2010**, *132*, 7238–7239.
  Abstract:



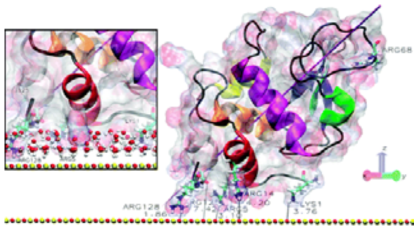
The syntheses of pure RG-I fragments of key plant matrix biomolecule pectin using a counterintuitive late-stage convergent *cis*-glycosylation has allowed detailed analyses of their solution-phase conformations, metal binding affinities, pK_a values, self-assembly equilibria, and diffusional kinetics. These reveal a striking, right-handed 3_1-helix that provides an effective and repeating lateral display of putative liganding carboxylates. Moreover, these heteropolymeric structures allow units as short as tetrasaccharides to self-assemble through carbohydrate−carbohydrate interactions that are induced by the presence of Ca(II), a known dynamic trigger in planta. These self-assembly properties can be switched simply by the addition or removal of a single methyl group in this repeating unit through methyl (de)esterification, another known dynamic trigger in planta. Together, the combined effect of Ca(II) and methylation revealed here suggests a concerted molecular basis for these two major dynamic modifications in planta.

- Oligopyrenotides: Abiotic, Polyanionic Oligomers with Nucleic Acid-like Structural Properties
  Häner, R.; Garo, F.; Wenger, D.; Malinovskii, V. L. *J. Am. Chem. Soc.* **2010**, *132*, 7466–7471.
  Abstract:



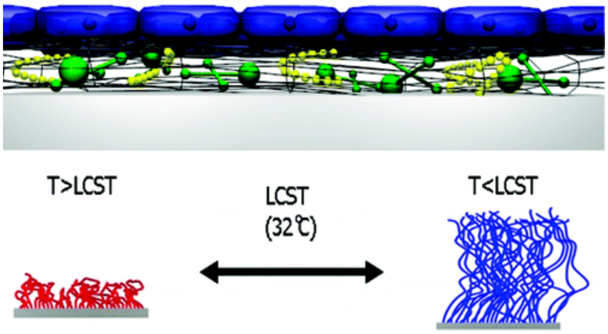
Oligopyrenotides, abiotic oligomers that exhibit significant structural analogies to the nucleic acids, are described. They are composed of achiral, phosphodiester-linked pyrene building blocks and a single chiral 1,2-diaminocyclohexane unit. These oligomers form stable hybrids in aqueous solution. Hybridization is based on stacking interactions of the pyrene building blocks. They show thermal denaturation/renaturation behavior that closely resembles DNA and RNA hybridization. In addition, oligopyrenotides display salt-concentration-dependent structural polymorphism. Thus, they possess a number of structural attributes that are typical of nucleic acids and therefore may serve as model systems for the design of artificial self-replicating systems.

- What Governs Protein Adsorption and Immobilization at a Charged Solid Surface?
  Kubiak-Ossowska, K.; Mulheran, P. A. *Langmuir* **2010**, *26,* 7690–7694.
  <u>Abstract:</u>



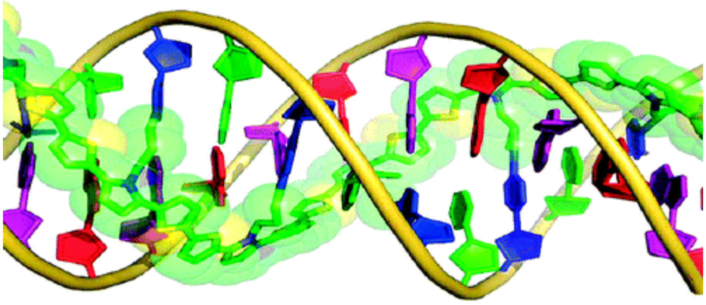
The adsorption of hen egg white lysozyme at a model charged surface is studied using fully atomistic molecular dynamics simulations. The simulations are performed over a 90 ns time scale which is sufficient to observe rotational and translational steps in the adsorption process. Electrostatics is found to play a key role in guiding the protein to the favorable binding orientation with the N,C-terminal face against the substrate. However, full immobilization appears to only occur through the strong interaction of Arg128 with the surface, facilitated by the protein’s flexibility at the terminal face. Simulated mutation at this residue confirms its crucial role. This work demonstrates that electrostatics alone might not be sufficient to guide the development of material systems that exploit protein adsorption and immobilization Encapsulating Light-Emitting Polymers in Block Copolymer Micelles.

- Biological Cell Detachment from Poly(*N*-isopropyl acrylamide) and Its Applications
  Cooperstein, M. A. ; Canavan, H. E. *Langmuir* **2010**, *26*, 7695–7707.
  <u>Abstract:</u>



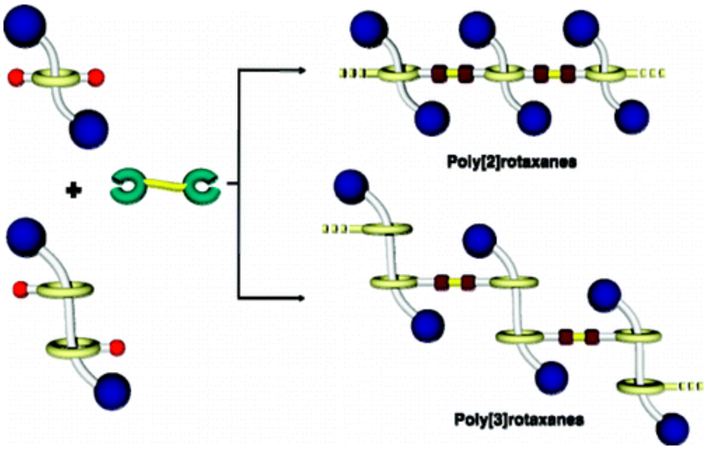
Over the past two decades, poly(*N*-isopropyl acrylamide) (pNIPAM) has become widely used for bioengineering applications. In particular, pNIPAM substrates have been used for the nondestructive release of biological cells and proteins. In this feature article, we review the applications for which pNIPAM substrates have been used to release biological cells, including for the study of the extracellular matrix (ECM), for cell sheet engineering and tissue transplantation, the formation of tumorlike spheroids, the study of bioadhesion and bioadsorption, and the manipulation or deformation of individual cells. The articles reviewed include submissions from our own group as well as from those performing research in the field.

- Development of Self-Organizing, Self-Directing Molecular Nanowires: Synthesis and Characterization of Conjoined DNA−2,5-Bis(2-thienyl)pyrrole Oligomers
  Chen, W.; Gler, G.; Kuruvilla, E.; Schuster, G. B. *Macromolecules* **2010**, *43*, 4032–4040.
  Abstract:



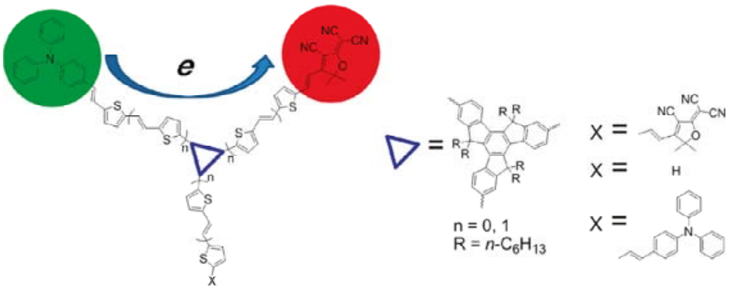
Specifically designed conducting polymers were prepared from monomers that are covalently linked to duplex DNA. These materials combine the self-assembly properties of DNA with those of conducting polymers and may be valuable in the development of self-directing molecular nanowires. Single-strand DNA oligomers having 2,5-bis(2-thienyl)pyrroles (SNS monomers) covalently linked at every other nucleobase along one strand form stable duplexes with their complementary strands. The duplex DNA serves as a scaffold that aligns the SNS monomers within its major groove. The reaction of these SNS-containing duplexes with horseradish peroxidase and H_2O_2 (an oxidant) results in the conversion of the SNS monomers to a conjoined (covalently linked) polymer having the optical properties of a conducting polymer. Examination of radiolabeled oligomers confirms bond formation between SNS monomers, and that conclusion is supported by AFM images. The conjoined polymers have structures that are determined and controlled by the DNA template

- Synthesis of Main-Chain-Type Polyrotaxanes by New Click Polymerization Using Homoditopic Nitrile *N*-Oxides via Rotaxanation−Polymerization Protocol
  Lee, Y.-G.; Koyama, Y.; Yonekawa, M.; Takata, T. *Macromolecules* **2010**, *43*, 4070–4080.
  Abstract:



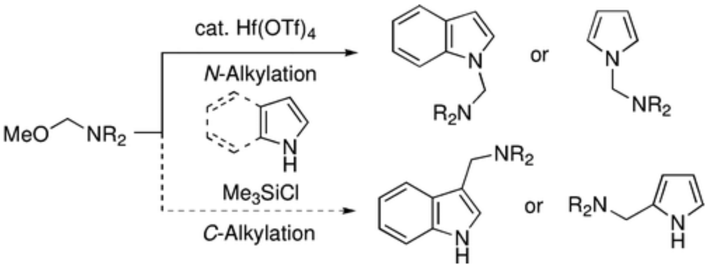
Main-chain-type poly[2]rotaxanes (**9** and **12**) and poly[3]rotaxanes (**10** and **13**) were synthesized by a new click polymerization using unstable and stable homoditopic nitrile *N*-oxides according to rotaxanation and polymerization protocol. Rotaxane monomers were prepared from ethynyl-functionalized crown ether and *sec*-ammonium salt via the typical urethane end-capping protocol. The homoditopic nitrile *N*-oxide **8′** was generated *in situ* through the reaction of the corresponding hydroxamoyl chloride **8** with molecular sieves 4 Å. The click polymerization of diethynyl-functionalized [2]rotaxane **5** and [3]rotaxane monomer **7** with **8′** efficiently proceeded in the absence of a catalyst to afford well-defined polyrotaxanes **9** and **10** containing a polyisoxazole backbone in high yields. The polymerization of a newly developed kinetically stabilized homoditopic nitrile *N*-oxide **11** with rotaxane monomers yielded well-defined polyrotaxanes **12** and **13** in high yields under similar conditions. The structures of poly[2]rotaxanes (**9** and **12**) and poly[3]rotaxanes (**10** and **13**) were confirmed by ^{1}H NMR, SEC, and IR analyses. The properties of polyrotaxanes such as solubility and thermal stability were evaluated. These polyrotaxanes showed relatively high thermal stability and good film-forming property based on their good solubility toward ordinary organic solvents.

- Star-Shaped Donor-π-Acceptor Conjugated Molecules: Synthesis, Properties, and Modification of Their Absorptions Features
  Tang, Z.-M.; Lei, T.; Wang, J.-L.; Ma, Y.; Pei, J. *J. Org. Chem.* **2010**, *75*, 3644–3655.
  <u>Abstract:</u>



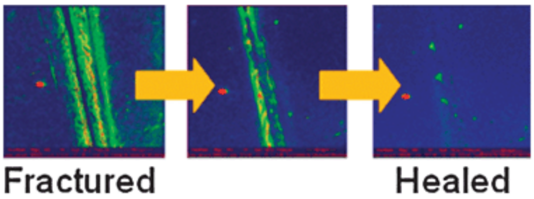
Well-defined star-shaped donor-π-acceptor *meta*-conjugated systems with broad absorption features were constructed through facilely synthetic routes, in which triphenylamine (**TPA**) moiety as an electron donor and 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (**TCF**) unit as an electron acceptor were introduced in various ratios. The investigation of the photophysical properties indicated that the absorption bands of these compounds covered the whole visible range from 300 to 800 nm. For instance, the absorption onset of **D1A2T2** was located at about 780 nm and peaked at 606 nm in thin film. The steady and transient emission spectra showed that these compounds possess an intramolecular energy transfer in such a *meta*-conjugation system, which was further supported by our computational investigation. Our systematic structural variation provides us insight into the tuning strategy of optical properties in D-π-A systems and offered us a series of broad absorption molecules.

- $Hf(OTf)_4$-Catalyzed Regioselective *N*-Aminomethylation of Indoles and Related NH-Containing Heterocycles
  Sakai, N.; Shimamura, K.; Ikeda, R.; Konakahara, T. *J. Org. Chem.* **2010**, *75*, 3923–3926.
  Abstract:



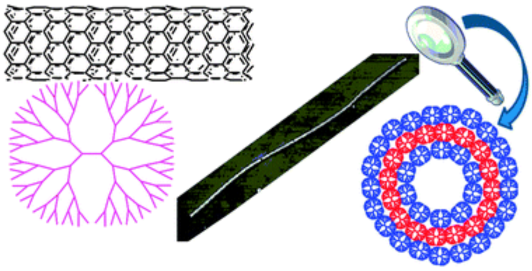
Under Lewis acidic conditions using $Hf(OTf)_4$, the aminomethylation of an indole derivative with a typical *N*,*O*-acetal preferentially produced kinetically favored *N*-aminomethylated indole derivatives instead of thermodynamically favored 3-aminomethylated índoles.

- Healable polymeric materials: a tutorial review
  Burattini, S.; Greenland, B. W.; Chappell, D.; Colquhoun, H. M.; Hayes, W. *Chem. Soc. Rev.* **2010**, *39*, 1973 – 1985.
  Abstract:



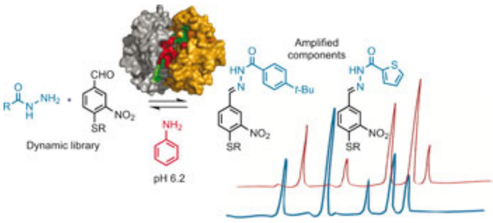
Given the extensive use of polymers in the modern age with applications ranging from aerospace components to microcircuitry, the ability to regain the mechanical and physical characteristics of complex pristine materials after damage is an attractive proposition. This *tutorial review* focusses upon the key chemical concepts that have been successfully utilised in the design of healable polymeric materials.

- Dendrimers and nanotubes: a fruitful association
  Caminade, A.-M.; Majoral, J.-P. *Chem. Soc. Rev.* **2010**, *39*, 2034 – 2047.
  Abstract:



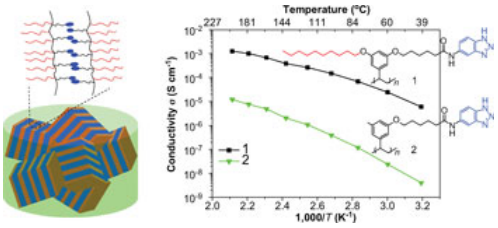
Dendrimers and nanotubes (particularly carbon nanotubes (CNTs)) are two types of nano-objects which have met independently a large success within the scientific community. Surprisingly, their association has been poorly studied up to now, despite some original properties recently reported and that will be emphasized in this *tutorial review*. One can name as a few, the elaboration of single-walled carbon nanotubes from dendrimers, CNTs functionalised with dendrimers displaying field effect transistor properties and/or used as biosensors, and modified biological properties (either enhanced biocompatibility or enhanced antimicrobial activity). However, not all the nanotubes are carbon nanotubes, and original properties were also reported for dendrimers associated with non-CNTs, such as the elaboration of specific nano-filters and of highly efficient and reusable catalysts. Furthermore, non-CNTs constituted of dendrimers, particularly those obtained by layer-by-layer deposition of positively and negatively charged dendrimers associated with quantum dots display an excellent detection limit for DNA hybridization (10 fM).

- Nucleophilic catalysis of acylhydrazone equilibration for protein-directed dynamic covalent chemistry
  Bhat, V. T.; Caniard, A. M.; Luksch, T.; Brenk, R.; Campopiano, D. J.; Greaney, M. F. *Nature Chemistry* **2010**, *2*, 490–497.
  Abstract:



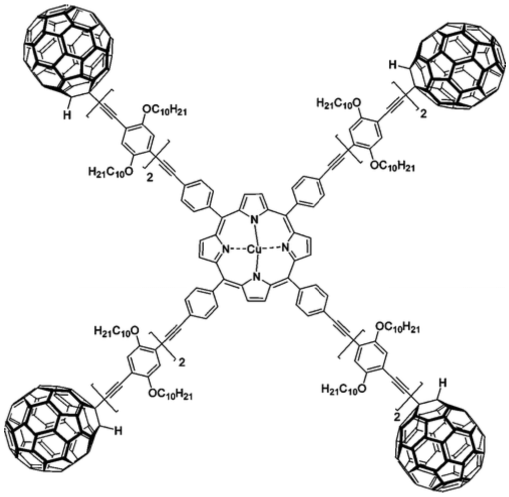
Dynamic covalent chemistry uses reversible chemical reactions to set up an equilibrating network of molecules at thermodynamic equilibrium, which can adjust its composition in response to any agent capable of altering the free energy of the system. When the target is a biological macromolecule, such as a protein, the process corresponds to the protein directing the synthesis of its own best ligand. Here, we demonstrate that reversible acylhydrazone formation is an effective chemistry for biological dynamic combinatorial library formation. In the presence of aniline as a nucleophilic catalyst, dynamic combinatorial libraries equilibrate rapidly at pH 6.2, are fully reversible, and may be switched on or off by means of a change in pH. We have interfaced these hydrazone dynamic combinatorial libraries with two isozymes from the glutathione *S*-transferase class of enzyme, and observed divergent amplification effects, where each protein selects the best-fitting hydrazone for the hydrophobic region of its active site.

- Enhancement of anhydrous proton transport by supramolecular nanochannels in comb polymers
  Chen, Y.; Thorn, M.; Christensen, S.; Versek, C.; Poe, A.; Hayward, R. C.; Tuominen, M. T.; Thayumanavan, S. *Nature Chemistry* **2010**, *2*, 503–508.
  Abstract:



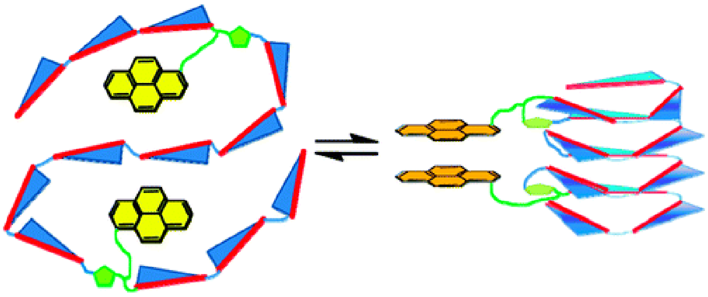
Transporting protons is essential in several biological processes as well as in renewable energy devices, such as fuel cells. Although biological systems exhibit precise supramolecular organization of chemical functionalities on the nanoscale to effect highly efficient proton conduction, to achieve similar organization in artificial systems remains a daunting challenge. Here, we are concerned with transporting protons on a micron scale under anhydrous conditions, that is proton transfer unassisted by any solvent, especially water. We report that proton-conducting systems derived from facially amphiphilic polymers that exhibit organized supramolecular assemblies show a dramatic enhancement in anhydrous conductivity relative to analogous materials that lack the capacity for self-organization. We describe the design, synthesis and characterization of these macromolecules, and suggest that nanoscale organization of proton-conducting functionalities is a key consideration in obtaining efficient anhydrous proton transport.

- Synthesis of a Porphyrin-Fullerene Pinwheel
  Sasaki, T.; Osgood, A. J.; Kiappes, J. L.; Kelly, K. F.; Tour, J. M. *Org. Lett.* **2008**, *10*, 1377–1380.
  Abstract:



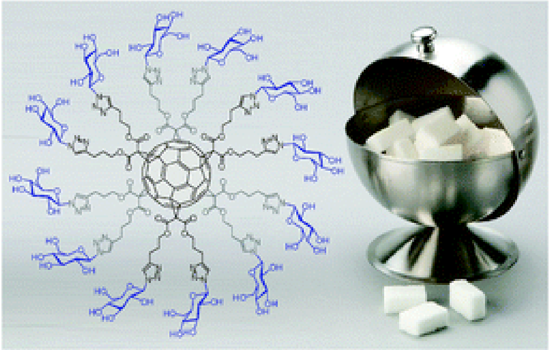
We disclose the synthesis of a porphyrin-fullerene pinwheel that was subsequently observed by scanning tunneling microscopy. The molecule was designed to further our understanding of fullerene-surface interactions, directional control, and surface-rolling versus pivoting capabilities of this class of nanomachines. The inner porphyrin provides the square planar configuration that might lead to realization of the pinwheel spiraling motion on surface.

- Efficient Construction of Oligocholate Foldamers via “Click” Chemistry and Their Tolerance of Structural Heterogeneity
  Pan, X.; Zhao, Y. *Org. Lett.* **2009**, *11*, 69–72.
  Abstract:



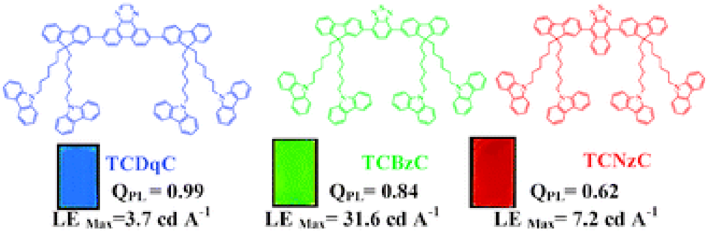
The 1,3-dipolar cycloaddition between an alkynyl-terminated cholate trimer and an azido-functionalized cholate hexamer readily afforded the nonamer and dodecamer derivatives, whereas amide coupling employed in previous oligocholate synthesis failed beyond the octamer. Unlike typical oligocholate foldamers with exclusively head-to-tail arrangement of the repeat units, the newly synthesized “clicked” oligocholates contained head-to-head arrangement and flexible tethers in the sequence. Despite large structural perturbations, the clicked oligocholates folded similarly as the parent foldamers, demonstrating the robustness of the solvophobically driven folding mechanism.

- Fullerene sugar balls
  Nierengarten, J.-F.; Iehl, J.; Oerthel, V.; Holler, M.; Illescas, B. M.; Muñoz, A.; Martín, N.; Rojo, J.; Sánchez-Navarro, M.; Cecioni, S.; Vidal, S.; Buffet, K.; Durka, M.; Vincent, S. P. *Chem. Commun.* **2010**, *46*, 3860 – 3862.
  Abstract:



Fullerene hexakis-adducts bearing 12 peripheral carbohydrate moieties have been prepared by grafting sugar derivatives onto the fullerene core through the copper mediated Huisgen 1,3-dipolar cycloaddition of azides and alkynes.

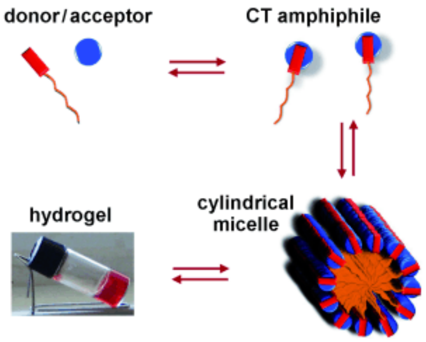
- Highly-efficient solution-processed OLEDs based on new bipolar emitters
  Zhang, M.; Xue, S.; Dong, W.; Wang, Q.; Fei, T.; Gu, C.; Ma, Y. *Chem. Commun.* **2010**, *46,* 3923 – 3925.
  Abstract:



A series of new bipolar solution-processable RGB materials are designed by considering the solubility, morphology, fluorescence efficiency and carriers balance. Solution-processable OLEDs are fabricated with high efficiencies, especially, the green TCBzC-based device shows the maximum luminous efficiency of 31.6 cd A^{-1}, which is among the best reported values.

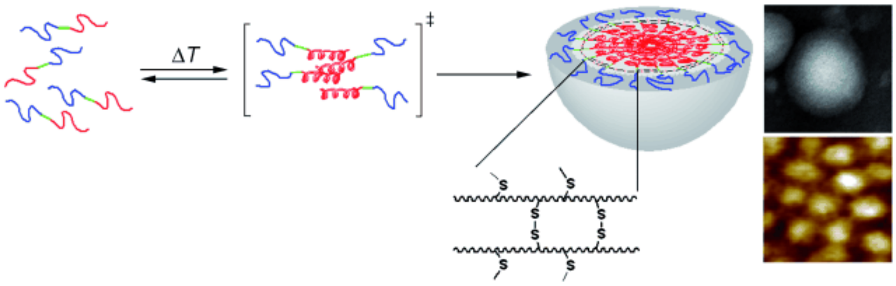
- Supramolecular Hydrogels and High-Aspect-Ratio Nanofibers through Charge-Transfer-Induced Alternate Coassembly
  Rao, K. V.; Jayaramulu, K.; Maji, T. K.; George, S. J. *Angew. Chem. Int. Ed*. **2010**, *49*, 4218 – 4222.

Abstract:



Gelling together: The alternate coassembly of a noncovalent donor-acceptor (D-A) amphiphilic pair in water results in very long nanofibers that form hydrogels (see scheme). Microscopic and single-crystal studies have provided an insight into the hierarchical self-assembly of the charge-transfer (CT) amphiphile, which consists of coronene and a viologen derivative, into cylindrical micelles and gels as the concentration of the D-A pair is increased.

- Self-Assembly of Thermally Responsive Amphiphilic Diblock Copolypeptides into Spherical Micellar Nanoparticles
  Kim, W.; Thévenot, J.; Ibarboure, E.; Lecommandoux, S.; Chaikof, E. L. *Angew. Chem. Int. Ed.* **2010,** *49*, 4257 –4260.
  Abstract:



Stable micellar structures were synthesized containing cysteine residues at the diblock interface to stabilize micellar structure (see picture). Self-assembly of these copolypeptides affords a new class of protein nanoparticles with potential applications in drug-delivery and bioimaging.

- Ferroelectrics: A new spin on spintronics
  Ramesh, R. *Nature materials* **2010**, *9*, 380-381.
  Abstract:

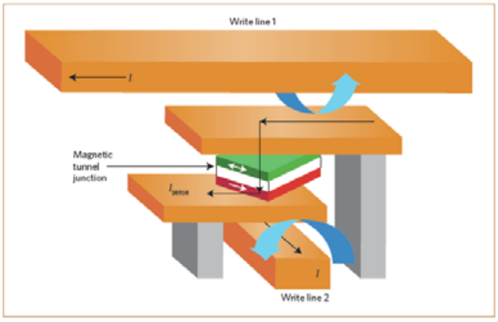
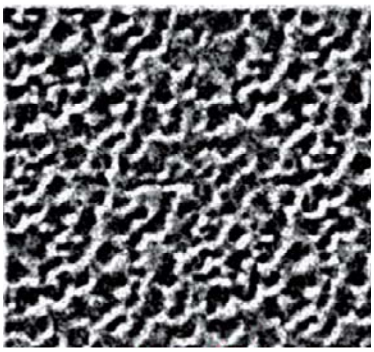


Figure 1 | Electric control of magnetism in a storage device. In magnetic random-access memory, an electric current I is used to apply a magnetic torque (blue arrows) that switches the magnetization (white arrows) in one layer (green) with respect to a layer with a fixed magnetization (red). I_{sense} denotes the sensing current. Figure adapted from ref. 1.

The use of a ferroelectric tunnel junction to control the spin polarization of adjacent magnetic electrodes promises. a new approach to the use of interface effects for low-power-consumption spintronic devices. he ever-increasing demand for faster, smaller and non-volatile electronics is pushing the limits of present semiconductor-based information processing and storage systems. Convoluting this development towards smaller device sizes is the fact that power-consumption requirements are increasing as transistor sizes shrink to the sub-100-nm regime.

- Irreversible nanogel formation in surfactant solutions by microporous flow
  Vasudevan, M.; Buse, E.; Lu, D.; Krishna, H.; Kalyanaraman, R.; Shen, A. Q.; Khomami, B.; Sureshkumar, R. *Nature materials* **2010**, 9, 436-441.
  Abstract:



Self-assembly of surfactant molecules into micelles of various shapes and forms has been extensively used to synthesize soft nanomaterials. Translucent solutions containing rod-like surfactant micelles can self-organize under flow to form viscoelastic gels. This flow-induced structure (FIS) formation has excited much fundamental research and pragmatic interest as a cost-effective manufacturing route for active nanomaterials. However, its practical impact has been very limited because all reported FIS transitions are reversible because the gel disintegrates soon after flow stoppage. We present a new microfluidics-assisted robust laminar-flow process, which allows for the generation of extension rates many orders of magnitude greater than is realizable in conventional devices, to produce purely flow-induced permanent nanogels.