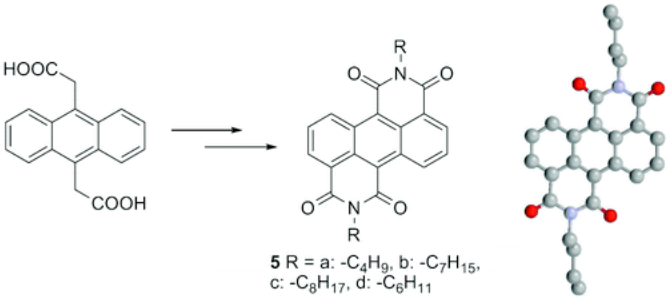
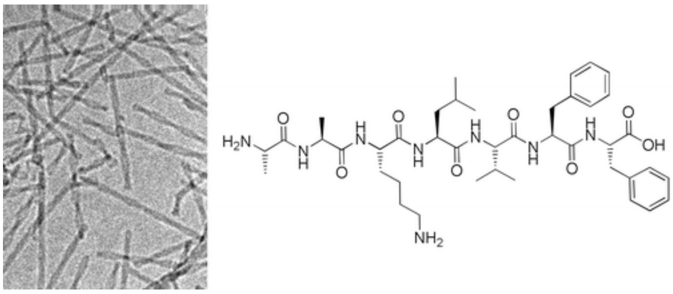
- Synthesis and Characterization of 2,8-Diazaperylene-1,3,7,9-tetraone, a New Anthracene Diimide Containing Six-Membered Imide Rings
  Mohebbi, A. R.; Munoz, C.; Wudl, F. *Org. Lett.* **2011**, *13*, 2560-2563.
  Abstract:



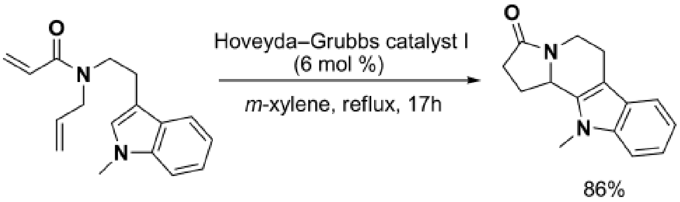
A successful synthesis of novel diimides, namely anthracene diimide containing six-membered imide rings, with potential application in organic electronics is reported. The single crystal of **5a** exhibits a close interplanar spacing of 3.45 Å between molecules in a stack.

- Genetic Expression of an Amyloid Peptide Fragment and Analysis of Formylated Product
  Cheng, G.; Krasel, C.; Zhou, H. G.; Chappell, D.; Hamley, I. W. *Org. Lett.* **2011**, *13*, 2572–2575.
  Abstract:



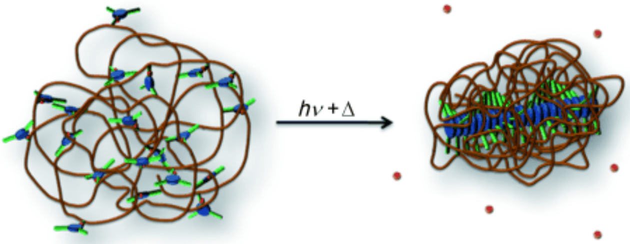
The model amyloid peptide AAKLVFF was expressed as a His-tagged fusion protein with the immunoglobulin-binding domain B1 of streptococcal protein G (GB1), a small (56 residues), stable, single-domain protein. It is shown that expression of this model amyloid peptide is possible and is not hindered by aggregation. Formylation side reactions during the CNBr cleavage are investigated via synthesis of selectively formylated peptides.

- Synthesis of Heterocycles through a Ruthenium-Catalyzed Tandem Ring-Closing Metathesis/Isomerization/N-Acyliminium Cyclization Sequence
  Ascic, E.; Jensen, J. F.; Nielsen, T. E. *Angew. Chem. Int. Ed.* **2011**, *50*, 5188–5191.
  Abstract:



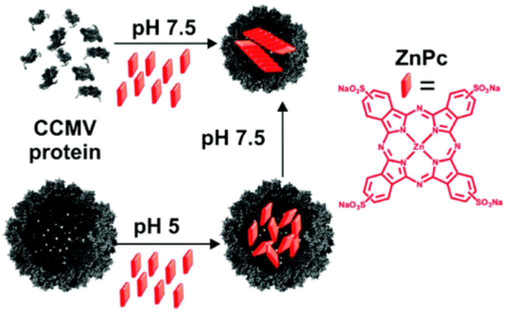
Tandem bicycle: In the title reaction double bonds created during ring-closing metathesis isomerize to generate reactive iminium intermediates that undergo intramolecular cyclization reactions with tethered heteroatom and carbon nucleophiles. In this way, a series of biologically interesting heterocyclic compounds can be made, including a known precursor for the total synthesis of the antiparasitic natural product harmicine.

- Single-Chain Polymeric Nanoparticles by Stepwise Folding
  Mes, T.; van der Weegen, R.; Palmans, A. R. A.; Meijer, E. W. *Angew. Chem. Int. Ed.* **2011**, *50*, 5085–5089.
  Abstract:



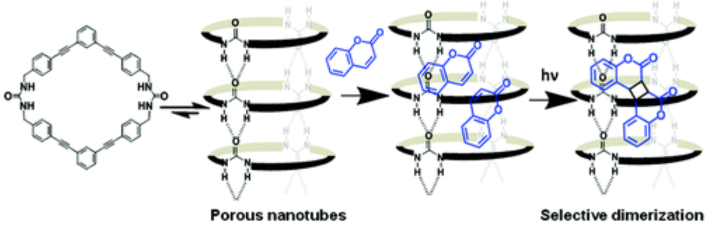
Light-induced self-assembly leads to the folding of synthetic random-coil polymers into highly stable single-chain polymeric chiral nanoparticles (see picture; green: side chains, blue: phenyl rings, red: nitrophenyl leaving groups). The folding of the polymer was aided by heating and cooling steps.

- Encapsulation of Phthalocyanine Supramolecular Stacks into Virus-like Particles
  Brasch, M.; de la Escosura, A.; Ma, Y.; Uetrecht, C.; Heck, A. J. R.; Torres, T.; Cornelissen, J. J. L. M. *J. Am. Chem. Soc.* **2011**, *133*, 6878-6881.
  Abstract:



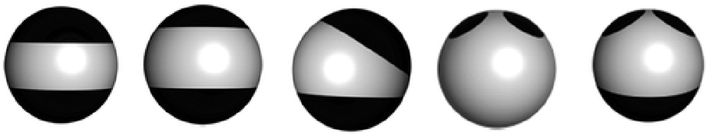
We report herein the encapsulation of a water-soluble phthalocyanine (Pc) into virus-like particles (VLPs) of two different sizes, depending on the conditions. At neutral pH, the cooperative encapsulation/templated assembly of the particles induces the formation of Pc stacks instead of Pc dimers, due to an increased confinement concentration. The Pc-containing VLPs may potentially be used as photosensitizer/vehicle systems for biomedical applications such as photodynamic therapy.

- Self-Assembled Phenylethynylene Bis-urea Macrocycles Facilitate the Selective Photodimerization of Coumarin
  Dawn, S.; Dewal, M. B.; Sobransingh, D.; Paderes, M. C.; Wibowo, A. C.; Smith, M. D.; Krause, J. A.; Pellechia, P. J.; Shimizu, L. S. *J. Am. Chem. Soc.* **2011**, *133*, 7025-7032.
  Abstract:



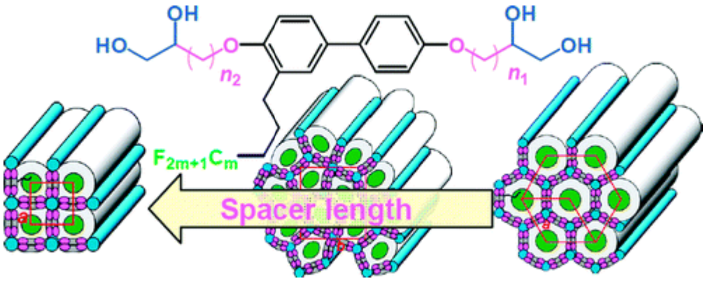
There is much interest in designing molecular sized containers that influence and facilitate chemical reactions within their nanocavities. On top of the advantages of improved yield and selectivity, the studies of reactions in confinement also give important clues that extend our basic understanding of chemical processes. We report here, the synthesis and self-assembly of an expanded bis-urea macrocycle to give crystals with columnar channels. Constructed from two C-shaped phenylethynylene units and two urea groups, the macrocycle affords a large pore with a diameter of 9 Å. Despite its increased size, the macrocycles assemble into columns with high fidelity to afford porous crystals. The porosity and accessibility of these channels have been demonstrated by gas adsorption studies and by the uptake of coumarin to afford solid inclusion complexes. Upon UV-irradiation, these inclusion complexes facilitate the conversion of coumarin to its anti-head-to-head (HH) photodimer with high selectivity. This is contrary to what is observed upon the solid-state irradiation of coumarin, which affords photodimers with low selectivity and conversion.

- Triblock Colloids for Directed Self-Assembly
  Chen, Q.; Diesel, E.; Whitmer, J. K.; Chul Bae, S.; Luijten, E.; Granick, S. *J. Am. Chem. Soc.* **2011**, *133*, 7725–7727.
  Abstract:



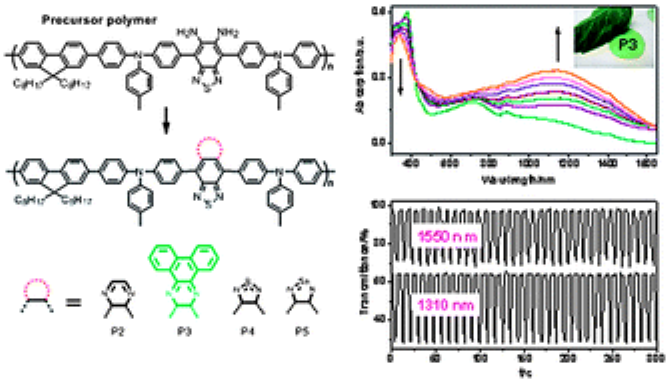
Methods for functionalizing micrometer-sized colloidal spheres with three or more zones of chemical functionality (ABA or ABC) are described. To produce ABA triblock colloids, we functionalized the north pole, south pole, and equator to produce what we call X, Y, and K functionality according to the number of allowed nearest neighbors and their spatial arrangements. These synthesis methods allowed targeting of various lattice structures whose bonding between neighboring particles in liquid suspension was visualized in situ by optical microscopy.

- Influence of Flexible Spacers on Liquid-Crystalline Self-Assembly of T-Shaped Bolaamphiphiles
  Cheng, X.; Liu, F.; Zeng, X.; Ungar, G.; Kain, J.; Diele, S.; Prehm, M.; Tschierske, C. *J. Am. Chem. Soc.* **2011**, *133*, 7872–7881.
  Abstract:



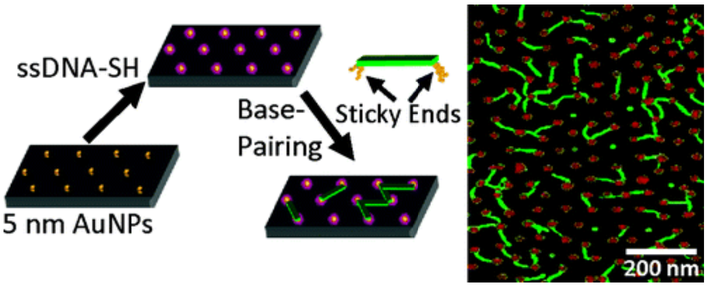
T-shaped bolaamphiphiles composed of a biphenyl rigid core, a semiperfluorinated lateral chain, two polar 1,2-diol groups in the terminal positions and flexible alkyl spacers connecting the polar groups with the biphenyl core have been synthesized and investigated by polarizing microscopy, DSC and X-ray scattering. The influence of spacer length and position of the spacer on the self-assembly in liquid-crystalline phases was studied. A series of four different columnar phases (Col$_{hex}$/*p6mm*, Col$_{rec}$/*p2gg*, Col$_{squ}$/*p4gm* and Col$_{squ}$/*p4mm*), representing liquid-crystalline honeycomb structures composed of cylinders having hexagonal, pentagonal, and square cross section, were found on increasing the spacer length. It is also shown that introduction of aliphatic spacers in the backbone of the T-shaped bolaamphiphiles replaces the $\mathrm{Col}_{rec}/c2mm$ phase made up of rhombic cylinders with the $\mathrm{Col}_{squ}/p4mm$ phase composed of square cylinders. It also causes the 2d lattice of pentagonal cylinders to increase the symmetry from $\mathrm{Col}_{rec}/p2gg$ to $\mathrm{Col}_{squ}/p4gm$. A temperature-dependent second-order phase transition between these two pentagonal cylinder structures was observed for the first time. Beside these effects on cylinder shape and phase symmetry the flexible spacer units also lead to reduced phase transition temperatures and allow adjustment of cylinder side length to envelop a wider range of side-chain sizes. Electron density maps suggest that this may involve sacrificing some of the hydrogen bonds.

- A precursor strategy for the synthesis of low band-gap polymers: an efficient route to a series of near-infrared electrochromic polymers
  Qian, G.; Abu, H.; Wang, Z. Y. *J. Mater. Chem.*, **2011**, *21*, 7678-7685.
  <u>Abstract:</u>



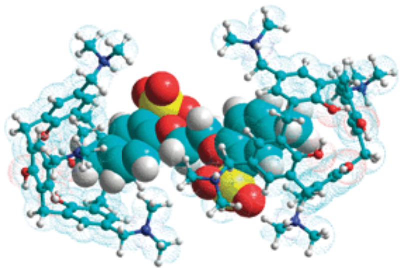
A precursor strategy for the synthesis and screening of a series of conjugated donor–acceptor polymers is demonstrated by successful preparation of low band-gap polymers (P2–P5) containing triphenylamine as an electron donor and several heterocycles as acceptors, such as [1,2,5]thiadiazolo[3,4-*g*]quinoxaline, [1,2,5]thiadiazolo[3,4-*i*]dibenzo[*a*,*c*]phenazine, benzo[1,2-*c*:4,5-*c*′]bis([1,2,5]thiadiazole), and selenadiazole[3,4-*f*]benzo[*c*][1,2,5]thiadiazole, that are transformed from a single reactive polymer (P1). Polymers P2–P5 have the band gap of 1.71–1.29 eV and show the absorption and emission in the near infrared (NIR) spectral region. All the polymers are also NIR electrochromic. In particular, polymer P3 is electrochemically switchable between leaf-like green coloring and near-infrared absorbing states with an efficiency of 479 $cm^2\ C^{-1}$ at 1310 nm or 232 $cm^2\ C^{-1}$ at 1550 nm, making it potentially useful for electrically switchable day-to-night camouflage applications.

- Chemical Alignment of DNA Origami to Block Copolymer Patterned Arrays of 5 nm Gold Nanoparticles
  Pearson, A. C.; Pound, E.; Woolley, A. T.; Linford, M. R.; Harb, J. N.; Davis, R. C. *Nano Lett.* **2011**, *11*, 1981–1987.
  <u>Abstract:</u>



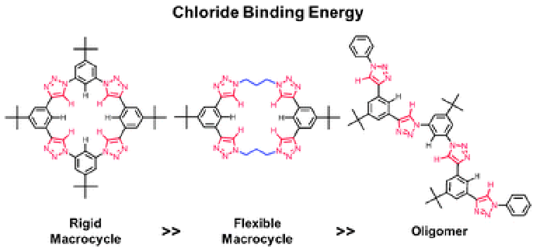
We have used block copolymer patterned arrays of 5 nm gold nanoparticles (AuNPs) for chemically aligned surface attachment of DNA origami. Addition of single-stranded DNA-thiol to AuNPs allowed a base paired attachment of sticky end modified DNA origami. Results indicate a stable, selective attachment between the DNA origami and ssDNA modified AuNPs. Yield data showed 74% of AuNP binding sites forming an attachment with a DNA origami rectangle, and control surfaces showed less than 0.5% nonspecific adsorption.

- A gemini guest triggers the self-assembly of a calixarene capsule in water at neutral pH
  Bonaccorso, C.; Sgarlata, C.; Grasso, G.; Zito, V.; Sciotto, D.; Arena, G. *Chem. Commun.* **2011**, *47*, 6117-6119.
  Abstract:



A gemini guest having both aromatic units and negative charges induces the self-assembling of a homodimeric capsule when interacting with a positively charged calixarene at pH 7.

- Two levels of conformational pre-organization consolidate strong CH hydrogen bonds in chloride–triazolophane complexes
  Hua, Y.; Ramabhadran, R. O.; Karty, J. A.; Raghavachari, K.; Flood, A. H. *Chem. Commun.* **2011**, *47*, 5979-5981.
  Abstract:

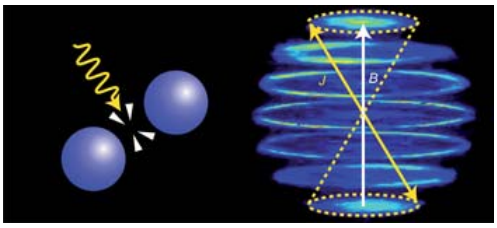


Structural rigidity is verified as a pre-organizational factor that acts together with the macrocyclic effect such that synthesis helps in paying the cost of bringing together electropositive CH donors ready for H-bonding with chloride.

- Control and imaging of O($^1D_2$) precession

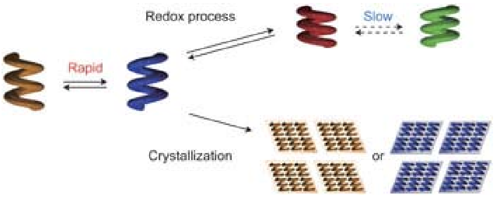
Wu, S.-M.; Radenovic, D. Č.; van der Zande, W. J.; Groenenboom, G. C.; Parker, D. H.; Vallance, C.; Zare, R. N. *Nature Chem.* **2011**, *3*, 28-33.

Abstract:



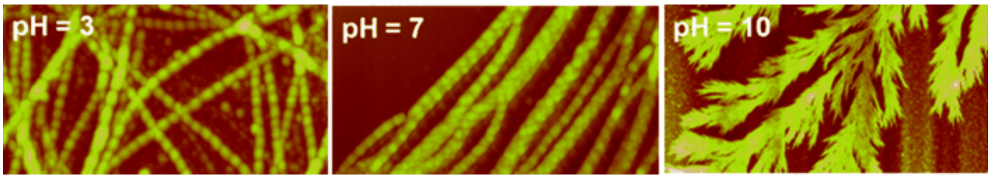
Larmor precession of a quantum mechanical angular momentum vector about an applied magnetic field forms the basis for a range of magnetic resonance techniques, including nuclear magnetic resonance spectroscopy and magnetic resonance imaging. We have used a polarized laser pump–probe scheme with velocity-map imaging detection to visualize, for the first time, the precessional motion of a quantum mechanical angular momentum vector. Photodissociation of O_2 at 157 nm provides a clean source of fast-moving $O(^1D_2)$ atoms, with their electronic angular momentum vector strongly aligned perpendicular to the recoil direction. In the presence of an external magnetic field, the distribution of atomic angular momenta precesses about the field direction, and polarization-sensitive images of the atomic scattering distribution recorded as a function of field strength yield ‘time-lapse-photography’ style movies of the precessional motion. We present movies recorded in various experimental geometries, and discuss potential consequences and applications in atmospheric chemistry and reaction dynamics.

- Redox-responsive molecular helices with highly condensed π-clouds
  Ohta, E.; Sato, H.; Ando, S.; Kosaka, A.; Fukushima, T.; Hashizume, D.; Yamasaki, M.; Hasegawa, K.; Muraoka, A.; Ushiyama, H.; Yamashita, K.; Aida, T. *Nature Chem.* **2011**, *3*, 68-73.
  Abstract:



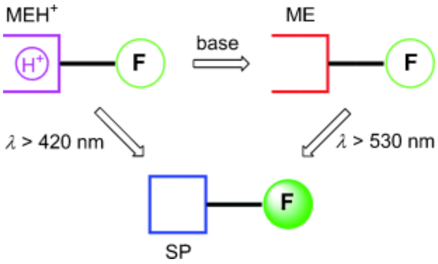
Helices have long attracted the attention of chemists, both for their inherent chiral structure and their potential for applications such as the separation of chiral compounds or the construction of molecular machines. As a result of steric forces, polymeric *o*-phenylenes adopt a tight helical conformation in which the densely packed phenylene units create a highly condensed π-cloud. Here, we show an oligomeric *o*-phenylene that undergoes a redox-responsive dynamic motion. In solution, the helices undergo a rapid inversion. During crystallization, however, a chiral symmetry-breaking phenomenon is observed in which each crystal contains only one enantiomeric form. Crystals of both handedness are obtained, but in a non-racemic mixture. Furthermore, in solution, the dynamic motion of the helical oligomer is dramatically suppressed by one-electron oxidation. X-ray crystallography of both the neutral and oxidized forms indicated that a hole, generated upon oxidation, is shared by the repeating *o*-phenylene units. This enables conformational locking of the helix, and represents a long-lasting chiroptical memory.

- Hierarchical Self-Assembly of Amphiphilic Peptide Dendrons: Evolution of Diverse Chiral Nanostructures Through Hydrogel Formation Over a Wide pH Range
  Duan, P.; Qin, L.; Zhu, X.; Liu, M. *Chem. Eur. J.* **2011**, *17,* 6389–6395.
  Abstract:



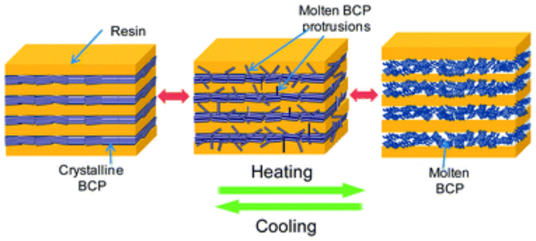
An amphiphilic dendron containing three dendrite L-glutamic acid units and a long alkyl chain was synthesized by a convergent method. It was found that the dendron could form hydrogels over a wide pH range from 2 to 13. Moreover, accompanying the pH change, the compounds self-assembled into various chiral structures: from helical nanotube, helical nanotube with a string of beads, and coiled superhelix to dendrite nanostructures, such as pine, feather, etc. A series of characterizations based on TEM observations, X-ray diffraction and FTIR spectroscopic measurements revealed that the dendron formed a bilayer first and then hierarchically self-assembled into various chiral nanostructures. The four carboxylic acid groups and three amide groups played an important role in the self-assembly. The interaction between the multiamide groups stabilized the bilayer structures, whereas the ionization degree of the carboxylic acids was responsible for the formation of various chiral structures. The work presented a hydrogel system with wide pH adaptability and showed the regulation on chiral structures by simple pH variations.

- Molecular Implementation of Sequential and Reversible Logic Through Photochromic Energy Transfer Switching
  Remón, P.; Hammarson, M.; Li, S.; Kahnt, A.; Pischel, U.; Andréasson, J. *Chem. Eur. J.* **2011**, *17,* 6492–6500.
  Abstract:



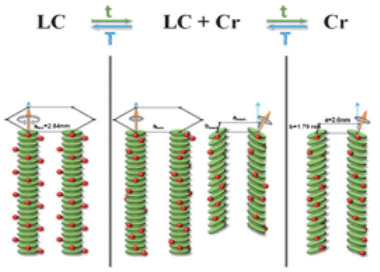
Photochromic spiropyrans modified with fluorophores were investigated as molecular platforms for the achievement of fluorescence switching through modulation of energy transfer. The dyads were designed in such a way that energy transfer is only observed for the open forms of the photochrome (merocyanine and protonated merocyanine), whereas the closed spiropyran is inactive as an energy acceptor. This was made possible through a deliberate choice of fluorophores (4-amino-1,8-naphthalimide, dansyl, and perylene) that produce zero spectral overlap with the spiro form and considerable overlap for the merocyanine forms. From the Förster theory, energy transfer is predicted to be highly efficient and in some cases of 100 % efficiency. The combined switching by photonic (light of λ>530 nm) and chemical (base) inputs enabled the creation of a sequential logic device, which is the basic element of a keypad lock. Furthermore, in combination with an anthracene-based acidochromic fluorescence switch, a reversible logic device was designed. This enables the unambiguous coding of different input combinations through multicolour fluorescence signalling. All devices can be conveniently reset to their initial states and repeatedly cycled.

- Permeable nanoconfinement of hierarchical block copolymer volume gratings
  Birnkrant, M.; Li, C.; Natarajan,L.; Tondiglia, V.; Sutherland, R.; Bunning, T. *Soft Matter* **2011**, *7*, 4729-4734.
  Abstract:



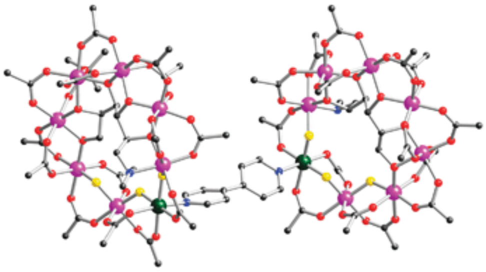
A hierarchical structure of poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL) block copolymer (BCP) confined between crosslinked resin was patterned into Bragg volume gratings using a holographic polymerization (HP) process. The BCP formed a lamellar structure confined between the layers of the grating created by HP. The periods of the volume grating and the BCP were controlled to be ~200 nm and 20 nm, respectively. These two different length scale layers were aligned parallel to one another yielding a polymeric film which exhibits distinct diffraction behavior due to a periodic refractive index variation. This system exhibits complex thermo-optical behavior during heating and cooling cycles with reversible changes in both the diffraction wavelength and efficiency induced by BCP melting and crystallization in the confined region. Transmission electron microscopy studies show reversible diffusion of PEO-*b*-PCL into and out of the crosslinked resin, indicating that the nanoconfinement imposed by the resin is soft and permeable for the BCP. The morphological changes in nanoconfinement with temperature account for the complex thermo-optical behavior of the grating and the system provides an interesting platform to investigate soft nanoconfinement of BCP materials.

- To tilt or not to tilt? Kinetics of structure formation in a discotic liquid crystal
  Grigoriadis, C.; Haase, N.; Butt, H-J.; Müllen, K; Floudas, G. *Soft Matter* **2011**, *7*, 4680-4689.
  Abstract:



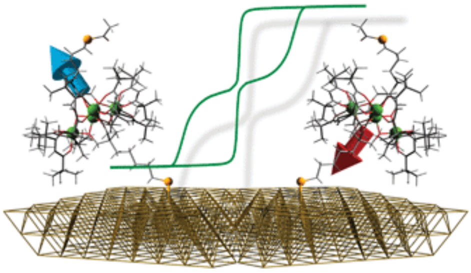
The distinctly different unit cells, dipolar dynamics and viscoelastic properties of the two columnar phases in a dipole-functionalized discotic liquid crystal (mono-iodine hexa-*peri*-hexabenzocoronene) were employed as fingerprints and allowed investigating the kinetic pathways towards formation of the crystalline phase. X-Ray scattering, dielectric spectroscopy and rheology revealed a nucleation and growth process. The transformation involved coexisting unit cells composed from columns with either tilted or non-tilted disks and the absence of intermediate states. The transition can be described as a transformation from a *structurally weakly ordered* but dipolar *well-ordered* liquid crystalline phase to a structurally *well-ordered* but *dipolar disordered* crystalline phase.

- Linking heterometallic rings for quantum information processing and amusement
  Timco, G. A.; Faust, T. B.; Tuna, F.; Winpenny, R. E. P. *Chem. Soc. Rev.* **2011**, *40*, 3067–3075.
  Abstract:



Linking polymetallic cages can be a method for creating new structures and new properties. In this *tutorial review* we use heterometallic anti-ferromagnetically coupled rings (AF-rings) as exemplars for three approaches that can be used to link cage compounds. The first of three routes involves an ion-pair interaction supported by hydrogen-bonding interactions, which allows the synthesis of hybrid rotaxanes among other materials. The second route involves functionalising the exterior of the AF-ring so that it will act as a Lewis base; complexes involving coordination of pyridine to bridging monometallic and dimetallic fragments are discussed. The third route involves creating a vacancy on one site of the AF-ring, and then using the ring as a Lewis acid. Di-imine ligands can then be used to link the AF-rings into dimers. A brief discussion of the physical properties of these systems is also included.

- Chemical strategies and characterization tools for the organization of single molecule magnets on surfaces
  Cornia, A.; Mannini, M.; Sainctavit, P.; Sessoli, R. *Chem. Soc. Rev.* **2011**, *40*, 3076–3091.
  Abstract:



Addressing individual bistable magnetic molecules, known as Single Molecule Magnets (SMMs), is a fascinating goal at the borderline between molecular magnetism and spin electronics. This *tutorial review* focuses on the first step towards single-molecule experiments, namely the organization of SMMs on surfaces. Both preparation and characterization of surface-supported SMMs prove to be quite demanding and a multidisciplinary approach is necessary, which is described here using selected examples. We first illustrate the chemical strategies devised to assemble SMMs and to control their orientation on surfaces. Then, we present characterization tools, which have been selected on the basis of their relevance to address specific points, *i.e.* the chemical composition of the deposited SMM films, the organization of the molecules on the surface, the intramolecular arrangement of the spins, the magnetic anisotropy of SMMs, and eventually the dynamics of their magnetization on surfaces. Particular attention is devoted to techniques exploiting synchrotron light.