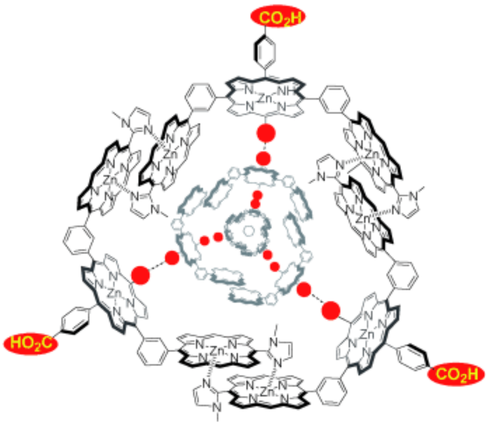
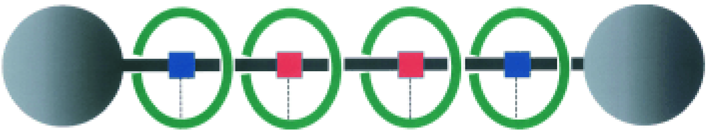
- Supramolecular Organization of Light-Harvesting Porphyrin Macrorings
  Satake, A.; Azuma, S.; Kuramochi, Y.; Hirota, S.; Kobuke, Y. *Chem.-Eur. J.* **2011**, *17*, 855-865.
  Abstract:



Porphyrin-based supramolecular nanostructures have been produced by the self-assembly of porphyrin macrorings with three benzoic acid groups (Acid-R) on each side of the rings through cooperative carboxyl–carboxyl hydrogen bonds. Structures of the organized Acid-R were analyzed by AFM, and two clear distribution peaks were observed at 3 and 27 nm in the height-distribution histogram. From the overall assessment, the higher objects are considered to be one-dimensional structures standing vertically on the mica substrate. The height corresponds to an 11-mer of a unit Acid-R. Light-harvesting functions were examined by using fluorescence titration, whereby an energy-acceptor molecule (Tripod **2**) was employed that strongly interacted with Acid-R units (association constant: 2.0×10^{8}□M^{-1}), specifically from the inner pore. The titration results showed that the apparent stoichiometry [Tripod **2**]/[Acid-R] was <0.5, and that the value was concentration dependent. Titration results reasonably account for the scheme in which Tripod **2** only interacts with each terminal in the organized Acid-R. The number of organization was fitted to a 10-mer of Acid-R in a 6.8×10^{-7}□M solution, and was consistent with that estimated from the AFM results. In the composites of organized Acid-R/Tripod **2**, a singlet excitation energy transfer occurred among the Acid-R units, and to Tripod **2**. The energy-transfer rate constants were estimated by using the decamer model, which employed kinetic parameters obtained from steady-state and time-resolved fluorescence experiments.

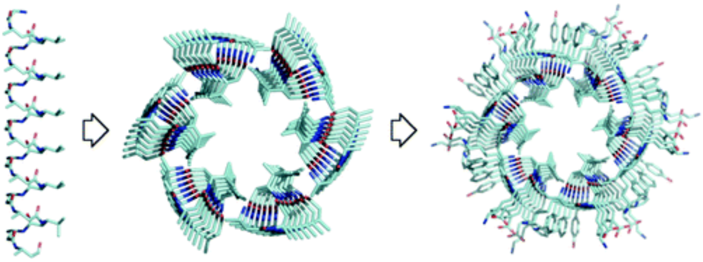
- Synthesis of [5]Rotaxanes Containing Bi- and Tridentate Coordination Sites in the Axis
  Collin, J.-P.; Durot, S.; Keller, M.; Sauvage, J. P.; Trolez, Y.; Cetina, M.; Rissanen, K. *Chem.-Eur. J.* **2011**, *17*, 947-957.
  Abstract:



A new example of a linear [5]rotaxane has been synthesized by using the traditional "gathering-and-threading" approach but based on an unusual axle incorporating a symmetrical bis(bidentate) chelating fragment built on a 4,7-phenanthroline core. The stoppering reaction is particularly noteworthy since, instead of using a trivial bulky stopper as precursor to the blocking group, two semistoppered copper-complexed [2]pseudorotaxanes (namely [2]semirotaxanes) are used, which leads to the desired [5]rotaxane in good yield. The efficiency of the method relies on the use of

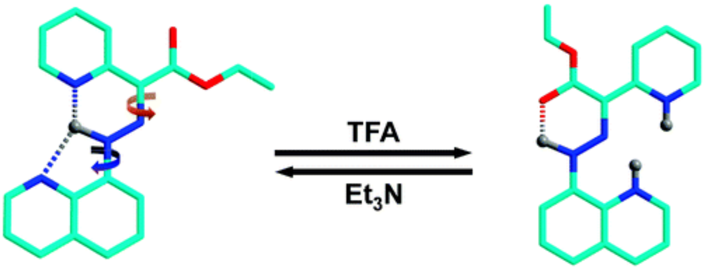
"click" chemistry, with its very mild conditions, and on the protection by a transition-metal (copper(I)) of the various coordinating groups present in the fragments to be interconnected (terpy and bidentate chelating groups), thus inhibiting potential detrimental side reactions during the copper-catalyzed stoppering reaction. Since the external fragments and the central core of the system contain tri- and bidentate chelating units, respectively, the axle of the final [5]rotaxane incorporates two types of coordinating units: two external terpy groups (terpy: 2,2′:6′,2″-terpyridine) and two central bidentate ligands. Such a situation enables the system to tidy two different metals centers, and to localize them in a priori well-defined positions. This is what was observed when mixing the free ligand with a mixture of Zn^{2+} and Li^{+}: the zinc(II) ions were unambiguously shown to occupy the external sites, whereas the Li^{+} cations were found in the central part of the [5]rotaxane. An X-ray diffraction study carried out on a [3]pseudorotaxane, the axis of which is similar to the central part of the [5]rotaxane axle, demonstrates that Zn^{2+} is clearly five-coordinate, the fifth ligand being a counterion, even when the coordination site of the pseudorotaxane is designed for four-coordinate metals, which is in marked contrast with copper(I) or Li^{+}.

- Computational Design of a Self-Assembling *β*-Peptide Oligomer
  Korendovych, I. V.; Ho Kim, Y.; Ryan, A. H.; Lear, J. D.; DeGrado, W. F.; Shandler, S. J. *Org. Lett.* **2010**, *12*, 5142-5145.
  Abstract:



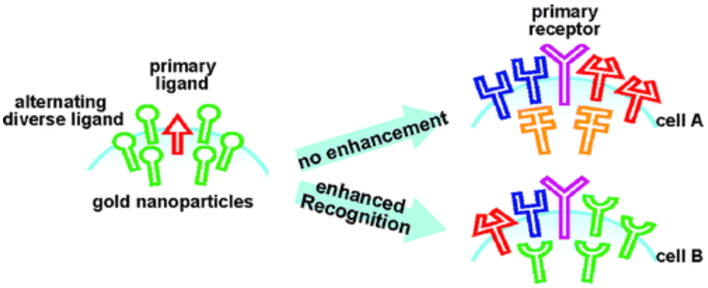
The first computationally designed self-assembling oligomer consisting of exclusively β-amino acids (βAAs) is presented. The packing of a β-3_{14} helix into coiled-coils of varying stoichiometries as a function of amino acid sequence is examined. β-Peptides with hVal repeating every third residue in the sequence appeared to have a strong propensity to pack into hexameric bundles. The designed sequence was synthesized and characterized with CD spectroscopy, NMR, and analytical ultracentrifugation, suggesting that the peptide adopts a well-folded hexameric structure.

- Switching Around Two Axles: Controlling the Configuration and Conformation of a Hydrazone-Based Switch
  Su, X.; Aprahamian, I. *Org. Lett.* **2011**, *13*, 30-33.
  Abstract:



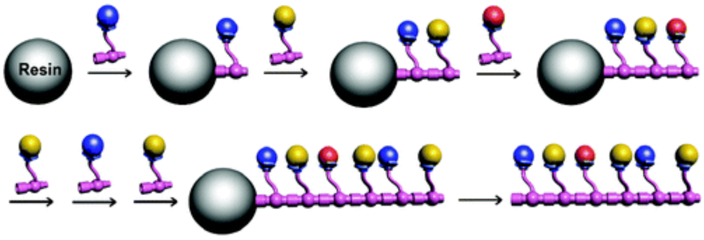
A hydrazone-based rotary switch, having a quinolinyl stator and a pyridine ring as part of the rotor, can be induced using pH to undergo a four-step switching sequence. This process yields three stable isomers and a fourth “metastable” one that can all be addressed separately based on the sequence of acid and base added. The switching process proceeds via conformational and/or configurational changes, allowing the molecule to rotate around two different axles.

- Enhancing Cell Recognition by Scrutinizing Cell Surfaces with a Nanoparticle Array
  Zhou, H.; Jiao, P.; Yang, L.; Li, X.; Yan, B. *J. Am. Chem. Soc.* **2011**, *133*, 680–682.
  Abstract:



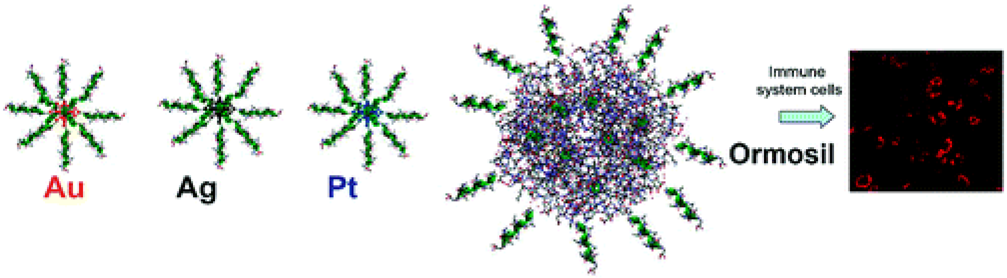
We report a dual-ligand nanoparticle array approach for discerning cells that have different surface receptor profiles surrounding a common primary receptor expressed at high or low levels. The achieved differentiation provides nanoparticles the ability for potential applications in treatment of patients at a personalized medicine level for drug delivery and radiation therapy with a much better safety profile.

- Synthesis of Metal−Organic Complex Arrays
  Vairaprakash, P.; Ueki, H.; Tashiro, K.; Yaghi, O. M. *J. Am. Chem. Soc.* **2011**, *133*, 759–761.
  Abstract:



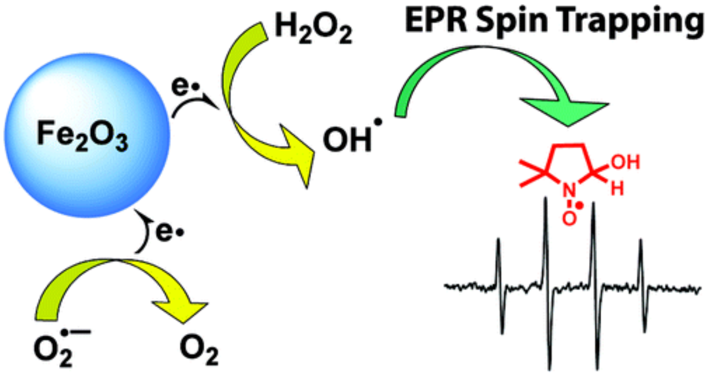
The Merrifield solid-phase peptide synthesis technique has been adapted to the synthesis of homo- and heterometallic metal−organic complex arrays (MOCAs). A terpyridine-appended and Fmoc-protected l-tyrosine derivative was metalated with Pt(II), Rh(III), or Ru(II) ions in solution and sequentially coupled at the surface of functionalized polymeric resin to give a metal complex triad (Rh−Pt−Ru), tetrad (Ru−Rh−Pt−Pt), pentad (Rh−Pt−Ru−Pt−Rh), and hexad (Rh−Pt−Ru−Pt−Rh−Pt) with specific metal sequence arrangements. These were cleaved from the resin, and their character was confirmed by mass spectrometry.

- Water-Soluble Peptide-Coated Nanoparticles: Control of the Helix Structure and Enhanced Differential Binding to Immune Cells
  Rio-Echevarria, I. M.; Tavano, R.; Causin, V.; Papini, E.; Mancin, F.; Moretto, A. *J. Am. Chem. Soc.* **2011**, *133*, 8–11.
  Abstract:



The stabilizing action of C^{α}-tetrasubstituted α-amino acids inserted into a sequence of short peptides allowed for the first time the preparation of water-soluble nanoparticles of different materials coated with a helix-structured undecapeptide. This peptide coating strongly favors nanoparticle uptake by human immune system cells.

- Surface-Mediated Production of Hydroxyl Radicals as a Mechanism of Iron Oxide Nanoparticle Biotoxicity
  Voinov, M. A.; Sosa Pagan, J. O.; Morrison, E.; Smirnova, T. I.; Smirnov, A. I. *J. Am. Chem. Soc.* **2011**, *133*, 35–41.
  Abstract:

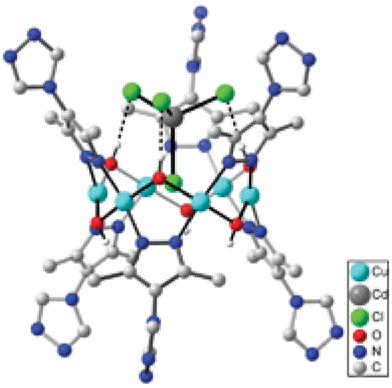


Emerging applications of nanosized iron oxides in nanotechnology introduce vast quantities of nanomaterials into the human environment, thus raising some concerns. Here we report that the surface of γ-Fe_2O_3 nanoparticles 20–40 nm in diameter mediates production of highly reactive hydroxyl radicals ($OH^•$) under conditions of the biologically relevant superoxide-driven Fenton reaction. By conducting comparative spin-trapping EPR experiments, we show that the free radical production is attributed primarily to the catalytic reactions at the nanoparticles' surface rather than being caused by the dissolved metal ions released by the nanoparticles as previously thought. Moreover, the catalytic centers on the nanoparticle surface were found to be at least 50-fold more effective in $OH^•$ radical production than the dissolved Fe^{3+} ions. Conventional surface modification methods such as passivating the nanoparticles' surface with up to 935 molecules of oleate or up to 18 molecules of bovine serum albumin per iron oxide core were found to be rather ineffective in suppressing production of the hydroxyl radicals. The experimental protocols developed in this study could be used as one of the approaches for developing analytical assays for assessing the free radical generating activity of a variety of nanomaterials that is potentially related to their biotoxicity.

- Self-assembly hexanuclear metallacontainer hosting halogenated guest species and sustaining structure of 3D coordination framework

Govor, E. V.; Lysenko, A. B.; Quiñonero, D.; Rusanov, E. B.; Chernega, A. N.; Moellmer, J.; Staudt, R.; Krautscheid, H.; Frontera, A.; Domasevitch, K. V. *Chem. Commun.* **2011**, *47*, 1764-1766.

Abstract:

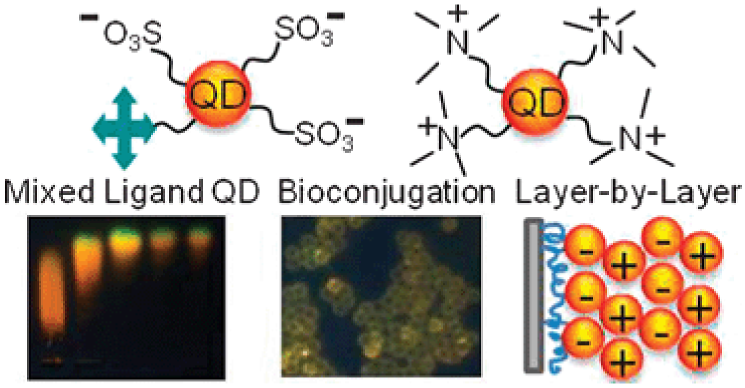


Chloride-centered hexanuclear hydroxopyrazolate reveals potential as a receptor of halomethane and halometallate species and as a molecular building block for coordination polymers.

- Strong polyelectrolyte quantum dot surface for stable bioconjugation and layer-by-layer assembly applications

  Jin, H.; Nam, J.; Park, J.; Jung, S.; Im, K.; Hur, J.; Park, J.-J.; Kim, J.-M.; Kim, S. *Chem. Commun.* **2011**, *47*, 1758-1760.

  Abstract:

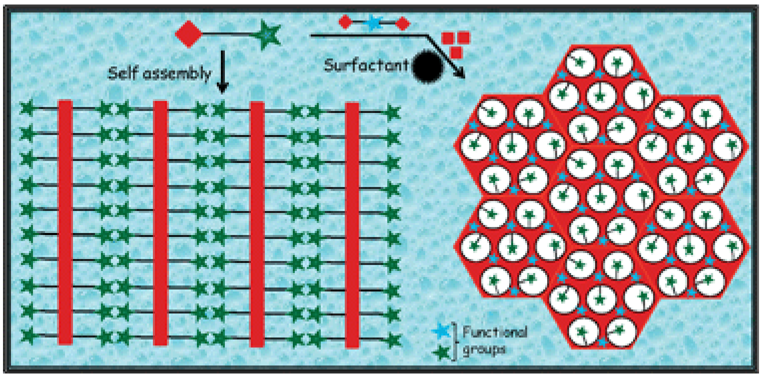


A series of quantum dot (QD) ligands are reported that can make strong polyelectrolyte QD surfaces with sulfonates or quaternary ammoniums, which can endow QDs with excellent colloidal stability independent of the pH and ionic strength, minimal hydrodynamic size, and can be exploited to achieve stable and flexible bioconjugations and layer-by-layer assembly.

- From molecular chemistry to hybrid nanomaterials. Design and functionalization

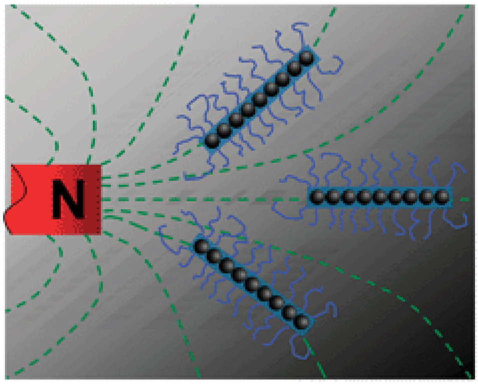
  Mehdi, A.; Reye, C.; Corriu, R. *Chem. Soc. Rev.* **2011**, *40*, 563-574.

  Abstract:



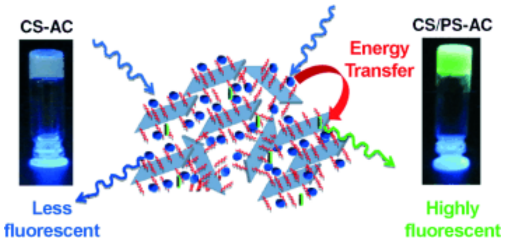
This *tutorial review* reports upon the organisation and functionalization of two families of hybrid organic–inorganic materials. We attempted to show in both cases the best ways permitting the organisation of materials in terms of properties at the nanometric scale. The first family concerns mesoporous hybrid organic–inorganic materials prepared in the presence of a structure-directing agent. We describe the functionalization of the channel pores of ordered mesoporous silica, that of the silica framework, as well as the functionalization of both of them simultaneously. This family is currently one of the best supports for exploring polyfunctional materials, which can provide a route to interactive materials. The second family concerns lamellar hybrid organic–inorganic materials which is a new class of nanostructured materials. These materials were first obtained by self-assembly, as a result of van der Waals interactions of bridged organosilica precursors containing long alkylene chains during the sol–gel process, without any structure directing agent. This methodology has been extended to functional materials. It is also shown that such materials can be obtained from monosilylated precursors.

- One-dimensional magnetic inorganic–organic hybrid nanomaterials
  Yuan, J.; Xu, Y.; Müller, A. H. E. *Chem. Soc. Rev.* **2011**, *40*, 640-655.
  Abstract:



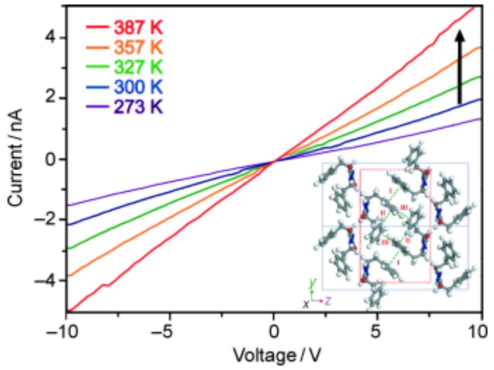
One-dimensional (1D) magnetic inorganic–organic hybrid nanomaterials bear both the intrinsic magnetic properties of the inorganic components and the functionality and responsiveness of their organic part. In this *tutorial review*, we first emphasize various synthetic strategies for this type of materials: (i) template-directed synthesis employs different preformed templates such as channels in solids, mesostructures self-assembled from block copolymers, cylindrical polymer brushes, 1D biological templates and other existing 1D templates; (ii) electrospinning, which provides a simple and efficient technique that can lead to a potential large-scale production; (iii) 1D conjugation of building blocks which combines the physical attraction of magnetic nanoparticles in a magnetic field with chemical crosslinking and stabilization. The properties, functions and the future trends of these materials are also briefly introduced. It is foreseeable that these hybrid materials will play more and more important roles in the ever-advancing miniaturization of functional devices.

- Light-Harvesting Hybrid Hydrogels: Energy-Transfer-Induced Amplified Fluorescence in Noncovalently Assembled Chromophore–Organoclay Composites
  Rao, K. V.; Datta, K. K. R.; Eswaramoorthy, M.; George, S. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 1179-1184.
  Abstract :



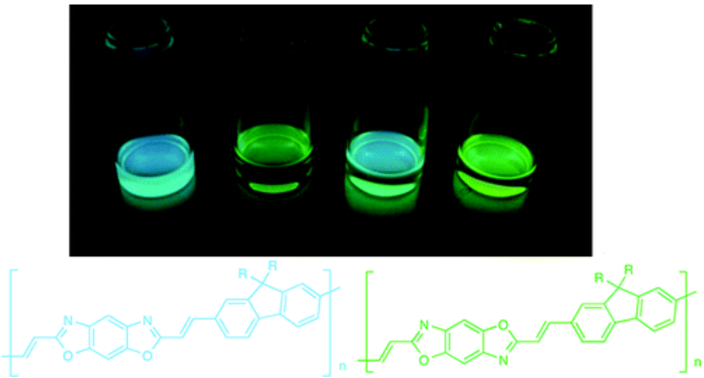
The noncovalent self-assembly of chromophores in an organoclay template results in the formation of fluorescent hybrid hydrogels and films. These clay–dye hybrids act as novel supramolecular scaffolds for light-harvesting as the aminoclay (AC) templates the spatial organization of donor and acceptor molecules to promote Förster resonant energy transfer (see picture; CS=coronene salt, PS=perylene salt).

- Self-Assembly of Semiconducting Photoluminescent Peptide Nanowires in the Vapor Phase
  Lee, J. S.; Yoon, I.; Kim, J.; Ihee, H.; Kim, B.; Park, C. B. *Angew. Chem. Int. Ed.* **2011**, *50*, 1164–1167.
  Abstract:



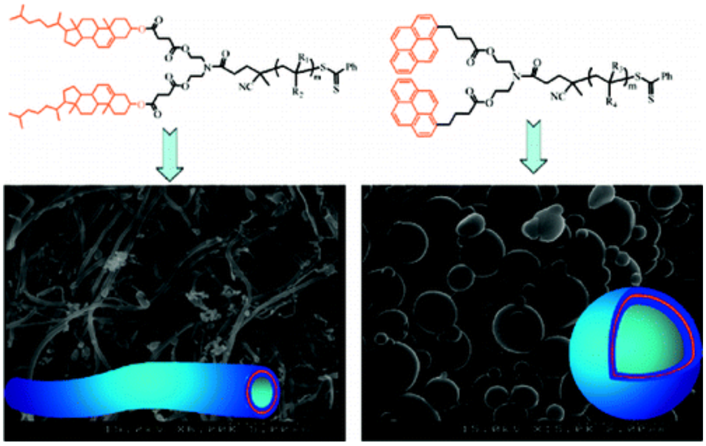
Down to the wire: A simple vapor-transport process using linear diphenylalanine as the starting material has resulted in the self-assembly of cyclodipeptide nanowires with an orthorhombic symmetry. Furthermore, the single-crystalline nanowires exhibit a strong blue luminescence centered at 465 nm and possess semiconducting properties (see picture).

- Synthesis and Characterization of Poly(9,9-dialkylfluorenevinylene benzobisoxazoles): New Solution-Processable Electron-Accepting Conjugated Polymers
  Intemann, J. J.; Mike, J. F.; Cai, M.; Bose, S.; Xiao, T.; Mauldin, T. C.; Roggers, R. A.; Shinar, J; Shinar, R.; Jeffries-EL, M. *Macromolecules* **2011**, *44*, 248–255.
  Abstract:



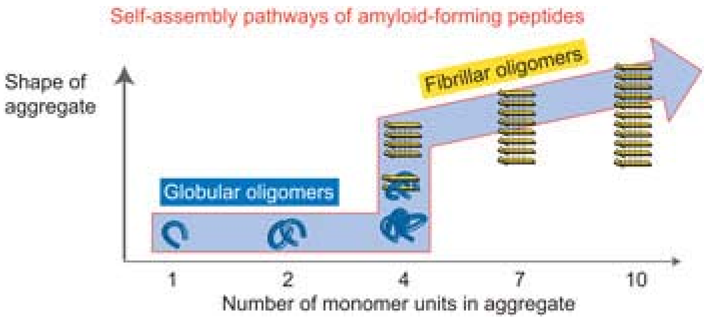
We present the synthesis of four new solution-processable, fluorescent poly(arylenevinylene)s containing benzobisoxazole and fluorene moieties. Two different moieties (cis- and trans-benzobisoxazole) and two different alkyl substituents (octyl and 3,7-dimethyloctyl) were used to study the impact of the structure on the electronic, optical, and thermal properties of these polymers. The polymers were characterized using UV–visible and fluorescence spectroscopy, cyclic voltammetry, thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). All of the polymers possess moderate molecular weights, good solubility in aprotic organic solvents, high fluorescence quantum efficiencies in dilute solutions, and high electron affinities. Cyclic voltammetry revealed quasi-reversible reduction for these polymers. Solution-processed light-emitting diodes using dilute blends of the polymer in a poly(N-vinyl carbazole) matrix gave blue emission with luminous efficiencies of up to 1 Cd/A at 470 nm which is very promising for deep blue-emitting polymer LEDs.

- Facile Access to Polymeric Vesicular Nanostructures: Remarkable ω-End group Effects in Cholesterol and Pyrene Functional (Co)Polymers
  Xu, J.; Tao, L.; Boyer, C.; Lowe, A. B.; Davis, T. P. *Macromolecules* **2011**, *44*, 299–312.
  Abstract:



Hydrophilic homopolymers of N,N-dimethylacrylamide (DMA) and N-(2-hydroxypropyl) methacrylamide (HPMA), as well as select examples of statistical copolymers with N-acryloxysuccinimide (NAS) were prepared with well-defined molecular characteristics employing a series of new RAFT chain transfer agents containing 1–4 hydrophobic functional groups in the R fragment based on pyrene, cholesterol, or octadecane, resulting in hydrophilic homopolymers containing between only 6–23 wt % hydrophobic end groups. PolyDMA (PDMA) and polyHPMA (PHPMA) homopolymers, of varying molar masses, with either bis pyrenyl or cholesteryl end groups self-assembled in aqueous media forming spherical vesicles with sizes in the range of several hundred nm up to ca. one micrometer. Lower molar mass PDMA−NAS copolymers with two cholesteryl end-groups at the ω-termini assemble to give clear tubular vesicles, whereas such copolymers of a higher molar mass preferentially form spherical polymersomes. The presence of two spatially close rigid rings at the ω-terminus is shown to be crucial in vesicle formation since a PDMA homopolymer with two octadecyl ω-end-groups self-assembles to yield polymeric micelles with an average hydrodynamic diameter of 20 nm as determined by dynamic light scattering. The presence of a C16 alkyl spacer in the R fragment in a novel dithioester CTA with two pyrenyl functional groups and its use in the polymerization of a PDMA homopolymer yields spherical polymersomes in water, in a similar manner to those formed using a CTA without a spacer, except there is no direct FE-SEM evidence of open-mouth species perhaps indicating that the added flexibility associated with the spacer groups helps facilitate full vesicle closure. The synthesis of a biodegradable bis-pyrenyl dithioester, containing disulfide bridges, facilitates the preparation of PDMA-based polymersomes capable of dithiothreitol-induced pyrene release as evidenced by fluorescence emission spectroscopy. The same biodegradable polymersomes are also shown to be able to sequester the hydrophilic model drug Rhodamine B whose controlled release is demonstrated to be dependent on the presence, or absence, of dithiothreitol as determined by UV−vis spectroscopy.

- Ion mobility–mass spectrometry reveals a conformational conversion from random assembly to β-sheet in amyloid fibril formation
  Bleiholder, C.; Dupuis, N. F.; Wyttenbach, T.; Bowers, M. T. *Nature Chemistry* **2011**, *3*, 172–177.
  Abstract:

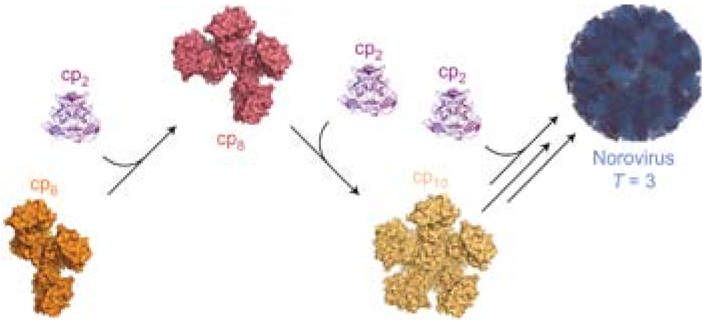


Amyloid cascades that lead to peptide β-sheet fibrils and plaques are central to many important diseases. Recently, intermediate assemblies of these cascades were identified as the toxic agents that interact with cellular machinery. The location and cause of the transformation from a natively unstructured assembly to the β-sheet oligomers found in all fibrils is important in understanding disease onset and the development of therapeutic agents. Largely, research on this early oligomeric region was unsuccessful because all the traditional techniques measure only the average oligomer properties of the ensemble. We utilized ion-mobility methods to deduce the peptide self-assembly mechanism and examined a series of amyloid-forming peptides clipped from larger peptides or proteins associated with disease. We provide unambiguous evidence for structural transitions in each of these fibril-forming peptide systems and establish the potential of this method for the development of therapeutic agents and drug evaluation.

- Interrogating viral capsid assembly with ion mobility–mass spectrometry

Uetrecht, C.; Barbu, I. M.; Shoemaker, G. K.; van Duijn, E.; Heck, A. J. R. *Nature Chemistry* **2011**, *3*, 126–132.

Abstract:

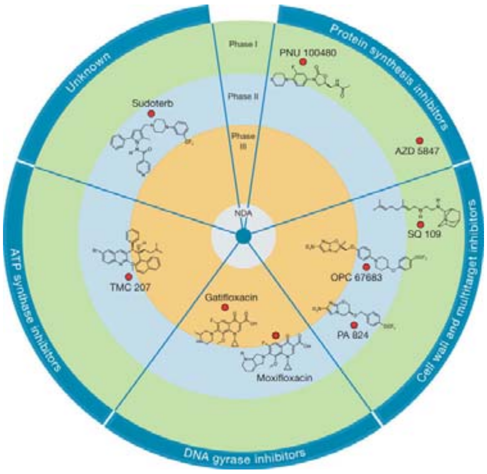


Most proteins fulfil their function as part of large protein complexes. Surprisingly, little is known about the pathways and regulation of protein assembly. Several viral coat proteins can spontaneously assemble into capsids *in vitro* with morphologies identical to the native virion and thus resemble ideal model systems for studying protein complex formation. Even for these systems, the mechanism for self-assembly is still poorly understood, although it is generally thought that smaller oligomeric structures form key intermediates. This assembly nucleus and larger viral assembly intermediates are typically low abundant and difficult to monitor. Here, we characterised small oligomers of Hepatitis B virus (HBV) and norovirus under equilibrium conditions using native ion mobility mass spectrometry. This data in conjunction with computational modelling enabled us to elucidate structural features of these oligomers. Instead of more globular shapes, the intermediates exhibit sheet-like structures suggesting that they are assembly competent. We propose pathways for the formation of both capsids.

- The challenge of new drug discovery for tuberculosis

  Koul, A.; Arnoult, E.; Lounis, N.; Guillemont, J.; Andries, K. *Nature* **2011**, *469*, 483–490.

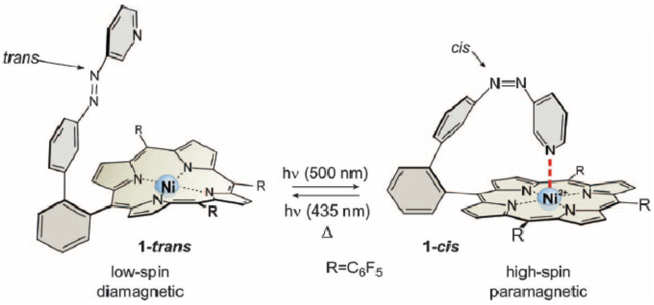
  Abstract:



Tuberculosis (TB) is more prevalent in the world today than at any other time in human history. *Mycobacterium tuberculosis,* the pathogen responsible for TB, uses diverse strategies to survive in a variety of host lesions and to evade immune surveillance. A key question is how robust are our approaches to discovering new TB drugs, and what measures could be taken to reduce the long and protracted clinical development of new drugs. The emergence of multi-drug-resistant strains of *M. tuberculosis* makes the discovery of new molecular scaffolds a priority, and the current situation even necessitates the re-engineering and repositioning of some old drug families to achieve effective

control. Whatever the strategy used, success will depend largely on our proper understanding of the complex interactions between the pathogen and its human host. In this review, we discuss innovations in TB drug discovery and evolving strategies to bring newer agents more quickly to patients.

- Magnetic Bistability of Molecules in Homogeneous Solution at Room Temperature
  Venkataramani, S.; Jana, U.; Dommaschk, M.; Sönnichsen, F. D.; Tuczek, F.; Herges, R. *Science* **2011**, *331*, 445-448.
  Abstract:



Magnetic bistability, as manifested in the magnetization of ferromagnetic materials or spin crossover in transition metal complexes, has essentially been restricted to either bulk materials or to very low temperatures. We now present a molecular spin switch that is bistable at room temperature in homogeneous solution. Irradiation of a carefully designed nickel complex with blue-green light (500 nanometers) induces coordination of a tethered pyridine ligand and concomitant electronic rearrangement from a diamagnetic to a paramagnetic state in up to 75% of the ensemble. The process is fully reversible on irradiation with violet-blue light (435 nanometers). No fatigue or degradation is observed after several thousand cycles at room temperature under air. Preliminary data show promise for applications in magnetic resonance imaging.