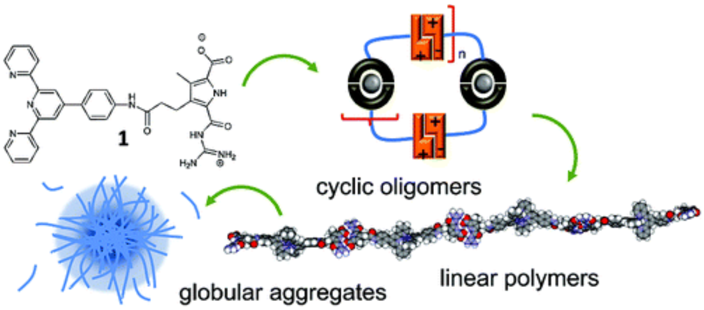
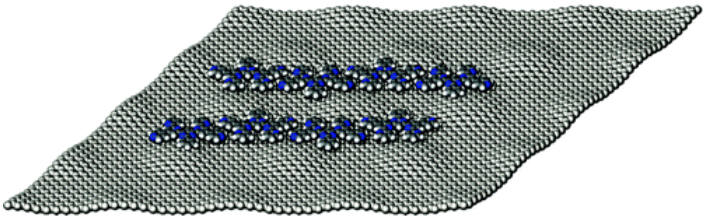
- Switchable Supramolecular Polymers from the Self-Assembly of a Small Monomer with Two Orthogonal Binding Interactions
  Gröger, G.; Meyer-Zaika, W.; Böttcher, C.; Gröhn, F.; Ruthard, C.; Schmuck, C. *J. Am. Chem. Soc.* **2011**, *133*, 8961-8971.
  Abstract:



The low molecular weight heteroditopic monomer 1 forms supramolecular polymers in polar solution as shown, for example, by infrared laser-based dynamic light scattering (DLS), small-angle neutron scattering (SANS), electron microscopy (TEM, cryo-TEM), and viscosity measurements. Self-assembly of 1 is based on two orthogonal binding interactions, the formation of a Fe(II)-terpyridine 1:2 metal–ligand complex and the dimerization of a self-complementary guanidiniocarbonyl pyrrole carboxylate zwitterion. Both binding interactions have a sufficient stability in polar (DMSO) and even aqueous solutions to ensure formation of linear polymers of considerable length (up to 100 nm). The supramolecular polymerization follows a ring–chain mechanism causing a significant increase in the viscosity of the solutions at millimolar concentrations and above. The linear polymers then further aggregate in solution into larger globular aggregates with a densely packed core and a loose shell. Both binding interactions can be furthermore switched on and off either by adding a competing ligand to remove the metal ion and subsequent readdition of Fe(II) or by reversible protonation and deprotonation of the zwitterion upon addition of acid or base. The self-assembly of 1 can therefore be switched back and forth between four different states, the monomer, a metal-complexed dimer or an ion paired dimer, and finally the polymer.

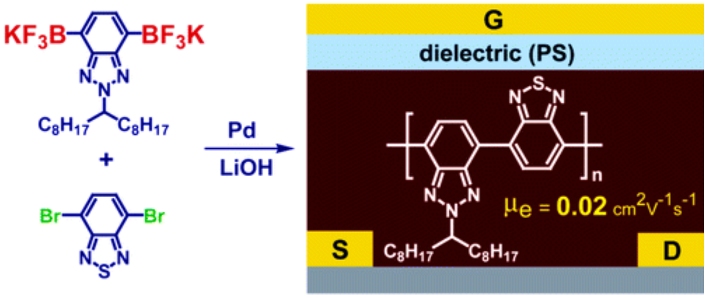
- Hierarchical Interactions and Their Influence upon the Adsorption of Organic Molecules on a Graphene Film
  Roos, M.; Künzel, D.; Uhl, B.; Huang, H.-H.; Brandao Alves, O.; Hoster, H. E.; Gross, A.; Behm, R. J. *J. Am. Chem. Soc.* **2011**, *133*, 9208-9211.
  Abstract:



The competition between intermolecular interactions and lateral variations in the molecule–substrate interactions has been studied by scanning tunneling microscopy (STM), comparing the phase formation of (sub)monolayers of the organic molecule 2,4′-BTP on buckled graphene/Ru(0001) and Ag(111) oriented thin films on Ru(0001). On the Ag films, the molecules form a densely packed 2D structure, while on graphene/Ru(0001), only the areas between the maxima are populated. The findings are rationalized by a high corrugation in the adsorption potential for 2,4′-BTP molecules on

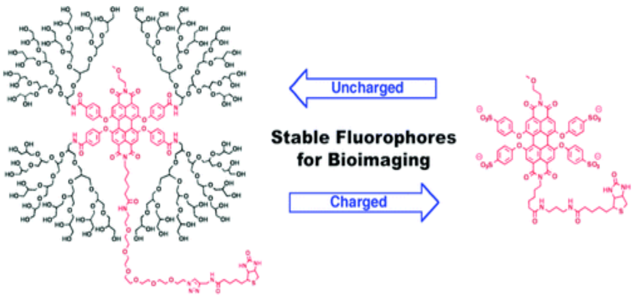
graphene/Ru(0001). These findings are supported by temperature programmed desorption (TPD) experiments and theoretical results.

- High-Performance Electron-Transporting Polymers Derived from a Heteroaryl Bis(trifluoroborate)
  Lee, J.-K.; Gwinner, M. C.; Berger, R.; Newby, C.; Zentel, R.; Friend, R. H.; Sirringhaus, H.; Ober, C. K. *J. Am. Chem. Soc.* **2011**, *133*, 9949–9951.
  Abstract:



In this communication, we report that dipotassium aryl bis(trifluoroborate)s make stable and easy-to-purify yet reactive monomers under Suzuki polycondensation reactions. A bis(trifluoroborate) of 2-alkylbenzotriazole was prepared successfully and copolymerized with dibromobenzothiadiazole in the presence of a Pd catalyst and LiOH, yielding high molecular weight conjugated polymers. This polymer (**P1**) composed of all electron-accepting units shows excellent electron-transport properties ($\mu_e = 0.02\ cm^2\ V^{-1}\ s^{-1}$), which proves the value of the aryl bis(trifluoroborate) monomers and suggests that many other types of semiconducting polymers that could not be accessed previously can be synthesized using this approach.

- Monovalent, Clickable, Uncharged, Water-Soluble Perylenediimide-Cored Dendrimers for Target-Specific Fluorescent Biolabeling
  Yang, S. K.; Shi, X.; Park, S.; Doganay, S.; Ha, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2011**, *133*, 9964–9967.
  Abstract:

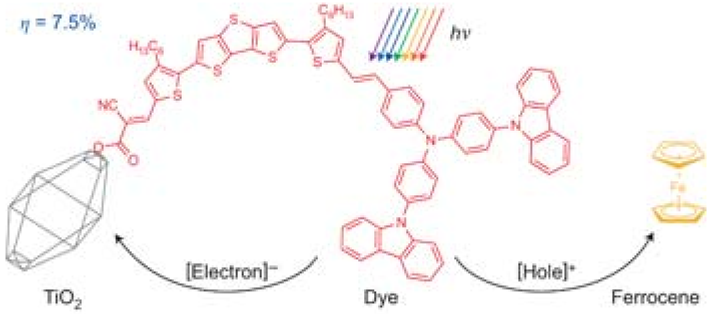


Herein we report the synthesis of water-soluble polyglycerol-dendronized perylenediimides with a single reactive group that undergoes high-yielding click reactions. Single-molecule studies and target-specific biolabeling are reported, including the highly specific labeling of proteins on the surface of living bacterial and mammalian cells.

- High-efficiency dye-sensitized solar cells with ferrocene-based electrolytes

Daeneke, T.; Kwon, T.-H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. *Nature Chemistry* **2011**, *3*, 211-215.

Abstract:

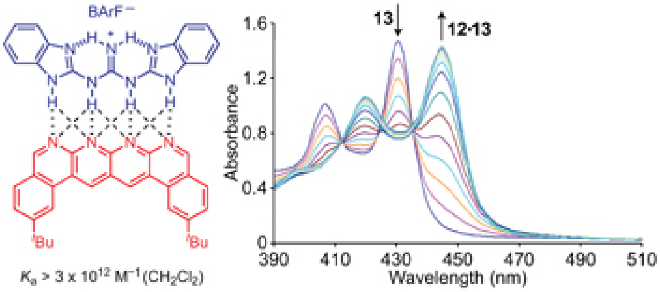


Dye-sensitized solar cells based on iodide/triiodide (I^-/I_3^-) electrolytes are viable low-cost alternatives to conventional silicon solar cells. However, as well as providing record efficiencies of up to 12.0%, the use of I^-/I_3^- in such solar cells also brings about certain limitations that stem from its corrosive nature and complex two-electron redox chemistry. Alternative redox mediators have been investigated, but these generally fall well short of matching the performance of conventional I^-/I_3^- electrolytes. Here, we report energy conversion efficiencies of 7.5% (simulated sunlight, AM1.5, 1,000Wm^{-2}) for dye-sensitized solar cells combining the archetypal ferrocene/ferrocenium (Fc/Fc$^+$) single-electron redox couple with a novel metal-free organic donor–acceptor sensitizer (Carbz-PAHTDTT). These Fc/Fc$^+$-based devices exceed the efficiency achieved for devices prepared using I^-/I_3^- electrolytes under comparable conditions, revealing the great potential of ferrocene-based electrolytes in future dye-sensitized solar cells applications. This improvement results from a more favourable matching of the redox potential of the ferrocene couple with that of the new donor–acceptor sensitizer.

- An AAAA–DDDD quadruple hydrogen-bond array

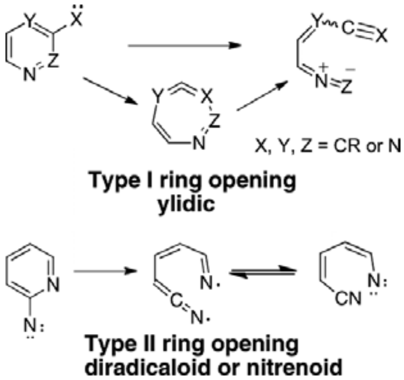
  Blight, B. A.; Hunter, C. A.; Leigh, D. A.; McNab, H.; Thomson, P. I. T. *Nature Chemistry* **2011**, *3*, 244-248.

  Abstract:



Secondary electrostatic interactions between adjacent hydrogen bonds can have a significant effect on the stability of a supramolecular complex. In theory, the binding strength should be maximized if all the hydrogen-bond donors (D) are on one component and all the hydrogen-bond acceptors (A) are on the other. Here, we describe a readily accessible AAAA–DDDD quadruple hydrogen-bonding array that exhibits exceptionally strong binding for a small-molecule hydrogen-bonded complex in a range of different solvents ($K_a > 3 \times 10^{12}$ M^{-1} in CH_2Cl_2, 1.5×10^6 M^{-1} in CH_3CN and 3.4×10^5 M^{-1} in 10% v/v DMSO/$CHCl_3$). The association constant in CH_2Cl_2 corresponds to a binding free energy (ΔG) in excess of –71 kJ mol^{-1} (more than 20% of the thermodynamic stability of a carbon–carbon covalent bond), which is remarkable for a supramolecular complex held together by just four intercomponent hydrogen bonds.

- Nitrenes, Carbenes, Diradicals, and Ylides. Interconversions of Reactive Intermediates
  Wentrup, C. *Acc. Chem. Res.* **2011**, *44*, 393–404.
  Abstract:



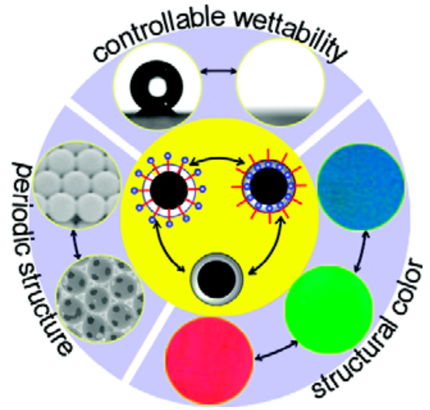
Rearrangements of aromatic and heteroaromatic nitrenes and carbenes can be initiated with either heat or light. The thermal reaction is typically induced by flash vacuum thermolysis, with isolation of the products at low temperatures. Photochemical experiments are conducted either under matrix isolation conditions or in solution at ambient temperature. These rearrangements are usually initiated by ring expansion of the nitrene or carbene to a seven-membered ring ketenimine, carbodiimide, or allene (that is, a cycloheptatetraene or an azacycloheptatetraene when a nitrogen is involved).

Over the last few years, we have found that two types of ring opening take place as well. Type I is an ylidic ring opening that yields nitrile ylides or diazo compounds as transient intermediates. Type II ring opening produces either dienylnitrenes (for example, from 2-pyridylnitrenes) or 1,7-(1,5)-diradicals (such as those formed from 2-quinoxalinylnitrenes), depending on which of these species is better stabilized by resonance. In this Account, we describe our achievements in elucidating the nature of the ring-opened species and unraveling the connections between the various reactive intermediates.

Both of these ring-opening reactions are found, at least in some cases, to dominate the subsequent chemistry. Examples include the formation of ring-opened ketenimines and carbodiimides, as well as the ring contraction reactions that form five-membered ring nitriles (such as 2- and 3-cyanopyrroles from pyridylnitrenes, *N*-cyanoimidazoles from 2-pyrazinyl and 4-pyrimidinylnitrenes, *N*-cyanopyrazoles from 2-pyrimidinylnitrenes and 3-pyridazinylnitrenes, and so forth). The mechanisms of formation of the open-chain and ring-contraction products were unknown at the onset of this study. In the course of our investigation, several reactions with three or more consecutive reactive intermediates have been unraveled, such as nitrene, seven-membered cyclic carbodiimide, and open-chain nitrile ylide. It has been possible in some cases to observe them all and determine their interrelationships by means of a combination of matrix-isolation spectroscopy, photochemistry, flash vacuum thermolysis, and computational chemistry.

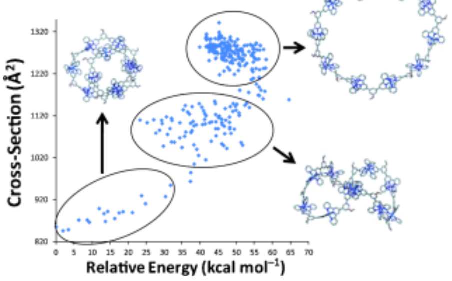
These studies have led to a deeper understanding of the nature of reactive intermediates and chemical reactivity. Moreover, the results indicate new directions for further exploration: ring-opening reactions of carbenes, nitrenes, and cyclic cumulenes can be expected in many other systems.

- Bioinspired Colloidal Photonic Crystals with Controllable Wettability
  Wang, J.; Zhang, Y.; Wang, S.; Song, Y.; Jiang, L. *Acc. Chem. Res.* **2011**, *44*, 405–415.
  Abstract:



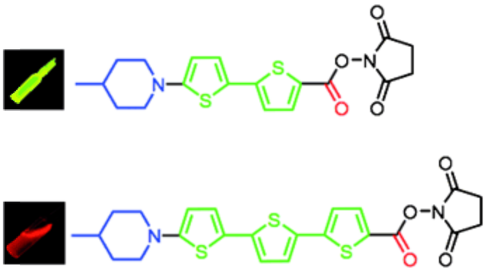
Because of the combinatorial advantage of their unique light manipulation properties and potential applications in novel optical devices, colloidal photonic crystals (PCs), the periodic arrangement of monodispersed latex spheres, have attracted interest from researchers. In particular, colloidal PCs exhibit structural colors based on interference effects within their periodic structures. The wavelength of these colors lies in the visible range, making them particularly attractive for a variety of applications. Colloidal PCs are extensively used in templating, catalysis, and chromatographic separations. Inspired by biological PCs with both structural color and specific wettability, researchers have fabricated colloidal PCs with controllable wettability as described in this Account. The wettability can be adjusted by the intrinsic roughness of colloidal crystals in combination with the tunable chemical composition of latex surfaces. Changes in the chemical composition of the latex surface under external stimuli, such as light, electricity, and heat, can reversibly control the wettability of PCs. Furthermore, the hierarchical structure of latex particles can effectively alter the water adhesive force of superhydrophobic colloidal PCs. Patterned PCs with a variety of wettabilities can be assembled using inkjet printing from well-designed latex suspensions.
By combining their structural color and specific wettability, we also exemplify some of the promising applications of colloidal PCs as templates for the construction of hierarchical structures, as indicators for controllable transport of liquid droplets, and as color-based sensors for the monitoring changes in their environment. These findings offer innovative insights into the design of novel colloidal PCs and will be of great importance for further applications of these materials.

- Towards Larger Polygonal Architectures: Synthesis and Characterization of Iron(II)– and Ruthenium(II)–Bis(terpyridine) Metallomacrocycles
  Chan, Y. T.; Li, X.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem. Eur. J.* **2011**, *17,* 7750–7754.
  Abstract:



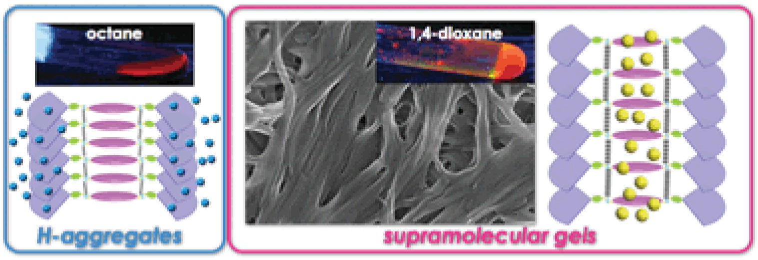
Five- through ten-membered homo- and heteronuclear metallomacrocycles possessing <tpy-Fe^{II} (or Ru^{II})-tpy> connectivity have been prepared and isolated. Characterization includes a detailed analysis using traveling wave ion-mobility mass spectrometry, which allows the separation and identification of individual conformers based on size and charge. Conformer size derived from molecular modeling agrees well with collision cross-sections determined by the mass spectrometry experiments (see graphic).

- Push–Pull Amino Succinimidyl Ester Thiophene-Based Fluorescent Dyes: Synthesis and Optical Characterization
  Sotgiu, G.; Galeotti, M.; Samorí, C.; Bongini, A.; Mazzanti, A. *Chem. Eur. J.* **2011**, *17,* 7947–7952.
  Abstract:



The design and synthesis of new fluorescent dyes with emission range at 490–650 nm are described. Their structural and electronic properties have been characterized by both experimental techniques and quantum-chemical calculations. The chromophores are donor–π-bridge–acceptor push–pull compounds with a π bridge of phenyl and thiophene rings and their combination. Compared with previous thiophene fluorophores, these dyes show significant redshift in the absorption and emission spectra and offer compact, red-emitting fluorophores. The dyes have amino succinimidyl active ester and can be readily conjugated to proteins, polymers and other amino-group-containing materials.

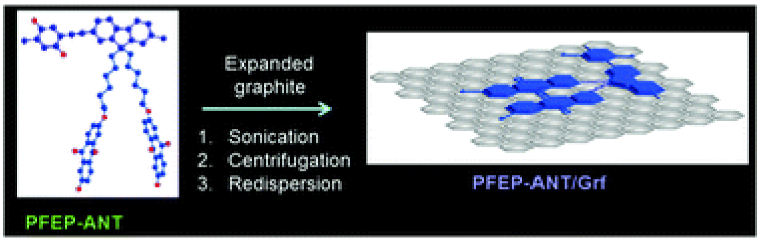
- Solvent-dependent supramolecular assemblies of π-conjugated anion-responsive acyclic oligopyrroles
  Maeda, H.; Terashima, Y. *Chem. Commun.* **2011**, *47*, 7620-7622.
  Abstract:



Amide-attached pyrrole-based π-conjugated anion receptors showed solvent-dependent assembled modes such as H-aggregates that were soluble in octane and highly organized structures that provided supramolecular gels in CH_2Cl_2 and 1,4-dioxane in the absence of π–π stacking.

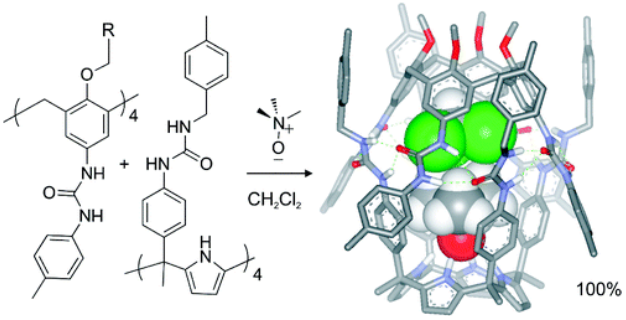
- Supramolecular assembly of graphene with functionalized poly(fluorene-*alt*-phenylene): the role of the anthraquinone pendant groups
  Castelaín, M.; Salavagione, H. J.; Gómez, R.; Segura, J. L. *Chem. Commun.* **2011**, *47*, 7677-7679.

Abstract:



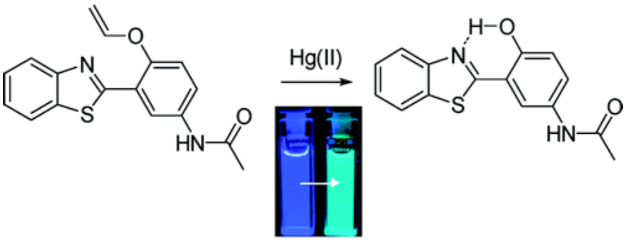
Supramolecular assembled graphene/conjugated polymer materials with intriguing electronic and electrochemical properties are prepared.

- Exclusive Self-Assembly of a Polar Dimeric Capsule between Tetraurea Calix[4]pyrrole and Tetraurea Calix[4]arene
  Chas, M.; Gil-Ramrez, G.; Ballester, P. *Org. Lett.* **2011**, *13*, 3402–3405.
  Abstract:



The exclusive self-sorting observed in the self-assembly process between tetraurea benzyl calix[4]pyrroles and tetraurea tolyl calix[4]arene to afford unprecedented hybrid dimeric capsules with polar interiors is described. The coencapsulation of a solvent molecule with an organic guest yields four particle aggregates in which the guests are confined and restricted into single hemispheres due to the polar requirements of the internal cavity.

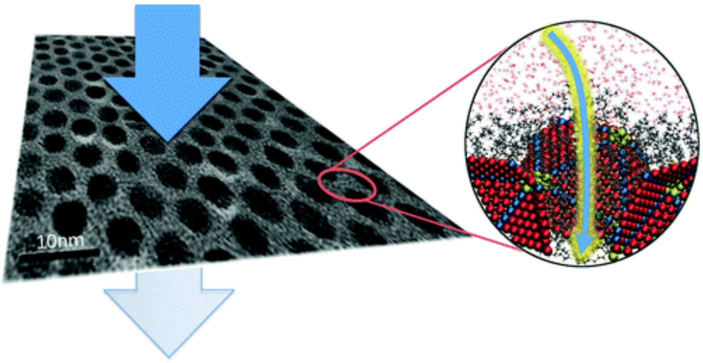
- A “Reactive” Ratiometric Fluorescent Probe for Mercury Species
  Santra, M.; Roy, B.; Han Ahn, K. *Org. Lett.* **2011**, *13*, 3422–3425.
  Abstract:



A ratiometric fluorescent probe for mercury species is developed based on the metal-promoted hydrolysis of a vinyl ether derivative of 2-(benzothiazol-2-yl)phenol in a buffer solution. The probe responds selectively to mercury species over various other metal ions with a marked fluorescence change from blue to cyan through the excited state intramolecular proton transfer (ESIPT) process. The fluorescence titration is complete with 0.5 equiv of $HgCl_2$, which indicates that the probe also responds to organomercury species, RHgCl.

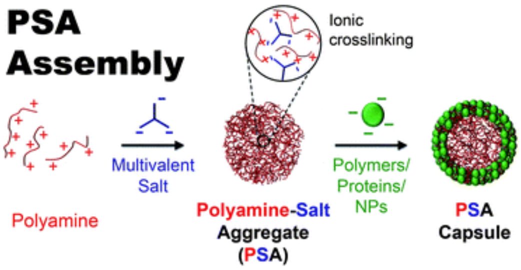
- Diffusion and Filtration Properties of Self-Assembled Gold Nanocrystal Membranes

He, J.; Lin, X.-M.; Chan, H.; Vukovi, L.; Kral, P.; Jaeger, H. M. *Nano Lett.* **2011**, *11* , 2430–2435.
Abstract:



Close-packed nanoparticle monolayers have recently been shown to form mechanically robust, free-standing membranes. We report the first measurements of molecular transport through such ultrathin sheets, self-assembled from dodecanethiol-ligated gold nanocrystals. For aqueous solutions we find filtration coefficients 2 orders of magnitude larger than those observed in polymer-based filters, sieving of large solutes, and for smaller solutes a pronounced dependence of rejection on being charged. These results open up new possibilities for controlled delivery and separation of nano-objects.

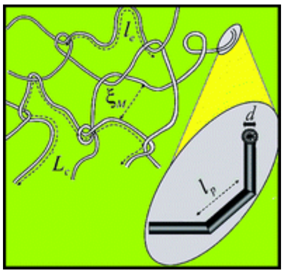
- Polyamine–salt aggregate assembly of capsules as responsive drug delivery vehicles
  Bagaria, H. G.; Wong, M. S. *J. Mater. Chem.* **2011**, *21*, 9454-9466.
  Abstract:



Responsive capsular delivery systems that can partly mimic the complexity of cellular systems hold great promise for the future of medicine. Simple self-assembled systems like liposomes are already in clinical use and others like polymeric micelles are under clinical trials. Unlike these self-assembled systems, the greater flexibility and versatility offered by template-based routes will likely drive the development of sophisticated capsules. The focus of this review is to introduce one such template-based route, which is based on polyamine–salt aggregate or 'PSA' assembly. The basic synthesis premise involves the assembly of cationic polymer (like poly-L-lysine) by ionic crosslinking with multivalent anionic salts (like citrate) into metastable templates for cargo encapsulation and shell material deposition. The technique offers several benefits: (i) the synthesis procedure involves simple mixing at ambient conditions, (ii) the capsule size is easy to control in the sub-100 nm to micron range, and (iii) a wide range of formulations is readily available with the use of different polymer, salt, cargo, and shell-forming precursors. In this review, the current state of this technique, the materials chemistry of the capsule assembly, and the demonstrated applications, including photothermal therapy, MRI contrast agent development and protease-responsive NIR imaging, will be discussed.

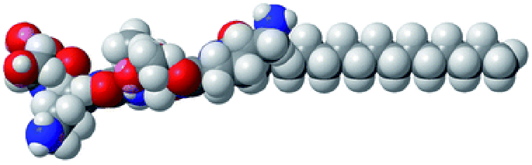
- Microrheology of solutions embedded with thread-like supramolecular structures

Lopez-Diaz, D., Castillo, R. *Soft Matter* **2011**, *7*, 5926-5937.
Abstract:



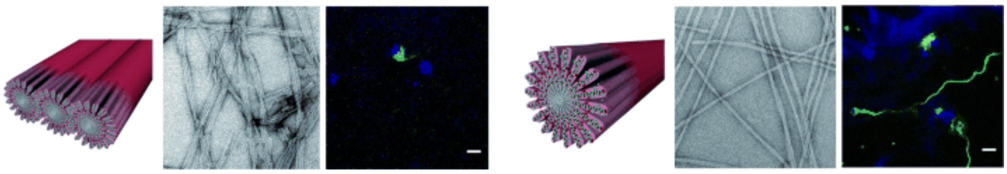
A family of methods uses colloidal particles as a mechanical probe for deforming the medium in conjunction with a procedure to trace the movement of the particles to get rheological information in a very wide frequency range. All of them are under the heading of microrheology. In the last decade, they have been developed up to the point of being a useful tool for understanding the structure and the dynamics of solutions with embedded thread-like supramolecular structures. This is the case of wormlike micellar solutions, which is the main interest of the paper. Here the impact of microrheology has been essential, providing structural information not easily obtained by other methods. Microrheology has also made an important contribution to the understanding of other threadlike system, as in the case of F-actin or fd virus solutions; they will also be discussed.

- Self-assembly of amphiphilic peptides
  Hamley, I. W. *Soft Matter* **2011**, *7*, 4122-4138.
  Abstract:



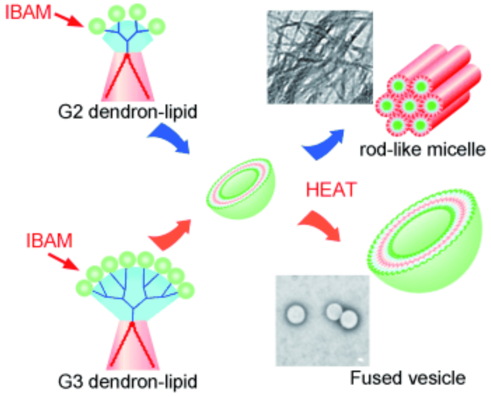
The self-assembly of amphiphilic peptides is reviewed. The review covers surfactant-like peptides with amphiphilicity arising from the sequence of natural amino acids, and also peptide amphiphiles (PAs) in which lipid chains are attached to hydrophilic peptide sequences containing charged residues. The influence of the secondary structure on the self-assembled structure and vice versa is discussed. For surfactant-like peptides structures including fibrils, nanotubes, micelles and vesicles have been reported. A particularly common motif for PAs is β-sheet based fibrils, although other structures have been observed. In these structures, the peptide epitope is presented at the surface of the nanostructure, providing remarkable bioactivity. Recent discoveries of potential, and actual, applications of these materials in biomedicine and bionanotechnology are discussed.

- Electrostatic Control of Bioactivity
  Goldberger, J. E.; Berns, E. J.; Bitton, R.; Newcomb, C. J.; Stupp, S. I. *Angew. Chem. Int. Ed.* **2011**, *50*, 6292–6295.
  Abstract:



The power of independence: When exhibited on the surface of self-assembling peptide-amphiphile nanofibers, the hydrophobic laminin-derived IKVAV epitope induced nanofiber bundling through interdigitation with neighboring fibers and thus decreased the bioactivity of the resulting materials. The inclusion of charged amino acids in the peptide amphiphiles disrupted the tendency to bundle and led to significantly enhanced neurite outgrowth (see picture).

- Thermosensitive Molecular Assemblies from Poly(amidoamine) Dendron-Based Lipids
  Kono, K.; Murakami, E.; Hiranaka, Y.; Yuba, E.; Kojima, C.; Harada, A.; Sakurai, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 6332–6336.
  Abstract:



The heat is on: Vesicles formed from poly(amidoamine) dendron-based lipids with terminal isobutyramide (IBAM) groups undergo a temperature-dependent structural transition through a change in hydration of the vesicle surface. The vesicles are stable at low temperature, but form aggregates above a specific temperature and transform to inverted rodlike micelles or fused vesicles (see picture; G2/G3=second/third generation).