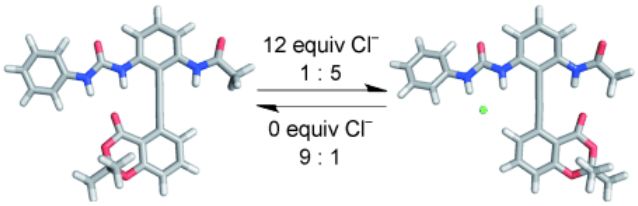
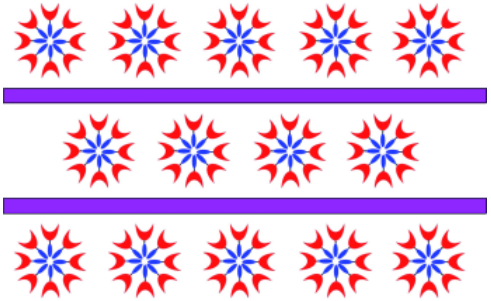
- Anion-Dependent Switching: Dynamically Controlling the Conformation of Hydrogen-Bonded Diphenylacetylenes
  Jones, I. M.; Hamilton, A. D. *Angew. Chem. Int. Ed.* **2011**, *50*, 4597–4600.
  Abstract:



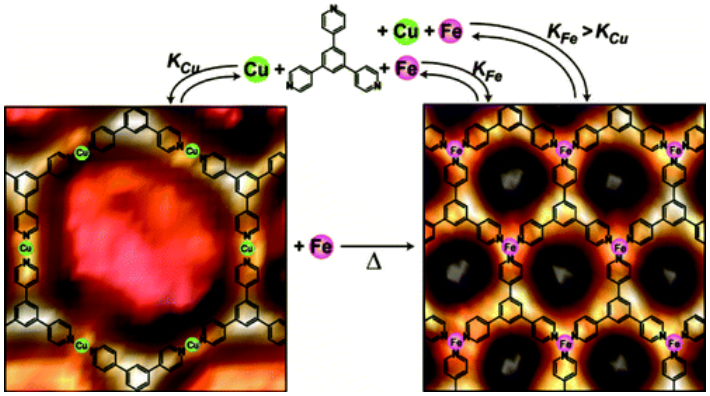
With a grain of salt: An anion-dependent switch based on an intramolecularly H-bonded diphenylacetylene is reported. The addition of Cl^- causes the conformation of the H-bond acceptor to switch from the urea protons to the amide proton (see scheme; blue N, red O, green Cl), suggesting the use of such systems as fluorescent anion sensors.

- Self-Assembling Ligands for Multivalent Nanoscale Heparin Binding
  Rodrigo, A. C.; Barnard, A.; Cooper, J.; Smith, D. K. *Angew. Chem. Int. Ed.* **2011**, *50*, 4675–4679.
  Abstract:



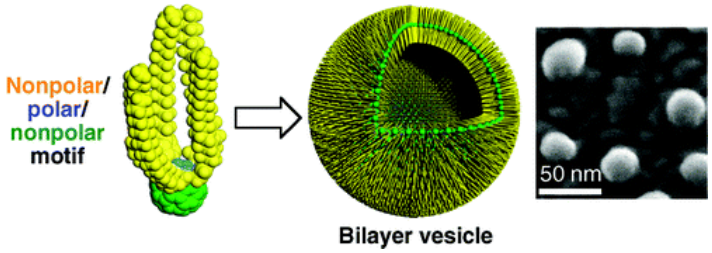
Supramolecular string of pearls: Polycationic ligands are designed to self-assemble into spherical pseudo-dendrimers that are capable of binding polyanionic heparin with affinities and binding modes similar to covalent nanostructures such as dendrimers and proteins (see picture; purple: heparin, red/blue: self-assembling ligand). Binding of the ligands to heparin induces nanoscale organization of the formed nanostructures.

- Thermodynamics and Selectivity of Two-Dimensional Metallo-supramolecular Self-Assembly Resolved at Molecular Scale
  Shi, Z.; Liu, J.; Lin, T.; Xia, F.; Liu, P. N.; Lin, N. *J. Am. Chem. Soc.* **2011**, *133*, 6150-6153.
  Abstract:



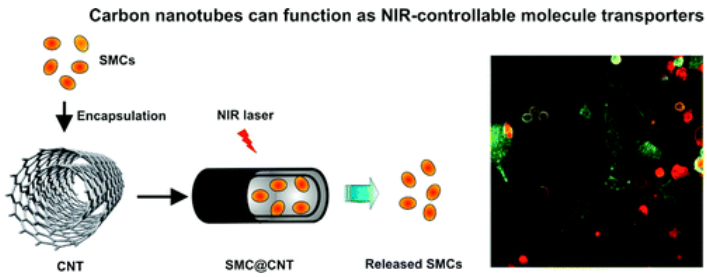
We investigated the thermodynamic processes of two-dimensional (2D) metallo-supramolecular self-assembly at molecular resolution using scanning tunneling microscopy and variable-temperature low-energy electron diffraction. On a Au(111) substrate, tripyridyl ligands coordinated with Cu in a twofold Cu–pyridyl binding mode or with Fe in a threefold Fe–pyridyl binding mode, forming a 2D open network structure in each case. The network structures exhibited remarkable thermal stability (600 K for the Cu-coordinated network and 680 K for the Fe-coordinated network). The Fe–pyridyl binding was selected thermodynamically as well as kinetically in self-assembly involving both modes. The selectivity can be effectively suppressed in a specifically designed self-assembly route.

- Preparation and Properties of Vesicles Made of Nonpolar/Polar/Nonpolar Fullerene Amphiphiles
  Homma, T.; Harano, K.; Isobe, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 6364-6370.
  Abstract:



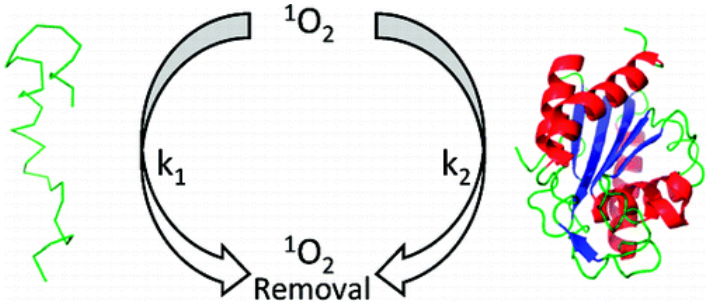
Twenty potassium complexes of penta-[(4-substituted)phenyl][60]fullerene anions were synthesized and examined for their ability to form bilayer vesicles in water. The 4-substituents include alkyl groups ranging from methyl to icosanyl groups and perfluoromethyl, perfluorobutyl, and perfluorooctyl groups. The overall structure of the amphiphiles can be described as a nonpolar/polar/nonpolar (n–p–n′) motif as opposed to the usual polar/nonpolar motif of lipid amphiphiles. Despite the hydrophobicity of the fullerene moiety (n-part) and alkyl/perfluoroalkyl chains (n′-part), all compounds except for the one with perfluoromethyl groups were soluble in water because of the centrally located fullerene cyclopentadienide (p-part) and spontaneously formed a vesicle of 25- to 60-nm diameter with a narrow unimodal size distribution. The vesicles are stable upon heating to 90 °C or standing over one year in air, as well as on a solid substrate in air or in vacuum, maintaining their spherical form. The vesicle membrane consists of an interdigitated bilayer of the amphiphile molecules, in which the fullerene n-part is inside and the n′-side is exposed to water. These vesicles, in particular the one bearing icosanyl chains, exhibit the smallest water permeability coefficient ever found for a self-assembled membrane in water.

- Controllable Delivery of Small-Molecule Compounds to Targeted Cells Utilizing Carbon Nanotubes
  Su, Z.; Zhu, S.; Donkor, A. D.; Tzoganakis, C.; Honek, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 6874–6877.
  Abstract:



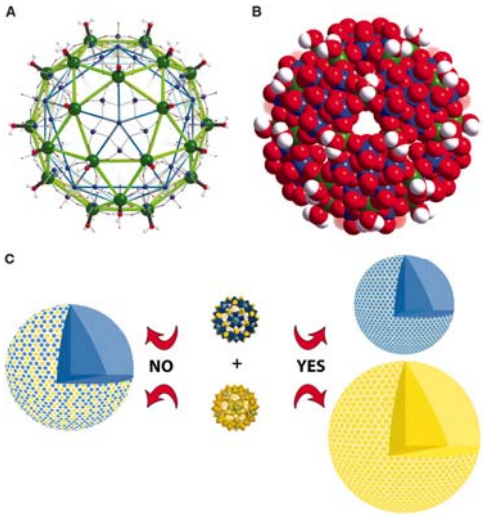
Carbon nanotubes (CNTs) have emerged as a new alternative and efficient tool for transporting molecules with biotechnological and biomedical applications, because of their remarkable physicochemical properties. Encapsulation of functional molecules into the hollow chambers of CNTs can not only stabilize encapsulated molecules but also generate new nanodevices. In this work, we have demonstrated that CNTs can function as controllable carriers to transport small-molecule compounds (SMCs) loaded inside their hollow tunnels onto targeted cells. Using indole as model compound, CNTs can protect indole molecules during transportation. Labeling indole-loaded CNTs (indole@CNTs) with EphB4-binding peptides generates cell-homing indole@CNTs (CIDs). CIDs can selectively target EphB4-expressing cells and release indole onto cell surfaces by near-infrared (NIR) irradiation. Released indole molecules exhibit significant cell-killing effects without causing local overheating. This establishes CNTs as excellent near-infrared controllable delivery vehicles for SMCs as selective cell-killing agents.

- Singlet Oxygen's Response to Protein Dynamics
  Jensen, R. L.; Arnbjerg, J.; Birkedal, H.; Ogilby, P. R. *J. Am. Chem. Soc.* **2011**, *133*, 7166–7173.
  Abstract:



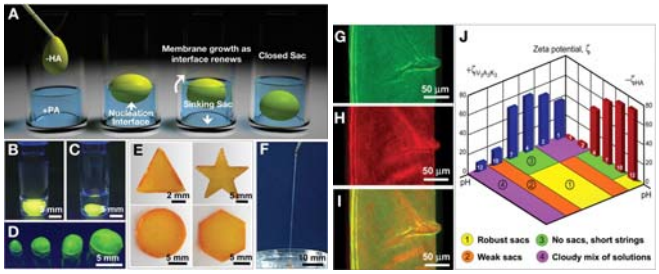
Singlet molecular oxygen, $O_2(a^1\Delta_g)$, is an intermediate in a variety of processes pertinent to the function of biological systems, including events that result in cell death. Many of these processes involve a reaction between singlet oxygen and a given protein. It is acknowledged that the behavior of a protein can change upon reaction with singlet oxygen, as a result of a structural alteration and/or a direct chemical modification of an active site. However, the converse, where one considers how the behavior of singlet oxygen can be altered by changes in protein structure, has received little attention. In this report, we use a variety of proteins to demonstrate how the rate constant for singlet oxygen removal by a protein responds to (a) protein denaturation, (b) macromolecular crowding of the protein, (c) ligand binding by the protein, and (d) polymerization of the protein. From one perspective, the data show that the kinetics of singlet oxygen removal can be used to monitor protein dynamics. Most importantly, however, the data indicate that protein structural changes that either reveal or cloak a given amino acid residue can have a measurable effect on the overall rate constant for singlet oxygen removal which, in turn, can have ramifications for singlet-oxygen-mediated intracellular events that perturb cell function.

- Self-Recognition Among Different Polyprotic Macroions During Assembly Processes in Dilute Solution
  Liu, T.; Langston, M. L. K.; Li, D.; Pigga, J. M.; Pichon, C.; Todea, A. M.; Müller, A. *Science* **2011**, *331*, 1590-1592.
  Abstract:



We report a self-recognition phenomenon based on an assembly process in a homogeneous dilute aqueous solution of two nano-scaled, spherical polyprotic metal oxide–based macroions (neutral species in crystals), also called Keplerates of the type $[(linker)_{30}(pentagon)_{12}]$[$\{M(H_2O)\}_{30}\{(Mo)Mo_5\}_{12}$] where M is Fe^{III} or Cr^{III}. Upon deprotonation of the neutral species, the resulting macroions assemble into hollow "blackberry"-type structures through very slow homogeneous dimer-oligomerization processes. Although the geometrical surface structures of the two macroions are practically identical, mixtures of these form homogeneous superstructures, rather than mixed species. The phase separation is based on the difference in macroionic charge densities present during the slow homogeneous dimer or oligomer formation. The surface water ligands' residence times of Cr^{III} and Fe^{III} differ markedly and lead to very different interfacial water mobilities between the Keplerates.

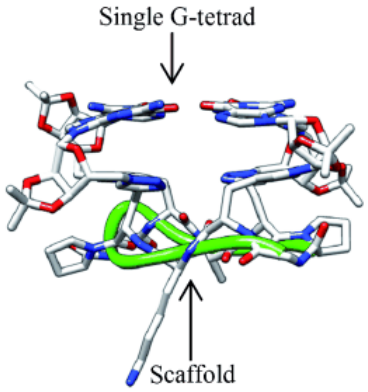
- Self-Assembly of Large and Small Molecules into Hierarchically Ordered Sacs and Membranes
  Capito, R. M.; Azevedo, H. S.; Velichko, Y. S.; Mata, A.; Stupp, S. I. *Science* **2008**, *319*, 1812-1816.
  Abstract:



We report here the self-assembly of macroscopic sacs and membranes at the interface between two aqueous solutions, one containing a megadalton polymer and the other, small self-assembling molecules bearing opposite charge. The resulting structures have a highly ordered architecture in which nanofiber bundles align and reorient by nearly 90° as the membrane grows. The formation of a diffusion barrier upon contact between the two liquids prevents their chaotic mixing. We

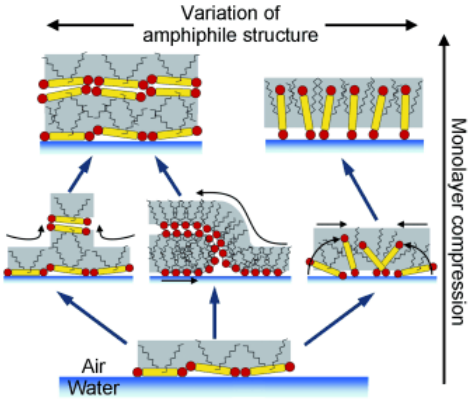
hypothesize that growth of the membrane is then driven by a dynamic synergy between osmotic pressure of ions and static self-assembly. These robust, self-sealing macroscopic structures offer opportunities in many areas, including the formation of privileged environments for cells, immune barriers, new biological assays, and self-assembly of ordered thick membranes for diverse applications.

- The Use of a Peptidic Scaffold for the Formation of Stable Guanine Tetrads: Control of a H-bonded Pattern in Water
  Murat, P.; Gennaro, B.; Garcia, J.; Spinelli, N.; Dumy, P.; Defrancq, E. *Chem. Eur. J.* **2011**, *17*, 5791–5795.
  Abstract :



With a little help from a scaffold: The pre-organization of guanine units onto a peptidic scaffold allows a remarkable stabilization of the G-quartet motif (see graphic). Indeed, the quartet motif was found to be stable even in water without addition of salts. The present study shows the first formation of a single synthetic G-tetrad under these aqueous conditions.

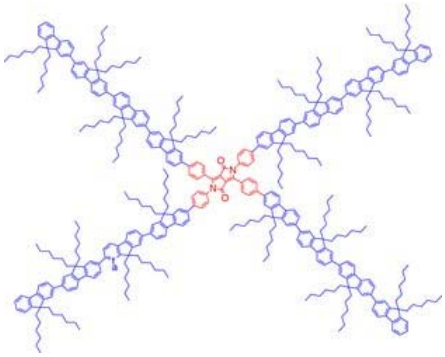
- Aggregation and Layering Transitions in Thin Films of X-, T-, and Anchor-Shaped Bolaamphiphiles at the Air–Water Interface
  Nitoń, P.; Zywociński, A.; Paczesny, J.; Fiałkowski, M.; Hołyst, R.; Glettner, B.; Kieffer, R.; Tschierske, C.; Pociecha, D.; Górecka, E. *Chem. Eur. J.* **2011**, *17*, 5861–5873.
  Abstract:



Aggregation in Langmuir films is usually understood as being a disorderly grouping of molecules turning into chaotic three-dimensional aggregates and is considered an unwanted phenomenon causing irreversible changes. In this work we present the studies of 11 compounds from the group of specific surfactants, known as bolaamphiphiles, that exhibit reversible aggregation and, in many

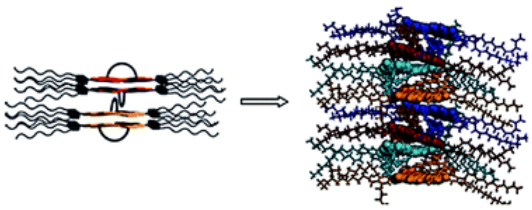
cases, transition to well-defined multilayers, which can be considered as a layering transition. These bolaamphiphiles incorporate rigid π-conjugated aromatics as hydrophobic cores, glycerol-based polar groups and hydrophobic lateral chains. Molecules of different shapes (X-, T-, and anchor) were studied and compared. The key property of these compounds is the partial fluorination of the lateral chains linked to the rigid cores of the molecules. The most interesting feature of the compounds is that, depending on their shape and degree of fluorination, they are able to resist aggregation and preserve a monolayer structure up to relatively high surface pressures (T-shaped and some X-shaped molecules), or create well-defined trilayers (X- and anchor-shaped molecules). Experimental studies were performed using Langmuir balance, surface potential and X-ray reflectivity measurements.

- Well-Defined and Monodisperse Linear and Star-Shaped Quaterfluorene-DPP Molecules: the Significance of Conjugation and Dimensionality
  Kanibolotsky, A. L.; Vilela, F.; Forgie, J. C.; Elmasly, S. E. T.; Skabara, P. J.; Zhang, K.; Tieke, B.; McGurk, J.; Beltoun, C. R.; Stavrinou, P. N.; Bradley, D. D. C. *Adv. Mater.* **2011**, *23*, 2093-2097.
  Abstract:



The synthesis of three new 1,4-diketo-3,6-diphenyl-pyrrolo[3,4-c]pyrrole (DPP) macromolecules appended with two or four quaterfluorene arms is reported. The compounds absorb mainly through the oligofluorene units and emit through the DPP core. Optical gain has been observed for Linear-c, a two-armed structure in which the quaterfluorene units are conjugated through the core unit.

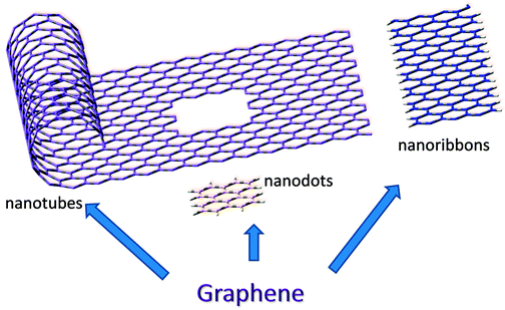
- Impact of core chirality on mesophase properties of perylene bisimides
  Safont-Sempere, M. M.; Stepanenko, V.; Lehmann M.; Würthner, F. *J. Mater. Chem.* **2011**, *21*, 7201-7209.
  Abstract:



The three-dimensional organisation of a racemic core-twisted perylene bisimide (PBI) 1 and its pure atropo-enantiomers ((*P*)-1 and (*M*)-1) are compared in the condensed state to elucidate the impact of core chirality in such materials. Our studies revealed distinctive differences in the condensed state properties of the racemic and enantiopure PBIs. While the racemic material forms a soft crystalline phase, the pure enantiomers (*P*)-1 and (*M*)-1 exhibit a smectic liquid crystalline mesophase of much lower viscosity as evidenced by differential scanning calorimetry (DSC), polarization optical microscopy (POM), X-ray diffraction of extruded samples and atomic force microscopy (AFM)

investigations. Two different packing models for the condensed state of the racemate and its pure enantiomers have been proposed based on the observed mesophase properties and force field calculations.

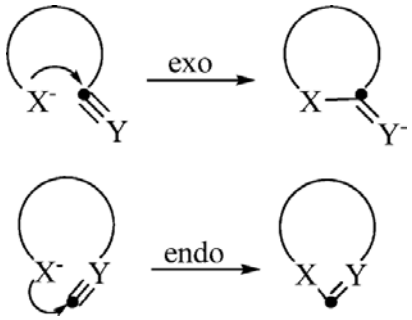
- Accurate Prediction of the Electronic Properties of Low-Dimensional Graphene Derivatives Using a Screened Hybrid Density Functional
  Barone, V.; Hod, O.; Peralta, J. E.; Scuseria, G. E. *Acc. Chem. Res.* **2011**, *44*, 269–279.
  Abstract:



Over the last several years, low-dimensional graphene derivatives, such as carbon nanotubes and graphene nanoribbons, have played a central role in the pursuit of a plausible carbon-based nanotechnology. Their electronic properties can be either metallic or semiconducting depending purely on morphology, but predicting their electronic behavior has proven challenging. The combination of experimental efforts with modeling of these nanometer-scale structures has been instrumental in gaining insight into their physical and chemical properties and the processes involved at these scales. Particularly, approximations based on density functional theory have emerged as a successful computational tool for predicting the electronic structure of these materials. In this Account, we review our efforts in modeling graphitic nanostructures from first principles with hybrid density functionals, namely the Heyd−Scuseria−Ernzerhof (HSE) screened exchange hybrid and the hybrid meta-generalized functional of Tao, Perdew, Staroverov, and Scuseria (TPSSh).
These functionals provide a powerful tool for quantitatively studying structure−property relations and the effects of external perturbations such as chemical substitutions, electric and magnetic fields, and mechanical deformations on the electronic and magnetic properties of these low-dimensional carbon materials. We show how HSE and TPSSh successfully predict the electronic properties of these materials, providing a good description of their band structure and density of states, their work function, and their magnetic ordering in the cases in which magnetism arises. Moreover, these approximations are capable of successfully predicting optical transitions (first and higher order) in both metallic and semiconducting single-walled carbon nanotubes of various chiralities and diameters with impressive accuracy. This versatility includes the correct prediction of the trigonal warping splitting in metallic nanotubes.
The results predicted by HSE and TPSSh provide excellent agreement with existing photoluminescence and Rayleigh scattering spectroscopy experiments and Green's function-based methods for carbon nanotubes. This same methodology was utilized to predict the properties of other carbon nanomaterials, such as graphene nanoribbons. Graphene nanoribbons may be viewed as unrolled (and passivated) carbon nanotubes. However, the emergence of edges has a crucial impact on the electronic properties of graphene nanoribbons. Our calculations have shown that armchair nanoribbons are predicted to be nonmagnetic semiconductors with a band gap that oscillates with their width. In contrast, zigzag graphene nanoribbons are semiconducting with an

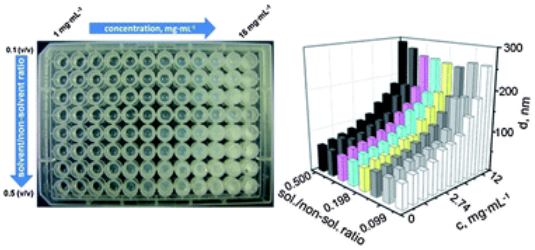
electronic ground state that exhibits spin polarization localized at the edges of the carbon nanoribbon. The spatial symmetry of these magnetic states in graphene nanoribbons can give rise to a half-metallic behavior when a transverse external electric field is applied. Our work shows that these properties are enhanced upon different types of oxidation of the edges. We also discuss the properties of rectangular graphene flakes, which present spin polarization localized at the zigzag edges.

- Synthesis of Heterocycles via Electrophilic Cyclization of Alkynes Containing Heteroatom
  Godoi, B.; Schumacher, R. F.; Zeni, G. *Chem. Rev.* **2011**, *111*, 2937–2980.
  Abstract:



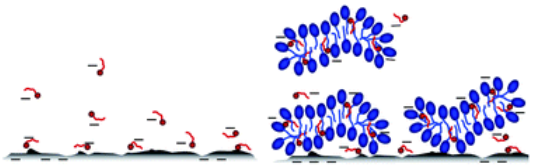
The interest in synthesizing heterocycles has always been enormous. The literature contains a variety of synthetic approaches to the heterocycle ring structures, much of which has been compiled into comprehensive reviews, including a special issue of *Chemical Reviews* devoted to this field. Among heterocycles, the six- and five-membered *O*- and *N*-heterocycles are probably one of the most common structural motifs spread across natural products, from simple glucose to structurally complex metabolites present in the structure of several biologically interesting compounds. Among a variety of synthetic methodologies, transition-metal-catalyzed cyclization reactions of simple acyclic precursors are one of the most attractive ways to directly construct complex heterocycles under mild conditions. In this context, palladium is one of the most common transition metals used, although the use of expensive transition metals together with the relatively complicated stepwise procedure employed limits the scope and general effectiveness of this method. Consequently, during the last few years an explosive increase of interest in electrophilic heteroatom cyclization has taken place, thus becoming an extremely active and original field of heterocycle synthesis. This methodology takes advantages, in most cases, of the presence of a residual halogen atom which is suitable to suffer further transformations. Electrophilic cyclizations have been demonstrated as an efficient tool in the synthesis of highly functionalized indoles, furan, thiophene, selenophene, benzo[*b*]furan, benzo[*b*]thiophene, benzo[*b*]selenophene, and pyrroles, employing electrophiles like I_2, ICl, or organochalcogen derivatives.

- Examination and optimization of the self-assembly of biocompatible, polymeric nanoparticles by high-throughput nanoprecipitation
  Perevyazko, I.; Delaney, J.; Vollrath, A.; Pavlov, G.; Schubert, S.; Schubert, U. *Soft Matter* **2011**, *7*, 5030-5035.
  Abstract:



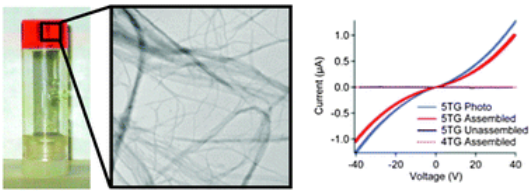
In recent years, the development of polymer nanoparticle suspensions by nanoprecipitation has gained increased attention both by industry and academia. However, the process by which such formulations are prepared is a highly empirically driven enterprise, whereby developing optimized formulations remains an iterative process. In this contribution, a new approach towards exploration of the materials space for these systems is reported, based on systematically varying processing and formulation to understand their influence on the characteristics of the resulting materials. Taking advantage of the tools and techniques that have already been standardized by informatics-driven life sciences disciplines, we have prepared libraries of nanoparticle formulations of poly(methyl methacrylate-*stat*-acrylate), poly(lactic-*co*-glycolic acid), and acetal-derivatized dextran by using a pipetting robot. They were subsequently characterized using a dynamic light scattering plate reader, analytical ultracentrifugation, and scanning electron microscopy. With this high-throughput nanoprecipitation approach, large numbers of materials can be prepared, screened, and the formulation rationally optimized.

- Interactions between large colloids and surfactants
  Iglesias, G.; Wachter, W.; Ahualli, S.; Glatter, O. *Soft Matter* **2011**, *7*, 4619-4622.
  Abstract:



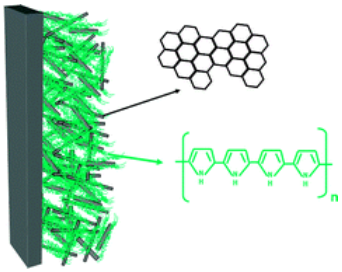
The interfacial adsorption of an anionic SDS and a nonionic surfactant $C_{12}E_5$, above the *cmc* onto submicron-sized, negatively charged silica particles in aqueous solution has been investigated by using electrokinetics, conductometry and static light scattering. It was found that both surfactants are prone to being adsorbed onto the silica/water interface. Addition of $C_{12}E_5$ to the silica dispersion leads to a decrease in mobility. This reduced surface charge causes a decrease in the stability of the silica particles. Surprisingly, the addition of SDS brings about an increase in the negative electrophoretic mobility of the anionic silica particles, leading to a *super-charging* effect. Subsequent addition of $C_{12}E_5$ gives rise to even higher negative electrophoretic mobilities. This unexpected hyper-charging effect can only be understood as a cooperative effect based on mixed micelles of $C_{12}E_5$ and non-adsorbed SDS. Not so unexpectedly, the sequence of surfactant addition was found to be decisive, as quite different results are obtained when $C_{12}E_5$ is added before SDS.

- Self-assembly and conductivity of hydrogen-bonded oligothiophene nanofiber networks
  Stone, D. A.; Tayi, A. S.; Goldberger, J. E.; Palmer, L. C.; Stupp, S. I. *Chem. Commun.* **2011**, *47*, 5702-5704.
  Abstract:



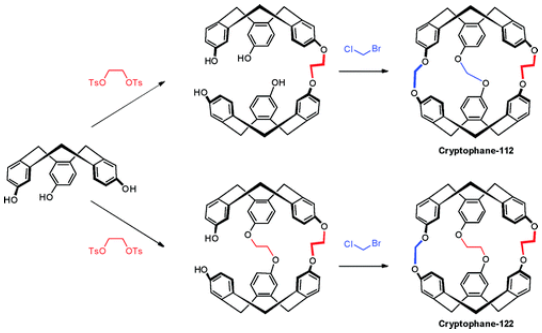
Symmetric oligothiophene derivatives containing hydrogenbonding groups form self-supporting organogels with conductive supramolecular networks of 1D nanostructures.

- Highly super capacitive electrodes made of graphene/poly(pyrrole)
  Mini, P. A.; Balakrishnan, A.; Nair, S. V.; Subramanian, K. R. V. *Chem. Commun.* **2011**, *47*, 5753-5755.
  Abstract:



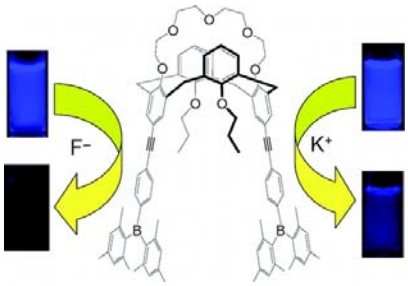
This communication reports on the development of high performance supercapacitor electrodes synthesized using a graphene/poly(pyrrole) composite layer.

- Design and Synthesis of New Cryptophanes with Intermediate Cavity Sizes
  Kotera, N.; Delacour, L.; Traor; T.; Tassali, N.; Berthault, P.; Buisson, D.-A.; Dognon, J.-P.; Rousseau, B. *Org. Lett.* **2011**, *13*, 2153–2155.
  Abstract:



The development of molecular imaging using hyperpolarized xenon MRI needs highly optimized biosensors. Cryptophane-111 and cryptophane-222 are promising candidates that show complementary encapsulation properties although they only differ by the length of the three alkane linkers joining two cyclotriphenolene units. Cryptophanes containing both methoxy and ethoxy linkers have never been synthesized. Here we synthesize two new cages with intermediate internal volumes, in two steps from cyclotriphenolene.

- A Highly Selective Bifunctional Luminescence Probe for Potassium and Fluoride Ions
  He, X.; Wing-Wah Yam , V. *Org. Lett.* **2011**, *13*, 2172–2175.
  Abstract:



A novel bifunctional molecule 1 by a combination of 1,3-alternate calix[4]-crown-5 and triarylborane moieties through alkynyl linkers has been designed and synthesized. Compound 1 shows intense fluorescence with a photoluminescence quantum yield of 0.70 in CH_2Cl_2 solution and can serve as a bifunctional luminescent probe for potassium and fluoride ions with high sensitivity and selectivity.