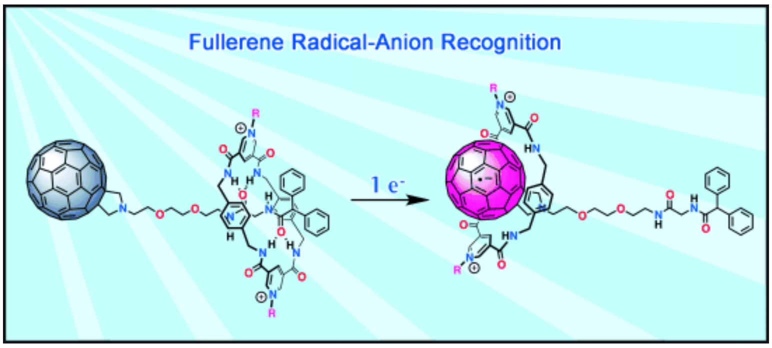
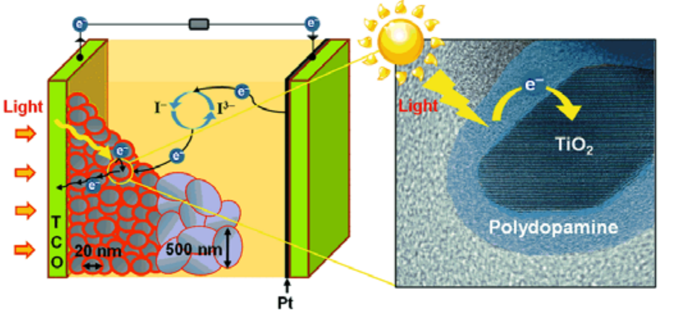
- A Molecular Shuttle Driven by Fullerene Radical-Anion Recognition
  Scarel, F.; Valenti, G.; Gaikwad, S.; Marcaccio, M.; Paolucci, F.; Mateo-Alonso, A. *Chem. Eur. J.* **2012**, *18*, 14063 – 14068.
  Abstract:



We describe a electrochemically driven molecular shuttle, in which shuttling takes place by means of fullerene radical-anion recognition that results in a very low operation potential ($E_{1/2}$=−0.580 V vs. decamethylferrocene). This has been achieved by introducing positive charges on the macrocycle, which strengthen the existing π–π interactions between the macrocycle and the electrogenerated fullerene radical anion by means of an electrostatic component. In addition, the synthesis of such a molecular shuttle has been accomplished by developing a new synthetic approach that exploits the controlled translocation of the macrocycle as a selective protecting group.

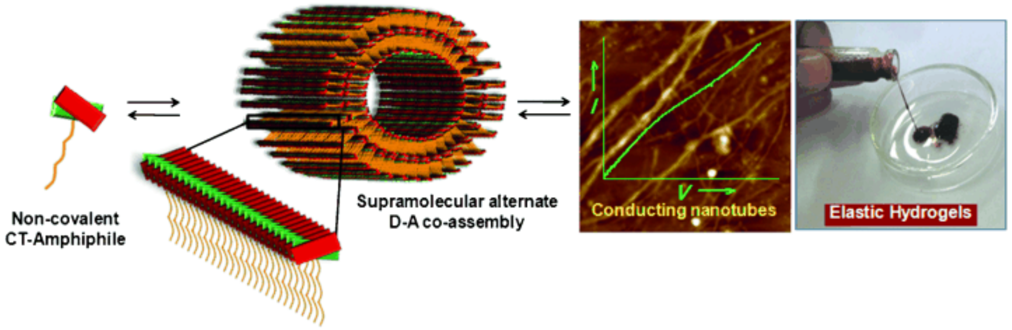
- A New Mussel-Inspired Polydopamine Sensitizer for Dye-Sensitized Solar Cells: Controlled Synthesis and Charge Transfer
  Nam, H. J.; Kim, B.; Ko,M. J.; Jin, M.; Kim, J. M.; Jung, D.-Y. *Chem. Eur. J.* **2012**, *18*, 14000 – 14007.
  Abstract:



The efficient electron injection by direct dye-to-TiO_2 charge transfer and strong adhesion of mussel-inspired synthetic polydopamine (PDA) dyes with TiO_2 electrode is demonstrated. Spontaneous self-polymerization of dopamine using dip-coating (DC) and cyclic voltammetry (CV) in basic buffer solution were applied to TiO_2 layers under a nitrogen atmosphere, which offers a facile and reliable synthetic pathway to make the PDA dyes, PDA-DC and PDA-CV, with conformal surface and perform an efficient dye-to-TiO_2 charge transfer. Both synthetic methods led to excellent photovoltaic results and the PDA-DC dye exhibited larger current density and efficiency values than those in the PDA-CV dye. Under simulated AM 1.5 G solar light (100 mW cm^{-2}), a PDA-DC dye exhibited a short circuit current density of 5.50 mW cm^{-2}, corresponding to an overall power conversion efficiency of 1.2 %, which is almost 10 times that of the dopamine dye-sensitized solar cell. The PDA dyes showed strong adhesion with the nanocrystalline TiO_2 electrodes and the interface engineering of a dye-adsorbed TiO_2 surface through the control of the coating methods, reaction times and solution concentration

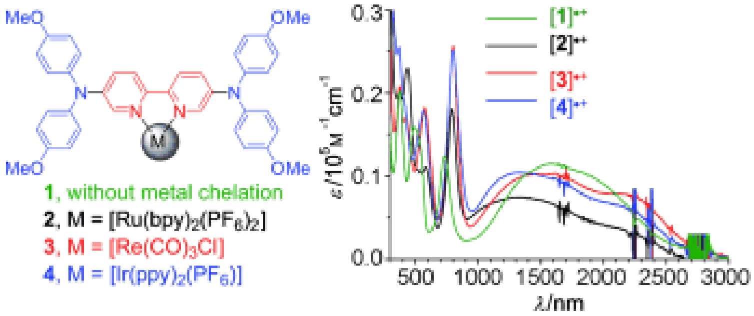
maximized the overall conversion efficiency, resulting in a remarkably high efficiency.

- Supramolecular Alternate Co-Assembly through a Non-Covalent Amphiphilic Design: Conducting Nanotubes with a Mixed D–A Structure
  Rao, K. V.; George, S. J. *Chem. Eur. J.* **2012**, *18*, 14286–14291.
  Abstract:



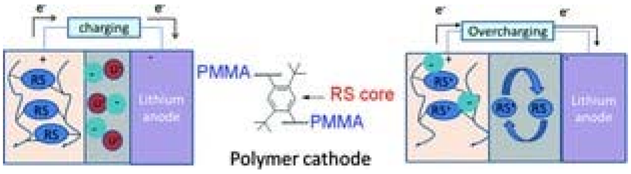
Mixing it up! The supramolecular alternate co-assembly of extended π-conjugated donor (D) and acceptor (A) molecules (i.e., oligo(phenylenevinylene) and perylenebisimide, respectively), to 1-D nanotubes with an unprecedented mixed stack D–A molecular structure is presented, through a non-covalent amphiphilic design strategy, which results in the formation of hydrogels with remarkable mechanical properties (see scheme).

- Electronic Coupling between Two Amine Redox Sites through the 5,5′-Positions of Metal-Chelating 2,2′-Bipyridines
  Nie, H.-J.; Chen, X.; Yao, C.-J.; Zhong, Y.-W.; Hutchison, G. R.; Yao, J. *Chem. Eur. J.* **2012**, *18*, 14497–14509.
  Abstract:



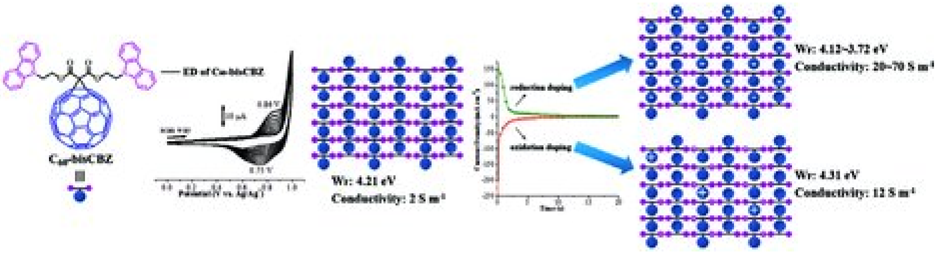
Electron delocalization of new mixed-valent (MV) systems with the aid of lateral metal chelation is reported. 2,2′-Bipyridine (bpy) derivatives with one or two appended di-*p*-anisylamino groups on the 5,5′-positions and a coordinated [Ru(bpy)2] (bpy=2,2′-bipyridine), [Re(CO)3Cl], or [Ir(ppy)2] (ppy=2-phenylpyridine) component were prepared. The single-crystal molecular structure of the bis-amine ligand without metal chelation is presented. The electronic properties of these complexes were studied and compared by electrochemical and spectroscopic techniques and DFT/TDDFT calculations. Compounds with two di-*p*-anisylamino groups were oxidized by a chemical or electrochemical method and monitored by near-infrared (NIR) absorption spectral changes. Marcus–Hush analysis of the resulting intervalence charge-transfer transitions indicated that electron coupling of these mixed-valent systems is enhanced by metal chelation and that the iridium complex has the largest coupling. TDDFT calculations were employed to interpret the NIR transitions of these MV systems.

- Smart Polymeric Cathode Material with Intrinsic Overcharge Protection Based on a 2,5-Di-*tert*-butyl- 1,4-dimethoxybenzene Core Structure
  Weng, W.; Zhang, Z.; Abouimrane, A.; Redfern, P. C.; Curtiss, L. A.; Amine, K. *Adv. Funct. Mater.* **2012**, *22*, 4485–4492.
  Abstract:



Polymer-based electroactive materials have been studied and applied in energy storage systems as a valid replacement for transition metal oxides. As early as 1999, Hass et al. proposed an interesting concept on the possible incorporation of both charge storage and overcharge protection functionality into a single material. However, there are virtually no examples of polymeric materials that can not only store the charge, but also consume the overcharge current. Herein, a new material based on a cross-linked polymer (**I**) with 2,5-di-*tert*-butyl-1,4-dimethoxybenzene as the core structure is reported. The cyclic voltammogram of the synthesized polymer shows a single oxidation/reduction peak at 3.9–4.0 V. At 1C rate (56 mA/g), polymer **I** shows stable cycling up to 200 cycles with <10% capacity loss. The redox shuttle mechanism remarkably can be activated when cell voltage is elevated to 4.3 V and the overcharge plateau at 4.2 V (2nd plateau) is persistent for more than 100 hours. The overcharge protection was due to the release of a chemical redox shuttle species in the electrolyte during the initial charging process. Both DFT calculations and NMR analysis of the aromatic signals in the ^{1}H-NMR spectrum of electrolytes from “overcharged” cells provide evidence for this hypothesis.

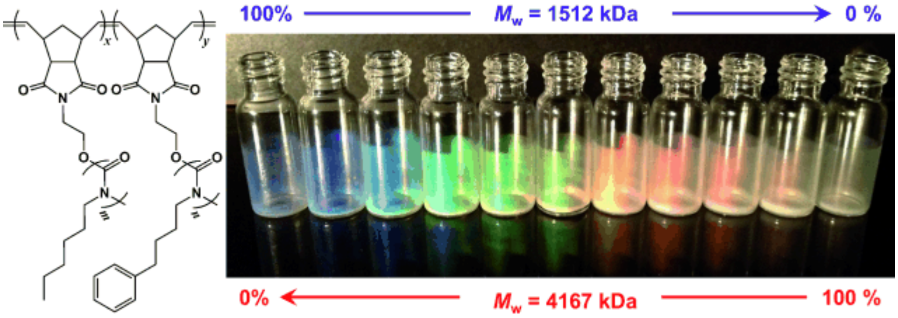
- In Situ Electrochemical Deposition and Doping of C_{60} Films Applied to High-Performance Inverted Organic Photovoltaics
  Gu, C.; Zhang, Z.; Sun, S.; Pan, Y.; Zhong, C.; Lv, Y.; Li, M.; Ariga, K.; Huang, F.; Ma, Y. *Adv. Mater.* **2012**, *24*, 5727–5731.
  Abstract:



Novel C_{60}-based cross-linked films formed by electrodeposition are produced and used as the electron-collection layer in inverted polymer solar cells (PSCs). The electrodeposited films exhibit a low work function of 4.2 eV and the PSCs perform well, with power conversion efficiencies of up to 6.31%. This new kind of electrodeposited film affords more opportunities to develop modified electrodes with a low work function.

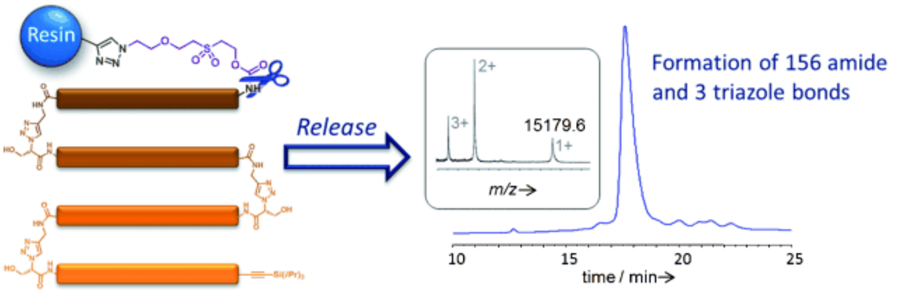
- Precisely Tunable Photonic Crystals From Rapidly Self-Assembling Brush Block Copolymer Blends
  Miyake, G. M.; Piunova, V. A.; Weitekamp, R. A.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2012**, *51*, 11246–11248.

Abstract:



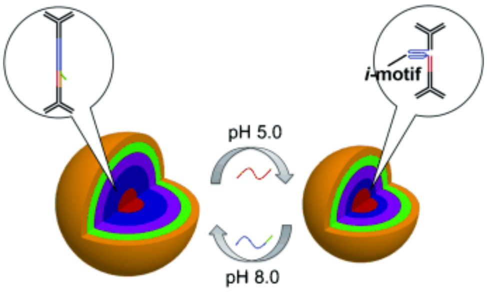
Colorful: Enabled by their reduced capacity for chain entanglement, high-molecular-weight brush block copolymers can rapidly self-assemble to photonic crystals. The blending of two polymers of different molecular weight can predictably modulate the sizes of the polymer domains, giving rise to a facile means of precision tuning of these photonic-band-gap materials.

- Towards the Simplification of Protein Synthesis: Iterative Solid-Supported Ligations with Concomitant Purifications
  Aucagne, V.; Valverde, I. E.; Marceau, P.; Galibert, M.; Dendane, N.; Delmas, A. F. *Angew. Chem. Int. Ed.* **2012**, *51*, 11320–11324.
  Abstract:



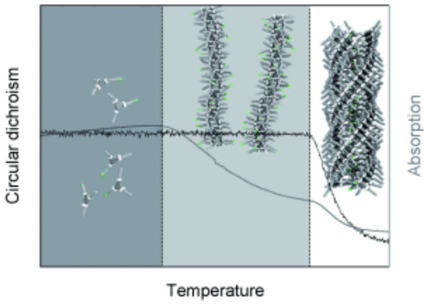
Please release me: A new linker for the temporary tagging of peptides at their N-terminus after solid-phase elongation, and its potential for capture/release purification is demonstrated. This concept is extended to a remarkably efficient self-purifying N-to-C iterative triazole ligation strategy, which is applied to the synthesis of a polypeptide having 160 residues, in a high purity without the need for chromatographic purification (see picture; orange blocks: peptide segments).

- pH-Responsive Size-Tunable Self-Assembled DNA Dendrimers
  Zhou, T.; Chen, P.; Niu, L.; Jin, J.; Liang, D.; Li, Z.; Yang, Z.; Liu, D. *Angew. Chem. Int. Ed.* **2012**, *51*, 11271–11274.
  Abstract:



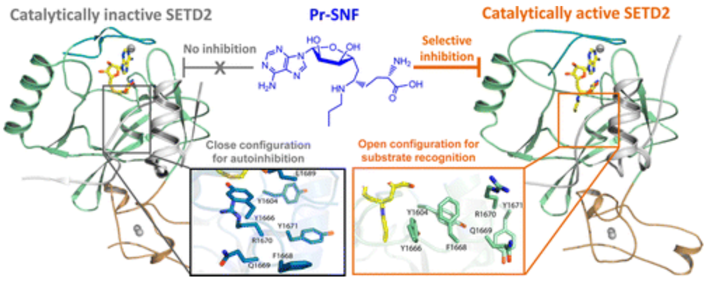
Putting the DNA in dendrimers: A strategy to swiftly prepare DNA dendrimers based solely on DNA self-assembly is presented. This technique produces highly pure DNA dendrimers with an excellent yield of high generation dendrimers. The incorporation of molecular motors (*i*-motifs) into the DNA dendrimers allows for a change in size (up to 30%) in response to changing pH values (see scheme).

- Symmetry Breaking in the Self-Assembly of Partially Fluorinated Benzene-1,3,5-tricarboxamides
  Stals, P. J. M.; Korevaar, P. A.; Gillissen, M. A. J.; de Greef, T. F. A.; Fitié, C. F. C.; Sijbesma, R. P.; Palmans, A. R. A.; Meijer, E. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 11297–11301.
  Abstract:



The interplay of two subsequent aggregation processes results in a symmetry-breaking phenomenon in an achiral self-assembling system. Partially fluorinated benzene-1,3,5-tricarboxamide molecules self-assemble into a racemic mixture of one-dimensional *P*- and *M*-helical aggregates, followed by bundling into optically active higher-order aggregates or fibers (see picture).

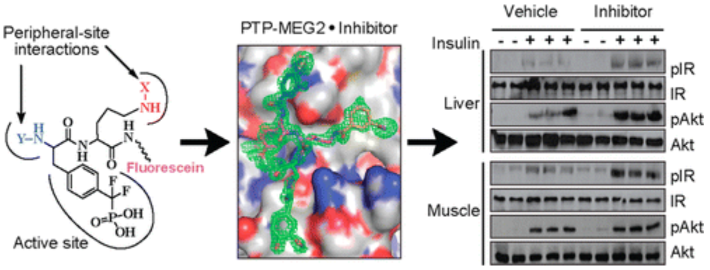
- Sinefungin Derivatives as Inhibitors and Structure Probes of Protein Lysine Methyltransferase SETD2
  Zheng, W.; Ibáñez, G.; Wu, H.; Blum, G.; Zeng, H.; Dong, A.; Li, F.; Hajian, T.; Allali-Hassani, A.; Amaya, M. F.; Siarheyeva, A.; Yu, W.; Brown, P. J.; Schapira, M.; Vedadi, M.; Min, J.; Luo, M. *J. Am. Chem. Soc.* **2012**, *134*, 18004–18014.
  Abstract:



Epigenetic regulation is involved in numerous physiological and pathogenic processes. Among the key regulators that orchestrate epigenetic signaling are over 50 human protein lysine methyltransferases (PKMTs). Interrogation of the functions of individual PKMTs can be facilitated by target-specific PKMT inhibitors. Given the emerging need for such small molecules, we envisioned an approach to identify target-specific methyltransferase inhibitors by screening privileged small-molecule scaffolds against diverse methyltransferases. In this work, we demonstrated the feasibility of such an approach by identifying the inhibitors of SETD2. N-propyl sinefungin (Pr-SNF) was shown to interact preferentially with SETD2 by matching the distinct transition-state features of SETD2's catalytically active conformer. With Pr-SNF as a structure probe, we further revealed the dual roles of SETD2's post-SET loop in regulating substrate access through a distinct topological reconfiguration.

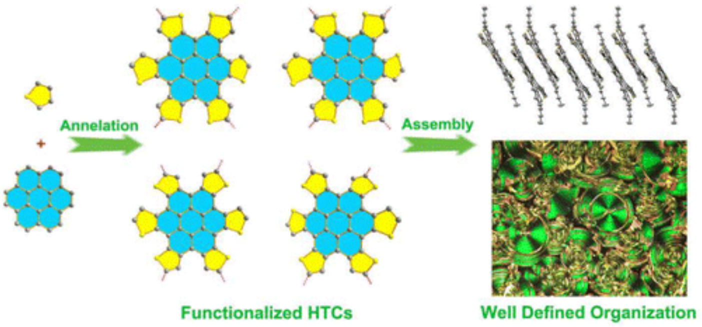
Privileged sinefungin scaffolds are expected to have broad use as structure and chemical probes of methyltransferases.

- A Highly Selective and Potent PTP-MEG2 Inhibitor with Therapeutic Potential for Type 2 Diabetes
  Zhang, S.; Liu, S.; Tao, R.; Wei, D.; Chen, L.; Shen, W.; Yu, Z.-H.; Wang, L.; Jones, D. R.; Dong, X. D.; Zhang, Z.-J. *J. Am. Chem. Soc.* **2012**, *134*, 18116–18124.
  <u>Abstract:</u>



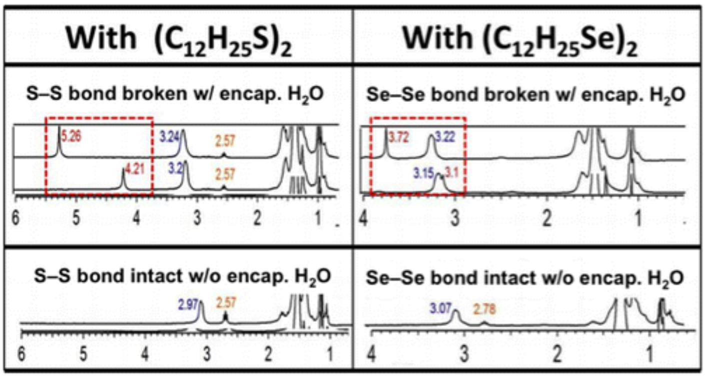
Protein tyrosine phosphatases (PTPs) constitute a large family of signaling enzymes that control the cellular levels of protein tyrosine phosphorylation. A detailed understanding of PTP functions in normal physiology and in pathogenic conditions has been hampered by the absence of PTP-specific, cell-permeable small-molecule agents. We present a stepwise focused library approach that transforms a weak and general non-hydrolyzable pTyr mimetic (F2Pmp, phosphonodifluoromethyl phenylalanine) into a highly potent and selective inhibitor of PTP-MEG2, an antagonist of hepatic insulin signaling. The crystal structures of the PTP-MEG2-inhibitor complexes provide direct evidence that potent and selective PTP inhibitors can be obtained by introducing molecular diversity into the F2Pmp scaffold to engage both the active site and unique nearby peripheral binding pockets. Importantly, the PTP-MEG2 inhibitor possesses highly efficacious cellular activity and is capable of augmenting insulin signaling and improving insulin sensitivity and glucose homeostasis in diet-induced obese mice. The results indicate that F2Pmp can be converted into highly potent and selective PTP inhibitory agents with excellent in vivo efficacy. Given the general nature of the approach, this strategy should be applicable to other members of the PTP superfamily.

- Hexathienocoronenes: Synthesis and Self-Organization
  Chen, L.; Puniredd, S. R.; Tan, Y.-Z.; Baumgarten, M.; Zschieschang, U.; Enkelmann, V.; Pisula, W.; Feng, X.; Klauk, H.; Müllen, K. *J. Am. Chem. Soc.* **2012**, *134*, 17869–17872.
  <u>Abstract:</u>



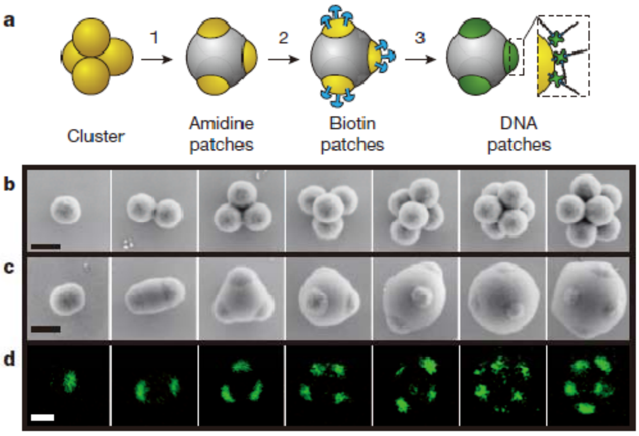
Here we report hexathienocoronenes (HTCs), fully thiophene-annelated coronenes in which six double bonds in the periphery are thieno-fused. The derivatives tetrasubstituted with hexyl and dodecyl chains show a phase formation that strongly depends on the chain length. HTCs are remarkably stronger donors than the known thiophene-annelated coronenes but do not readily assemble into well-ordered films when deposited from the vapor phase. Thus, thin-film transistors fabricated by vacuum deposition have only modest field-effect mobilities of 0.002 $cm^2\ V^{-1}\ s^{-1}$.

- Inverse-Micelle-Encapsulated Water-Enabled Bond Breaking of Dialkyl Diselenide/Disulfide: A Critical Step for Synthesizing High-Quality Gold Nanoparticles
  Zaluzhna, O.; Li, Y.; Allison, T. C.; Tong, Y. J. *J. Am. Chem. Soc.* **2012**, *134*, 17991–17996.
  Abstract:



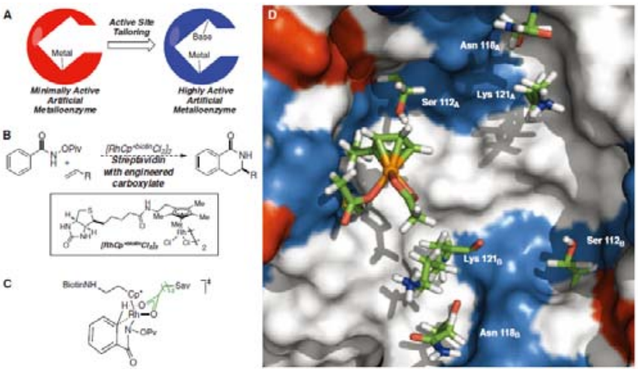
Inverse-micelle-encapsulated water formed in the two-phase Brust–Schiffrin method (BSM) synthesis of Au nanoparticles (NPs) is identified as essential for dialkyl diselenide/disulfide to react with the Au(III) complex in which the Se–Se/S–S bond is broken, leading to formation of higher-quality Au NPs.

- Colloids with valence and specific directional bonding.
  Wang, Y.; Wang, Y.; Breed, D. R.; Manoharan, V. N.; Feng, L.; Hollingsworth, A. D.; Weck, M.; Pine, D. J. *Nature* **2012**, *491*, 51-56.
  Abstract:



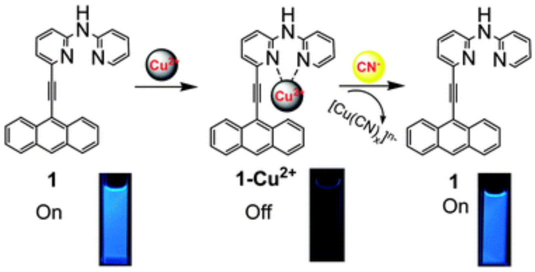
The ability to design and assemble three-dimensional structures from colloidal particles is limited by the absence of specific directional bonds. As a result, complex or low-coordination structures, common in atomic and molecular systems, are rare in the colloidal domain. Here we demonstrate a general method for creating the colloidal analogues of atoms with valence: colloidal particles with chemically distinct surface patches that imitate hybridized atomic orbitals, including *sp*, sp^2, sp^3, sp^3d, sp^3d^2 *and* sp^3d^3. Functionalized with DNA with single-stranded sticky ends, patches on different particles can form highly directional bonds through programmable, specific and reversible DNA hybridization. These features allow the particles to self-assemble into ‘colloidal molecules’ with triangular, tetrahedral and other bonding symmetries, and should also give access to a rich variety of new microstructured colloidal materials.

- Biotinylated Rh(III) Complexes in Engineered Streptavidin for Accelerated Asymmetric C–H Activation
  Hyster, T. K.; Knörr, L.; Ward, T. R.; Rovis, T. *Science* **2012**, *338*, 500-503.
  Abstract:



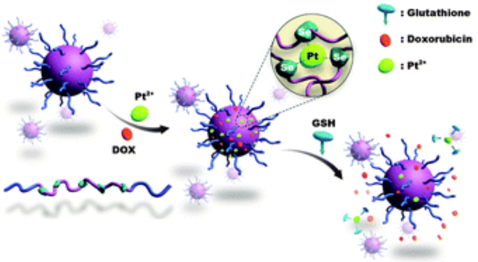
Enzymes provide an exquisitely tailored chiral environment to foster high catalytic activities and selectivities, but their native structures are optimized for very specific biochemical transformations. Designing a protein to accommodate a non-native transition metal complex can broaden the scope of enzymatic transformations while raising the activity and selectivity of small-molecule catalysis. Here, we report the creation of a bifunctional artificial metalloenzyme in which a glutamic acid or aspartic acid residue engineered into streptavidin acts in concert with a docked biotinylated rhodium(III) complex to enable catalytic asymmetric carbon-hydrogen (C–H) activation. The coupling of benzamides and alkenes to access dihydroisoquinolones proceeds with up to nearly a 100-fold rate acceleration compared with the activity of the isolated rhodium complex and enantiomeric ratios as high as 93:7.

- Selective, sensitive and reversible "turn-on" fluorescent cyanide probes based on 2,2′-dipyridylaminoanthracene–Cu^{2+} ensembles
  Xie, H.; Ding, Y.; Li, X.; Wang, C.; Hill, J. P.; Ariga, K.; Zhang, W.; Zhu, W. *Chem. Commun.* **2012,** *48,* 11513–11515.
  Abstract:



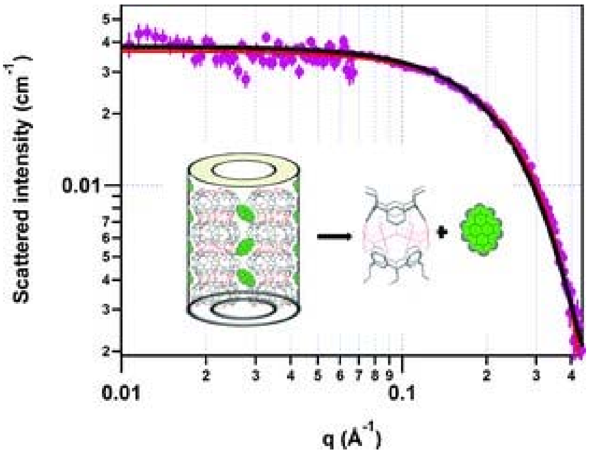
2,2′-Dipyridylamine and anthracene units were linked to afford highly emissive compounds whose Cu^{2+} ensembles were developed as effective fluorescence turn-on CN^- probes.

- Coordination-responsive selenium-containing polymer micelles for controlled drug release
  Cao, W.; Li, Y.; Yi ,Y.; Ji, S. ; Zeng, L.; Sun Z.; Xu, H. *Chem. Sci.*, **2012,** *3,* 3403–3408.
  Abstract:



A novel coordination-responsive system for the controlled release of doxorubicin was fabricated by complexing platinum cations with selenium-containing polymers. Doxorubicin loaded in the platinum-coordinating micelles can be released in a controlled manner through the competitive coordination of the platinum cations with glutathione. The coordination micelles are quite biocompatible as vehicles of drug delivery, thus opening a new avenue in multidrug systems for cooperative chemotherapy.

- Investigating Structural Alterations in Pyrogallol[4]arene-Pyrene Nanotubular Frameworks
  Kumari, H.; Kline, S. R.; Wycoff, W. G.; Atwood, J. L. *Small* **2012**, *8*, 3321–3325.
  Abstract:

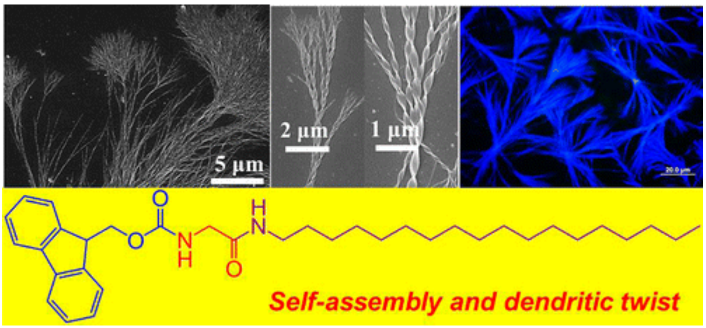


Small-angle neutron scattering (SANS) and diffusion NMR studies are performed to investigate the stability and geometry of hydrogen-bonded pyrene-guest-containing *C*-hexylpyrogallol[4]arene (PgC_6-pyrene) nanotubular frameworks in solution. In the solid state, hydrogen-bonded pyrogallol[4]arene tubes are formed; however, the scattering data for PgC_6-pyrene assemblies in acetone are best modeled as dimeric spheres of PgC_6 with no pyrene guest. The result of diffusion NMR study also indicates the rearrangement of tubular entity into spherical framework in acetone. This is the first example of structural transformation of pyrogallol[4]arene nanotubes (guest-exo) in solution. Individual hydrogen-bonded spheres of PgC_6 exhibits a uniform radius of ca. 8.6 Å and a diffusion coefficient of 9.12×10^{-10} m^2 s^{-1} in acetone. The diffusion NMR measurements further gave, for the first time, insights into how the type of solvent (acetone vs. methanol vs. acetontitrile/D_2O) governs the structural differences in these nanoassemblies. Solution-phase structural alteration observed for PgC_6-pyrene gives evidence of enhanced stability of pyrogallol[4]arene nanocapsules over nanotubes.

- Hierarchical Self-Assembly of Achiral Amino Acid Derivatives into Dendritic Chiral Nanotwists

Cao, H.; Yuan, Q.; Zhu, X.; Zhao, Y.-P.; Liu, M. *Langmuir* **2012**, *28*, 15410 –15417.

Abstract:

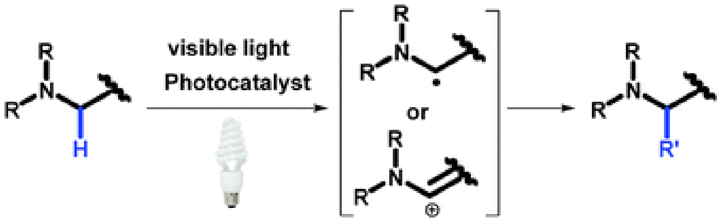


The organogel formation and self-assembly of a glycine-based achiral molecule were investigated. It has been found that the compound could gel organic solvents either at a lower temperature with lower concentration or at room temperature with higher concentration, which showed different self-assembled nanostructures. At a low temperature of −15 °C, the compound self-assembled into fibrous structures, whereas it formed distinctive flat microbelts at room temperature. When the organogel with nanofibers formed at −15 °C was brought into an ambient condition, chiral twist nanostructures were immediately evolved, which subsequently transferred to a giant microbelt through a hierarchical dendritic twist with the time. Although the compound is achiral, it formed chiral twist with both left- and right-handed twist structures simultaneously. When a trace analogical chiral trigger, l-alanine or d-alanine derivative, was added, a complete homochiral dendritic twist was obtained. Interestingly, a reverse process, i.e. the transformation of the microbelts into twists, could occur upon dilution of the organogel with microbelt structure. During the dilution, both left- and right-handed chiral twists could be formed again. Interestingly, the same branch from the microbelt formed the twist with the same handedness. A combination of the density functional theory (DFT), molecular mechanics (MM), and molecular dynamics (MD) simulations demonstrates that the temperature-induced twisting of the bilayer is responsible for the morphological transformation and evolution of the dendrite twist. This research sheds new light on the hierarchical transformation of the chiral structures from achiral molecules via controlled self-assembly.

- Photoredox functionalization of C–H bonds adjacent to a nitrogen atom

  Shi, L.; Xia, W. *Chem. Soc. Rev.* **2012,** *41***,** 7687-7697.

  Abstract:

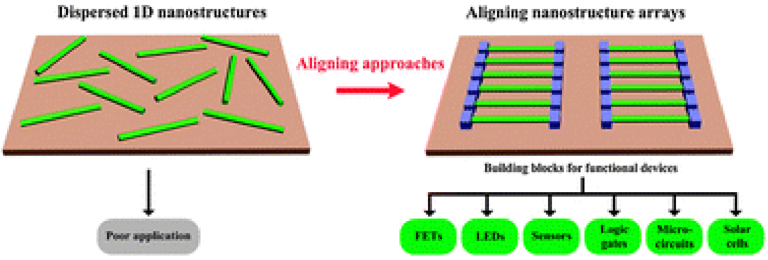


The functionalization of C–H bonds and the visible light photoredox catalysis represent two prominent challenges in organic chemistry. In this regard, the combination of visible-light catalysis and C–H bond functionalization adjacent to a tertiary amine has been successfully developed in the past three years. In this *tutorial review*, we aim to give a brief overview of this issue and state the main results obtained in the reactions.

- The art of aligning one-dimensional (1D) nanostructures

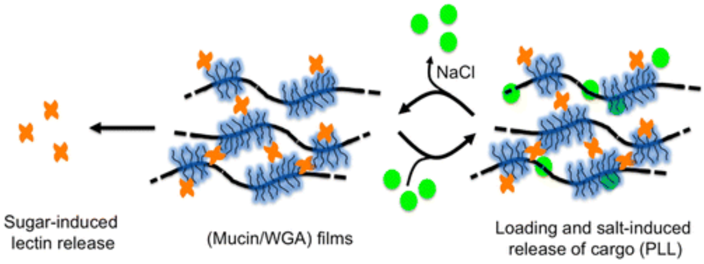
  Su, B.; Wu, Y.; Jiang, L. *Chem. Soc. Rev.* **2012**, *41*, 7832-7856.

Abstract:



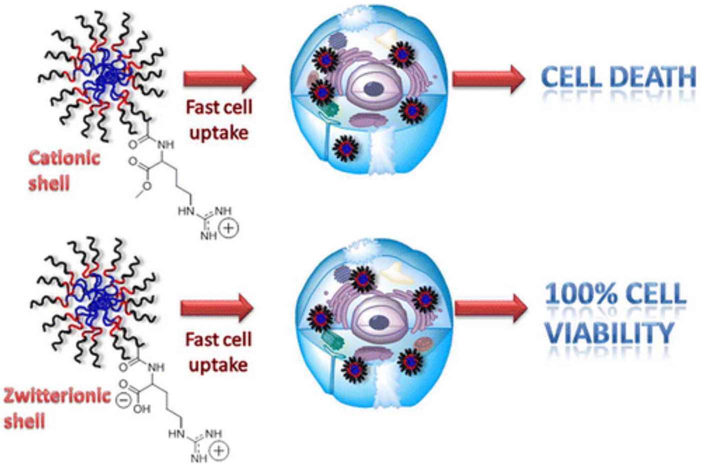
One-dimensional (1D) nanostructures, including polymeric, small molecule and inorganic types, are currently being investigated in great detail for their unique mechanical, optical, electronic properties and potential implementation as devices. To integrate 1D nanostructures into device applications, it is of importance to align such nanostructures in a parallel, scalable, and highly reproducible manner independent of the specific materials. Well aligned 1D nanostructures might exhibit superior properties that are not found in their disordered counterparts, allowing promising applications in diverse fields. This *critical review* summarizes the recent work in the alignment of polymeric, small molecule and inorganic 1D nanostructures, in particular, the advantages and drawbacks of various aligning approaches. Discussion is focused on an advanced strategy to precisely position each 1D nanostructure by superhydrophobic pillar-structured surfaces. The research prospects and directions of this rapidly developing field are also briefly addressed (123 references).

- Mucin Multilayers Assembled through Sugar–Lectin Interactions
  Crouzier, T.; Beckwitt, C. H.; Ribbeck, K. *Biomacromolecules* **2012**, *13*, 3401–3408.
  Abstract:



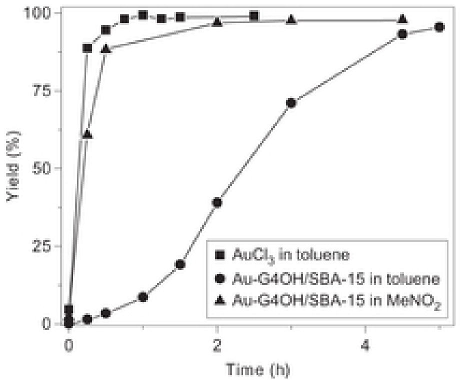
Multilayer films of biopolymers are attractive tools to exploit the extraordinary properties of certain biomacromolecules and introduce new functionalities to surfaces. Mucins, the gel-forming constituents of mucus, are versatile glycoproteins that have potential as new building blocks for biomaterial surface coatings. Multilayer films have mostly been assembled through the electrostatic pairing of polyelectrolytes, which results in limited pH and salt stability and screens charges otherwise available for useful payload binding. Here, we aim at assembling mucin multilayer films that differ from conventional paired polyelectrolyte assemblies to obtain highly stable and functional surface modifications. Using the lectin wheat germ agglutinin (WGA) to cross-link mucin-bound sugar residues, we show that (Mucin/WGA) films can grow into hydrated films and sustain exceptional resistance to extreme salt conditions and a large range of pH. Furthermore, we show that the addition of soluble *N*-acetyl-d-glucosamine can induce the controlled release of WGA from (Mucin/WGA) films. Last, we show that (Mucin/WGA) films can repeatedly incorporate and release a positively charged model cargo. The lubricating, hydration, barrier, and antimicrobial properties of mucins open multiple applicative perspectives for these highly stable mucin-based multilayer films.

- Zwitterionic Guanidine-Based Oligomers Mimicking Cell-Penetrating Peptides as a Nontoxic Alternative to Cationic Polymers to Enhance the Cellular Uptake of Micelles
  Kim, Y.; Binauld, S.; Stenzel, M. H. *Biomacromolecules* **2012**, *13*, 3418–3426.
  Abstract:



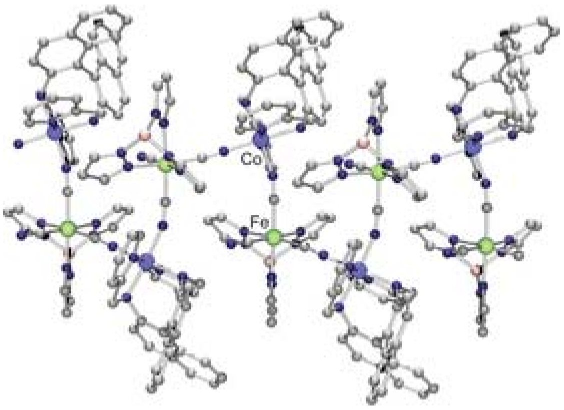
The aim of this work is to generate polymer micelles decorated with a synthetic version of cell-penetrating peptides, which are often rich in arginine with its positively charged guanidine group. A methacrylate-based monomer with guanidinium as functional groups was prepared using arginine (M-Arg) as a building block, resulting in a zwitterionic monomer. RAFT (reversible addition–fragmentation chain transfer) polymerization was employed to generate triblock copolymers with poly(methyl methacrylate)-*block*-poly(polyethylene glycol methyl ether methacrylate) as the first two blocks, which were subsequently chain extended with the guanidine-based monomer to generate micelles with guanidinium functional groups on the surface. To simulate the actual oligoarginine peptide, which only carries cationic charges, the carboxylate group of P(M-Arg) was methylated to convert the zwitterionic polymer into a cationic polymer P(Me-M-Arg). For comparison, micelles based on triblock copolymers with a third block with permanently cationic charges, poly(2-methacryolyloxy ethyl) trimethyl ammonium chloride (PTMA), was prepared. The hydrodynamic diameters of the micelles were approximately 30–40 nm based on DLS and TEM. A direct correlation between surface charge (zeta potential ζ) and cytotoxicity was observed. The micelles based on the zwitterionic P(M-Arg) were nontoxic (ζ = −10 mV at pH = 7), while the methylated version P(Me-M-Arg) with a high cationic charge (ζ = +35 mV at pH = 7) were observed to be toxic. The cellular uptake of the block copolymers by OVCAR-3 ovarian cancer cell lines was found to be relatively fast (about 35% in 3 min) reaching an equilibrium after approximately 30 min. Both micelles, with either P(M-Arg) or P(Me-M-Arg) on the surface, showed an enhanced uptake compared to micelles with P(PEGMEMA) as shell only. In fact, the percentage of uptake was similar, with the difference that cells incubated with micelles with P(M-Arg) (zwitterionic) stayed alive, while P(Me-M-Arg) (cationic) led to significant cell death.

- Control of selectivity in heterogeneous catalysis by tuning nanoparticle properties and reactor residence time
  Gross, E.; Liu, J. H.; Toste, F. D.; Somorjai, G. A. *Nature Chemistry* **2012**, *4*, 947–952.
  Abstract:



A combination of the advantages of homogeneous and heterogeneous catalysis could enable the development of sustainable catalysts with novel reactivity and selectivity. Although heterogeneous catalysts are often recycled more easily than their homogeneous counterparts, they can be difficult to apply in traditional organic reactions and modification of their properties towards a desired reactivity is, at best, complex. In contrast, tuning the properties of homogeneous catalysts by, for example, modifying the ligands that coordinate a metal centre is better understood. Here, using olefin cyclopropanation reactions catalysed by dendrimer-encapsulated Au nanoclusters as examples, we demonstrate that changing the dendrimer properties allows the catalytic reactivity to be tuned in a similar fashion to ligand modification in a homogeneous catalyst. Furthermore, we show that these heterogeneous catalysts employed in a fixed-bed flow reactor allow fine control over the residence time of the reactants and thus enables the control over product distribution in a way that is not easily available for homogeneous catalysts.

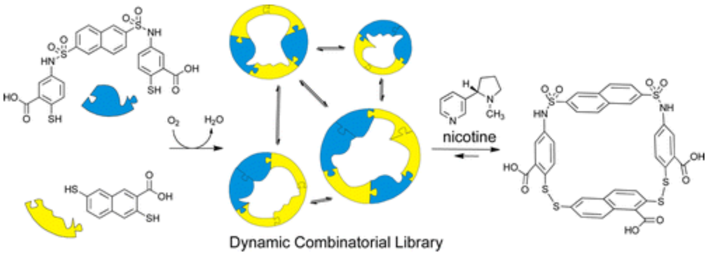
- Three-way switching in a cyanide-bridged [CoFe] chain
  Hoshino, N.; Iijima, F.; Newton, G. N.; Yoshida, N.; Shiga, T.; Nojiri, H.; Nakao, A.; Kumai, R.; Murakami, Y.; Oshio, H. *Nature Chemistry* **2012**, *4*, 921–926.
  Abstract:



Bistable compounds that exist in two interchangeable phases under identical conditions can act as switches under external stimuli. Among such switchable materials, coordination complexes have energy levels (or phases) that are determined by the electronic states of their constituent metal ions and ligands. They can exhibit multiple bistabilities and hold promise in the search for multifaceted materials that display different properties in different phases, accessible through the application of contrasting external stimuli. Molecular systems that exhibit both thermo- and photoinduced magnetic bistabilities are excellent candidates for such systems. Here we describe a cyanide-bridged [CoFe] one-dimensional chiral coordination polymer that displays both magnetic and electric bistabilities in the same temperature range. Both the electric and magnetic switching probably arise

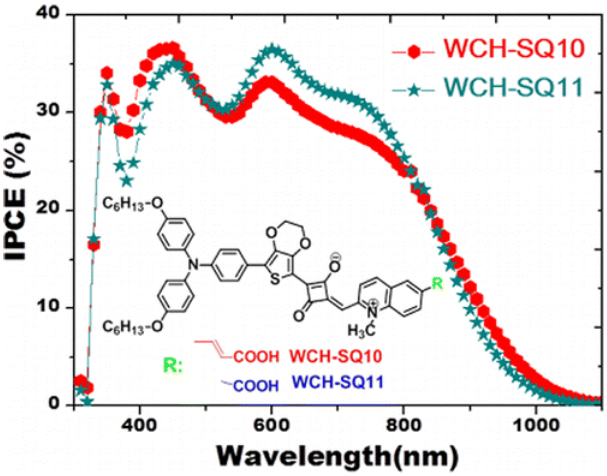
from the same electron-transfer coupled spin-transition phenomenon, which enables the reversible conversion between an insulating diamagnetic phase and either a semiconducting paramagnetic (thermoinduced) or a type of ferromagnetic single-chain magnet (photoinduced) state.

- A Synthetic Receptor for Nicotine from a Dynamic Combinatorial Library
  Hamieh, S.; Ludlow, R. F.; Perraud, O.; West, K. R.; Mattia, E.; Otto, S. *Org. Lett.* **2012**, *14*, 5404–5407.
  Abstract:



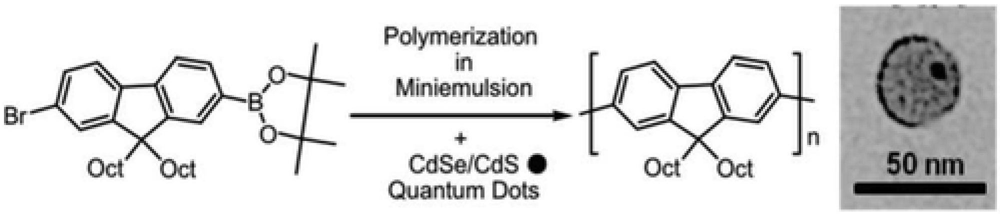
Designing synthetic receptors that bind biologically relevant guests in an aqueous solution remains a considerable challenge. We now report a new synthetic receptor for nicotine, selected from a dynamic combinatorial library, that binds this guest in water at neutral pH through a combination of hydrophobic and π–π interactions.

- Unsymmetrical Squaraines Incorporating Quinoline for Near Infrared Responsive Dye-Sensitized Solar Cells
  Li, J.-Y.; Chen, C.-Y.; Ho, W.-C.; Chen, S.-H.; Wu, C.-G. *Org. Lett.* **2012**, *14*, 5420–5423.
  Abstract:



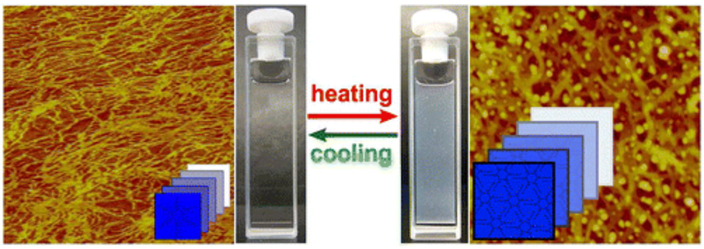
Two new unsymmetrical squaraines (WCH-SQ10 and WCH-SQ11), wherein the electron-rich 3,4-ethylenedioxy-thiophene conjugated fragment was linked unconventionally to the squaraine core and triphenyl amine donor, and carboxylic acid substituted quinoline was used as an acceptor, were prepared. WCH-SQ10 and WCH-SQ11 dyes in ethanol have the λmax of 686 and 673 nm, respectively. The corresponding photovoltaic devices exhibit an attractively panchromatic response over 1000 nm, suggesting that quinoline benefits the low energetic electron injection.

- Polyfluorene Nanoparticles and Quantum Dot Hybrids via Miniemulsion Polymerization
  Negele, C.; Haase, J.; Leitenstorfer, A.; Mecking, S. *ACS Macro Lett.* **2012**, *1*, 1343–1346.
  Abstract:



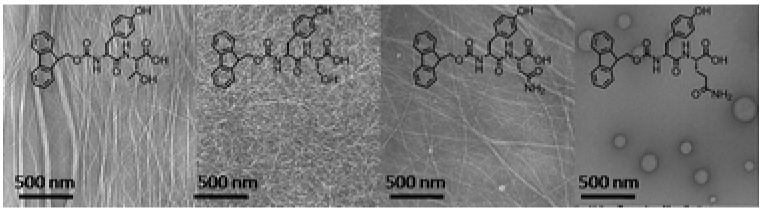
Suzuki–Miyaura polycondensation of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-bromo-9,9-dioctylfluorene in aqueous miniemulsion with only two equivalents of NaOH as a base yields colloidally stable nanoparticles of polyfluorene with M_n ca. 2×10^4 g mol^{-1} and particle sizes of 40–85 nm, depending on the surfactant concentration. Polymerization in the presence of CdSe/CdS core/shell quantum dots affords hybrid nanoparticles of nonaggregated quantum dots, in particular nanoparticles composed of a single quantum dot embedded in a polyfluorene shell. Microphotoluminescence spectroscopy on single hybrid particles reveals an enhanced photostability of the quantum dots and indicates an efficient Förster energy transfer from the polyfluorene shell to the quantum dot.

- Temperature-Controlled, Reversible, Nanofiber Assembly from an Amphiphilic Macrocycle
  Li, L.; Che, Y.; Gross, D. E. ; Huang, H. ; Moore, J. S.; Zang, L. *ACS Macro Lett.* **2012**, *1*, 1335–1338.
  Abstract:



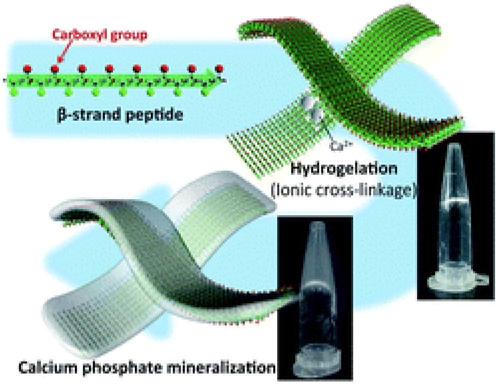
One-dimensional nanostructures are self-assembled from an amphiphilic arylene-ethynylene macrocycle (AEM) in solution phase. The morphology and size of the nanostructures are controlled by simply changing the temperature, reversibly switching between monomolecular cross-sectioned nanofibers and large bundles. At elevated temperature in aqueous solutions, the tri(ethylene glycol) (Tg) side chains of the AEM become effectively more hydrophobic, thus facilitating intermolecular association through side chain interactions. The enhanced intermolecular association causes the ultrathin nanofibers to be bundled, forming an opaque dispersion in solution. The reported observation provides a simple molecular design rule that may be applicable to other macrocycle molecules for use in temperature-controlled assembly regarding both size and morphology.

- Differential supramolecular organisation of Fmoc-dipeptides with hydrophilic terminal amino acid residues by biocatalytic self-assembly
  Hughes, M.; Birchall, L. S.; Zuberi, K.; Aitken, L. A.; Debnath, S.; Javid, N.; Ulijn, R. V. *Soft Matter* **2012**, *8*, 11565-11574.
  Abstract:



The study of enzymatically triggered self-assembly of aromatic peptide amphiphiles has become increasingly popular in recent years and has lead to a variety of nanoscale architectures. As hydrophobic interactions have been recognised as a major driving force in their self-assembly, typically, the peptide components are found to be hydrophobic in nature, containing aromatic or aliphatic amino acid residues. In this article, we use subtilisin triggered self-assembly of four closely related Fmoc-dipeptide amphiphiles with terminal hydrophilic amino acid residues, YT, YS, YN and YQ, in order to introduce a new functionality to the self-assembled systems, and determine the influence of each amino acid side chain. We use microscopy techniques, rheology, fluorescence, FTIR and CD to demonstrate differences in molecular assembly, mechanical properties and nanoscale architecture as a direct result of the subtle molecular variance of each system. We demonstrate that the amino acid side chain in position two directly affects the molecular packing abilities in the supramolecular structure, with YT, YS and YN forming nanoscale fibres with mechanical properties being linked to the functionality of the amino acid side chain, and YQ forming spherical structures due to steric effects associated with the glutamine side chain prohibiting the adoption of the typical π–β assembly.

- Calcium phosphate biomineralization in peptide hydrogels for injectable bone-filling materials
  Nonoyama, T.; Ogasawara, H.; Tanaka, M.; Higuchi, M.; Kinoshita, T. *Soft Matter* **2012**, *8*, 11531-11536.
  Abstract:



We performed amorphous calcium phosphate (ACP) and hydroxyapatite (HAp) mineralization in peptide hydrogels for the formation of a novel bone-filling material. We prepared two kinds of β-sheet peptides, $(LE)_8$ and $(VEVSVKVS)_2$, respectively, using hydrophilic glutamic acid (E), serine (S) and lysine (K), and hydrophobic leucine (L) and valine (V). Both peptides hierarchically self-assembled as nanofibers and formed hydrogels in the presence of calcium ions. The formation of the hydrogel was due to the ionic cross-linkage between carboxyl groups in the glutamic acid side chains of the peptide nanofibers and the calcium ion. $(LE)_8$ formed a clear hydrogel above a calcium ion concentration of 4.0×10^{-3} M and the hydrogel collapsed at 1.0×10^{-2} M, owing to excess ionic cross-linkage. On the other hand, $(VEVSVKVS)_2$ containing two glutamic acid residues per molecule retained the hydrogel structure at a higher concentration of calcium ions in the hydrogel where the $(LE)_8$ hydrogel collapsed. The viscoelastic property of both peptide hydrogels was increased by increasing the calcium ion concentration, showing adequate strength as a bone-filling material. When phosphate ion was added into the $(LE)_8$ hydrogel containing calcium ion, ACP was mineralized along the peptide nanofiber in the hydrogel under neutral pH. The $(VEVSVKVS)_2$ hydrogel, on the other hand, produced HAp under basic pH. In addition, the peptide hydrogel smoothly recovered its original moduli just after the shear deformation of the hydrogel. It was also clarified that calcium ions are not only a source of mineralization but also induce an increase in the mechanical strength of the hydrogels as a reinforcing agent. It was shown, moreover, that the crystallinity of the HAp was slightly dependent on the modulus of the peptide hydrogels. Therefore, it may be said that peptide hydrogels are applicable for tailor-made injectable bone-filling materials.