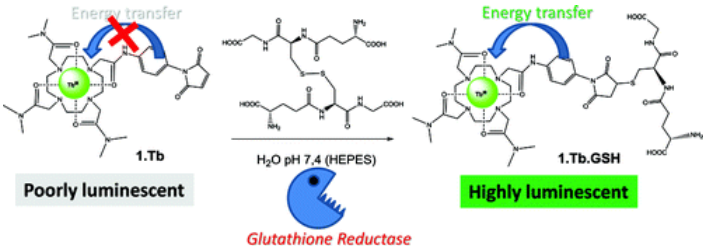
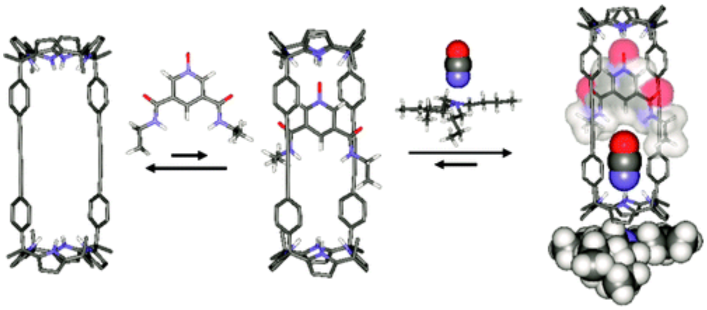
- Selective Detection of the Reduced Form of Glutathione (GSH) over the Oxidized (GSSG) Form Using a Combination of Glutathione Reductase and a Tb(III)-Cyclen Maleimide Based Lanthanide Luminescent 'Switch On' Assay
  McMahon, B. K.; Gunnlaugsson, T. *J. Am. Chem. Soc.* **2012**, *134*, 10725–10728.
  Abstract:



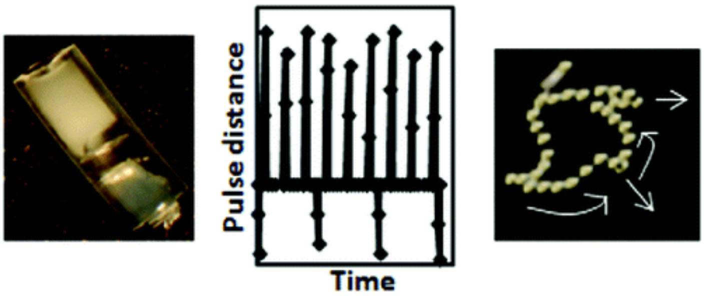
The synthesis of a novel Tb(III) luminescent probe for the detection of thiols is presented. The probe 1.Tb, possessing a maleimide moiety, as its sulfhydryl acceptor, was poorly emitting in aqueous pH 7 solution in the absence of a thiol. However, upon addition of thiols such as glutathione (GSH), large enhancements were observed, particularly within the physiological pH range. In contrast no enhancements were observed in the presence of the oxidized form of glutathione (GSSG), except in the presence of the enzyme *glutathione reductase* and NADPH which enabled 1.Tb to be used to observe the enzymatic reduction of GSSG to GSH in real time.

- Polyatomic Anion Assistance in the Assembly of [2]Pseudorotaxanes
  Valderrey, V.; Escudero-Adán, E. C.; Ballester, P. *J. Am. Chem. Soc.* **2012**, *134*, 10733–10736.
  Abstract:



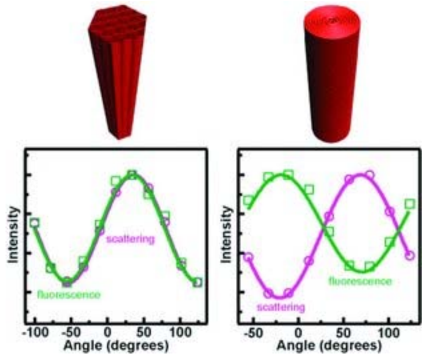
We describe the use of polyatomic anions for the quantitative assembly of ion-paired complexes displaying pseudorotaxane topology. Our approach exploits the unique ion-pair recognition properties exhibited by noncovalent neutral receptors assembled through hydrogen-bonding interactions between a bis-calix[4]pyrrole macrocycle and linear bis-amidepyridyl-*N*-oxides. The complexation of bidentate polyatomic anions that are complementary in size and shape to the receptor's cavity, in which six NH hydrogen-bond donors converge, induces the exclusive formation of four particle-threaded assemblies.

- Gel-Based Self-Propelling Particles Get Programmed To Dance
  Sharma, R.; Chang, S. T.; Velev, O. D. *Langmuir* **2012**, *28*, 10128-10135.
  Abstract:



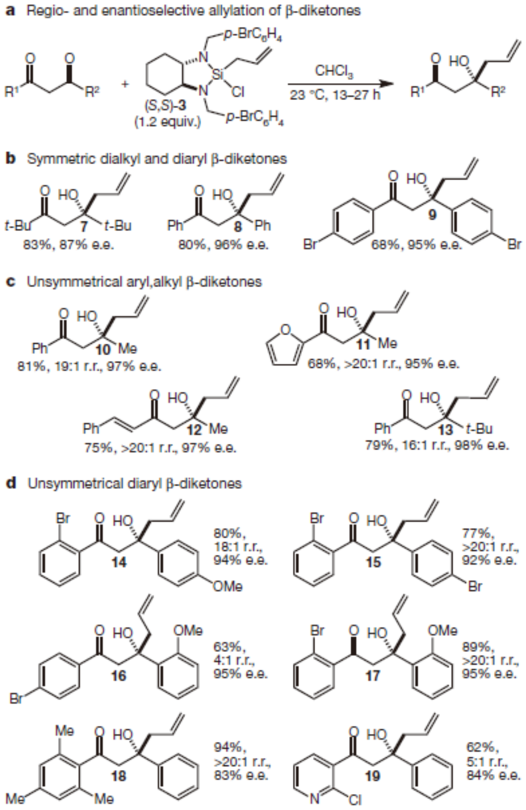
We present a class of gel-based self-propelling particles moving by the Marangoni effect in an oscillatory mode. The particles are made of an ethanol-infused polyacrylamide hydrogel contained in plastic tubing. These gel boats floating on the water surface exhibit periodic propulsion for several hours. The release of ethanol from the hydrogel takes place beneath the liquid surface. The released ethanol rises to the air–water interface by buoyancy and generates a self-sustained cycle of surface tension gradient driven motion. The disruption of the ethanol flux to the surface by the bulk flows around the moving particle results in their pulsating motion. The pulse interval and the distance propelled in a pulse by these gel floaters were measured and approximated by simple expressions based on the rate of ethanol mass-transfer through and out of the hydrogel. This allowed us to design a multitude of particles performing periodic steps in different directions or at different angles of rotation, traveling in complex preprogrammed trajectories on the surface of the liquid. Similar gel-based self-propelling floaters can find applications as mixers and cargo carriers in lab-on-a-chip devices, and in various platforms for sensing and processing at the microscale.

- Alignment Control of Polythiophene Chains with Mesostructured Silica Nanofibers Having Different Pore Orientations
  Yang, B.; Xiao, M.; Zhao, C.; Zhang, S.; Jiang, A.; Wang, J. *Small* **2012**, *8*, 2021–2026.
  Abstract:



Alignment control of polythiophene chains with mesostructured silica nanofibers through an organic–inorganic co-assembly approach is realized. Cationic ammonium surfactants with a polymerizable thiophene end group are synthesized and subsequently used as structure-directing agents to grow silica nanofibers with two different pore architectures. In situ polymerization produces mesostructured polythiophene−silica nanofibers with the polymer chains aligned along the pore channels.

- Direct and highly regioselective and enantioselective allylation of β-diketones
  Chalifoux, W. A.; Reznik, S. K.; Leighton, J. L. *Nature* **2012***, 487*, 86-89.
  Abstract:


a Regio- and enantioselective allylation of β-diketones

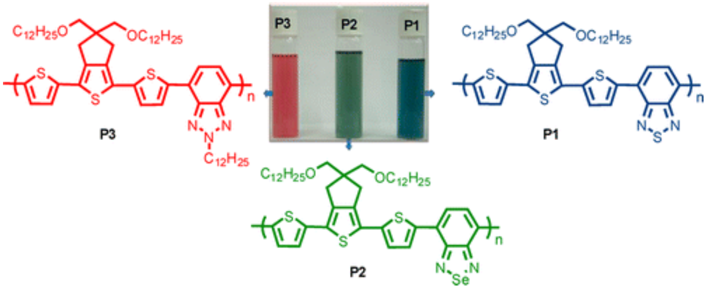
b Symmetric dialkyl and diaryl β-diketones

c Unsymmetrical aryl,alkyl β-diketones

d Unsymmetrical diaryl β-diketones

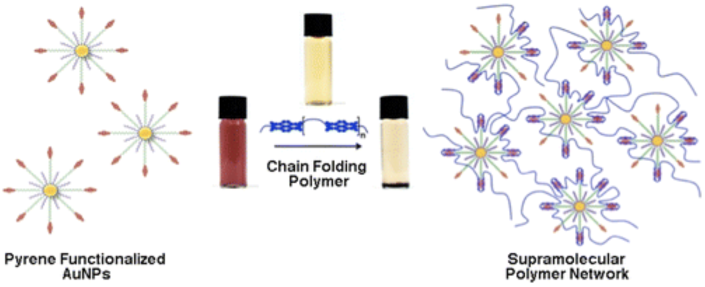
The enantioselective allylation of ketones is a problem of fundamental importance in asymmetric reaction design, especially given that only a very small number of methods can generate tertiary carbinols. Despite the vast amount of attention that synthetic chemists have given to this problem, success has generally been limited to just a few simple ketone types. A method for the selective allylation of functionally complex ketones would greatly increase the utility of ketone allylation methods in the chemical synthesis of important targets. Here we describe the operationally simple, direct, regioselective and enantioselective allylation of β-diketones. The strong tendency of β-diketones to act as nucleophilic species was overcome by using their enol form to provide the necessary Brøsted-acid activation. This reaction significantly expands the pool of enantiomerically enriched and functionally complex tertiary carbinols that may be easily accessed. It also overturns more than a century of received wisdom regarding the reactivity of β-diketones.

- Cyclopenta[*c*]thiophene-Based D–A Conjugated Copolymers: Effect of Heteroatoms (S, Se, and N) of Benzazole Acceptors on the Properties of Polymers
  Das, S.; Pati, P. B.; Zade, S. S. *Macromolecules* **2012**, *45*, 5410–5417.
  Abstract:



Three new donor–acceptor (D–A) type copolymers **P1**, **P2**, and **P3** have been synthesized by Stille condensation between the distannyl derivative of thiophene-capped cyclopenta[*c*]thiophene (CPT) with 4,7-dibromo[2,1,3]benzothiadiazole, 4,7-dibromo[2,1,3]benzoselenadiazole, and 4,7-dibromo[2,1,3]benzotriazole, respectively. These new CPT-based D–A copolymers showed an interesting trend of visible color (red, green, and blue) in solution as the acceptor was varied keeping the donor constant. The optical band gaps of the polymers, which were estimated by measuring the absorption onset in the UV–vis spectra of the film, were found to be 1.57, 1.44, and 1.86 eV for **P1**, **P2**, and **P3**, respectively. DFT calculations correlated the strength of the acceptors with the interesting trend in the colors of these $(D)_{nonvariant}–(A)_{variant}$ copolymers. Compared with the solution, the film state absorption of **P2** and **P3** was significantly red-shifted compared to that of **P1**, indicating the presence of strong interchain interactions due to efficient self-π-stacking in the solid state.

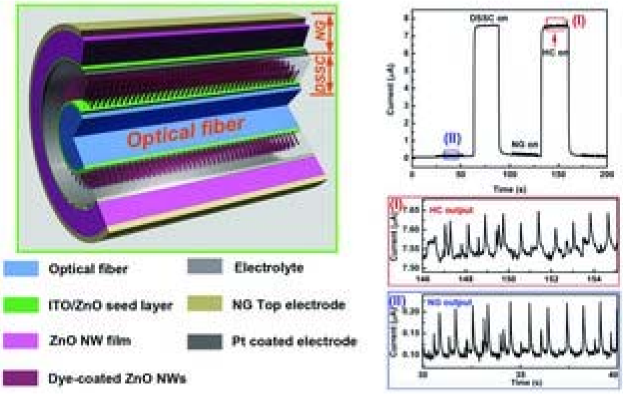
- Thermoresponsive Supramolecular Polymer Network Comprising Pyrene-Functionalized Gold Nanoparticles and a Chain-Folding Polydiimide
  Vaiyapuri, R.; Greenland, B. W.; Rowan, S. J.; Colquhoun, H. M.; Elliott, J. M.; Hayes, W. *Macromolecules* **2012**, *45*, 5567–5574.
  Abstract:



A thermoresponsive, supramolecular nanocomposite has been prepared by the addition of pyrenyl functionalized gold nanoparticles (AuNPs) to a polydiimide that contains receptor residues designed to form defined complexes with pyrene. The novel pyrenyl-functionalized AuNPs (P-AuNPs) were characterized by transmission electron microscopy, with surface functionalization confirmed by infrared and UV–visible spectroscopic analyses. Mixing solutions of the P-AuNPs and a π-electron-deficient polydiimide resulted in the formation of electronically complementary, chain-folded and π–π-stacked complexes, so affording a new supramolecular nanocomposite network which precipitated from solution. The P-AuNPs bind to the polydiimide via π–π stacking interactions to create supramolecular cross-links. UV–visible spectroscopic analysis confirmed the thermally reversible nature of the complexation process, and transmission electron microscopy (TEM), infrared spectroscopy (IR), and differential scanning calorimetry (DSC) were used to characterize the supramolecular-nanocomposite material. The supramolecular polymer network is insoluble at room temperature, yet may be dissolved at temperatures above 60 °C. The thermal reversibility of this system is maintained over five heat/cool cycles without diminishment of the network characteristics. In contrast to the individual components, the nanocomposite formed self-supporting films, demonstrating the benefit of the supramolecular network in terms of mechanical properties. Control experiments probing the interactions between a model diimide compound that can also form a π-stacked complex with the π-electron rich pyrene units on P-AuNPs showed that, while complexation was readily apparent, precipitation did not occur because a supramolecular cross-linked network system could not be formed with this system.

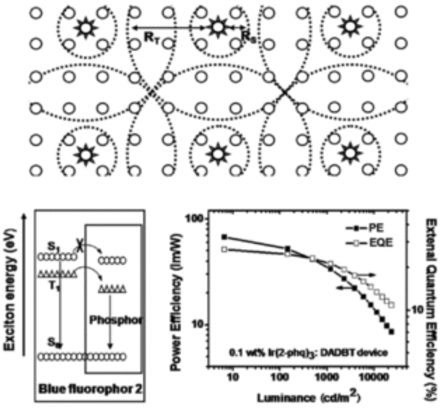
- Optical Fiber-Based Core–Shell Coaxially Structured Hybrid Cells for Self-Powered Nanosystems

Pan, C.; Guo, W.; Dong, L.; Zhu, G.; Wang, Z. L. *Adv. Mater.* **2012**, *24*, 3356–3361.
Abstract:



An optical fiber-based 3D hybrid cell consisting of a coaxially structured dye-sensitized solar cell (DSSC) and a nanogenerator (NG) for simultaneously or independently harvesting solar and mechanical energy is demonstrated. The current output of the hybrid cell is dominated by the DSSC, and the voltage output is dominated by the NG; these can be utilized complementarily for different applications. The output of the hybrid cell is about 7.65 μA current and 3.3 V voltage, which is strong enough to power nanodevices and even commercial electronic components.

- Management of Singlet and Triplet Excitons in a Single Emission Layer: A Simple Approach for a High-Efficiency Fluorescence/Phosphorescence Hybrid White Organic Light-Emitting Device
  Ye, J.; Zheng, C.-J.; Ou, X.-M.; Zhang, X.-H.; Fung, M.-K.; Lee, C.-S. *Adv. Mater.* **2012**, *24*, 3410–3414.
  Abstract:

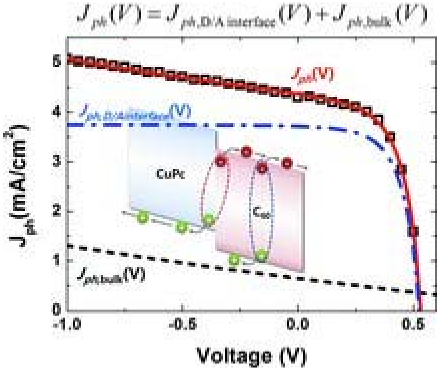


A high-efficiency single-emission-layer (EML) hybrid white organic light emitting device is fabricated based on an ideal sky-blue fluorophor, DADBT, using a novel doping concentration regulation strategy, which effectively separates and respectively utilizes the singlet and triplet excitons in the single-EML. The white device shows excellent electroluminescence performance with maximum total efficiencies of 26.6%, 53.5 cd A^{-1} and 67.2 lm W^{-1}.

- Formation Mechanism of Fullerene Cation in Bulk Heterojunction Polymer Solar Cells
  Yamamoto, S.; Ohkita, H.; Benten, H.; Ito, S. *Adv. Funct. Mater.* **2012**, *22*, 3075–3082.
  Abstract:

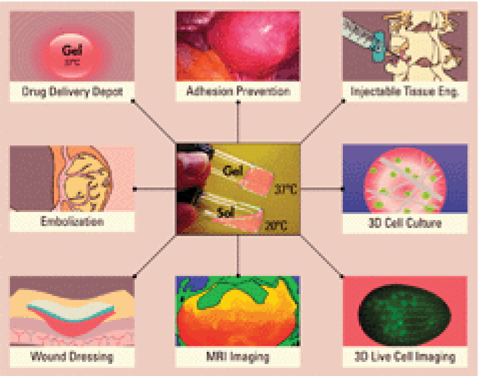
The charge carrier dynamics in blend films of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and conjugated polymers with different ionization potentials are measured using transient absorption spectroscopy to study the formation mechanism of PCBM radical cation, which was previously discovered for blend films of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and PCBM. On a nanosecond time scale after photoexcitation, polymer hole polaron and PCBM radical anion are observed but no PCBM radical cation is found in the blends. Subsequently, the fraction of polymer hole polarons decreases and that of PCBM radical cations increases with time. Finally, the fraction of PCBM radical cations becomes constant on a microsecond time scale. The final fraction of PCBM radical cation is dependent on the ionization potential of polymers but independent of the excitation wavelength. These findings show that the formation of PCBM radical cation is due to hole injection from polymer to PCBM domains. Furthermore, the energetic conditions for such hole injection in polymer/PCBM blend films are discussed on the basis of Monte Carlo analysis for hole hopping in a disordered donor/acceptor heterojunction with varying energetic parameters.

- Photoconductivity of C60 as an Origin of Bias-Dependent Photocurrent in Organic Photovoltaics
  Jeong, W.-I.; Lee, Y. E.; Shim, H.-S.; Kim, T.-M.; Kim, S.-Y.; Kim, J.-J. *Adv. Funct. Mater.* **2012**, *22*, 3089–3094.
  Abstract:



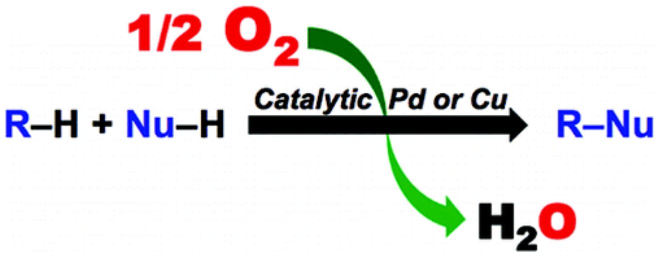
The bulk-ionized photoconductivity of C_{60} is reported as an origin of the bias-dependent linear change of the photocurrent in copper phthalocyanine (CuPc)/C_{60} planar heterojunction solar cells, based on the observation of the variation of the bias-dependent photocurrent on excitation wavelengths and the thickness-dependent photocurrent of the C_{60} layer. A theoretical model, which is a combination of the Braun-Onsager model for the dissociation of excitons at the donor/acceptor interface and the Onsager model for the bulk ionization of excitons in the C_{60} layer, describes the bias-dependent photocurrent in the devices very well. The bulk-ionized photoconductivity of C_{60} must generally contribute to the photocurrent in organic photovoltaics, since fullerene and fullerene derivatives are widely used in these devices.

- Temperature-responsive compounds as *in situ* gelling biomedical materials
  Moon, H. J.; Ko, D. Y.; Park, M. H.; Joo, M. K.; Jeong, B. *Chem. Soc. Rev.* **2012**, *41*, 4860-4883.
  Abstract:



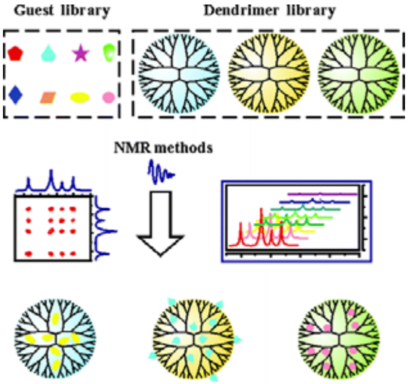
Aqueous solutions that undergo sol-to-gel transition as the temperature increases have been extensively studied during the last decade. The material can be designed by controlling the hydrophilic and hydrophobic balance of the material. Basically, the molecular weight of the hydrophilic block and hydrophobic block of a compound should be fine-tuned from the synthetic point of view. In addition, stereochemistry, microsequence, topology, and nanostructures of the compound also affect the transition temperature, gel window, phase diagram, and modulus of the gel. From a practical point of view, biodegradability, biocompatibility, and interactions between the material and drug or cell should be considered in designing a thermogelling material. The interactions are particularly important in that they control drug release profile and initial burst release of the drug in the drug delivery system, and affect cell proliferation, differentiation, and biomarker expression in three-dimensional cell culture and tissue engineering application. This review provides an in-depth summary of the recent progress of thermogelling systems including polymers, low molecular compounds, and nanoemulsions. Their biomedical applications were also comparatively discussed. In addition, perspectives on future material design of a new thermogelling material and its application are suggested.

- Overcoming the “Oxidant Problem”: Strategies to Use O_2 as the Oxidant in Organometallic C–H Oxidation Reactions Catalyzed by Pd (and Cu)
  Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**, *45*, 851–863.
  Abstract:



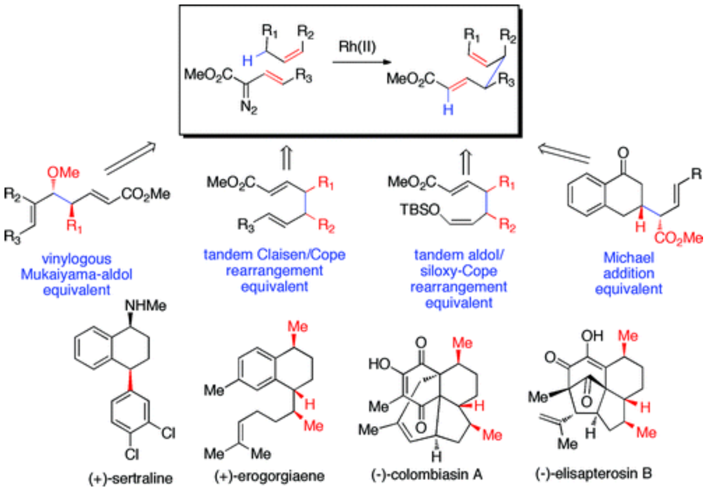
Methods for selective oxidation of C–H bonds have expanded significantly over the past decade, and their role in the synthesis of organic chemicals will continue to increase. Our group’s contributions to this field are linked to our broader interest in the development and mechanistic understanding of aerobic oxidation reactions. Molecular oxygen (O_2) is the ideal oxidant. Its low cost and lack of toxic byproducts make it a highly appealing reagent that can address key “green chemistry” priorities in industry. With strong economic and environmental incentives to use O_2, the commmodity chemicals industry often uses aerobic oxidation reactions. In contrast, O_2 is seldom used to prepare more-complex smaller-volume chemicals, a limitation that reflects, in part, the limited synthetic scope and utility of existing aerobic reactions.

- NMR Insights into Dendrimer-Based Host–Guest Systems
  Hu, J.; Xu, T.; Cheng, Y. *Chem. Rev.* **2012**, *112*, 3856–3891.
  Abstract:



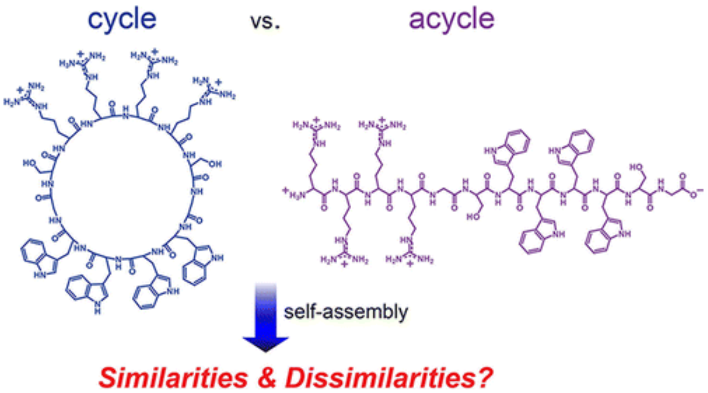
The aim of this critical review is to illustrate how new insights into dendrimer-based host–guest systems can be obtained by NMR studies. The theoretical background of NMR techniques was first introduced, including chemical shift titration, NOE analysis, diffusion NMR, relaxation measurement, and STD. Then the applications of NMR techniques in the analysis of dendrimer-based host–guest systems were discussed, such as qualitative and quantitative analysis of interactions between dendrimers and guest molecules, the localization of guest molecules within dendrimer scaffolds, the physicochemical properties of dendrimer-guest complexes, and methods proposed to screen dendrimer-binding compounds.

- The Combined C–H Functionalization/Cope Rearrangement: Discovery and Applications in Organic Synthesis
  Davies, H. M. L.; Lian, Y. *Acc. Chem. Res.* **2012**, *45*, 923–935.
  Abstract:



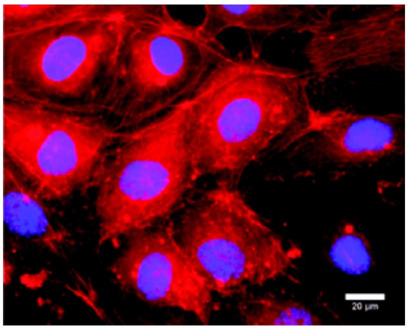
The development of methods for the stereoselective functionalization of sp^3 C–H bonds is a challenging undertaking. This Account describes the scope of the combined C–H functionalization/Cope rearrangement (CHCR), a reaction that occurs between rhodium-stabilized vinylcarbenoids and substrates containing allylic C–H bonds.

- Differential Self-Assembly Behaviors of Cyclic and Linear Peptides
  Choi, S.-J; Jeong, W.-J.; Kang, S.-K.; Lee, M.; Kim, E.; Ryu, D. Y.; Lim, Y.-B. *Biomacromolecules* **2012**, *13*, 1991–1995.
  Abstract:



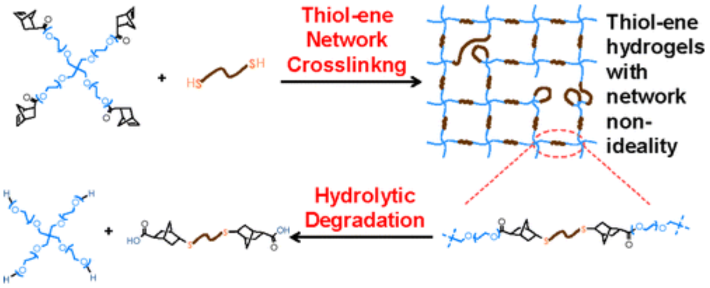
Here we ask the fundamental questions about the effect of peptide topology on self-assembly. The study revealed that the self-assembling behaviors of cyclic and linear peptides are significantly different in several respects, in addition to sharing several similarities. Their clear differences included the morphological dissimilarities of the self-assembled nanostructures and their thermal stability. The similarities include their analogous critical aggregation concentration values and cytotoxicity profiles, which are in fact closely related. We believe that understanding topology-dependent self-assembly behavior of peptides is important for developing tailor-made self-assembled peptide nanostructures.

- Collagen-Based Fibrillar Multilayer Films Cross-Linked by a Natural Agent
  Chaubaroux, C.; Vrana, E.; Debry, C.; Schaaf, P.; Senger, B.; Voegel, J.-C.; Haikel, Y.; Ringwald, C.; Hemmerlé, J.; Lavalle, P.; Boulmedais, F. *Biomacromolecules* **2012**, *13*, 2128–2135.
  Abstract:



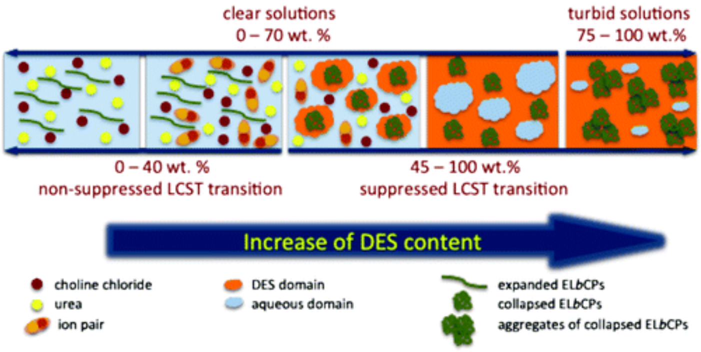
Surface functionalization plays an important role in the design of biomedical implants, especially when layer forming cells, such as endothelial or epithelial cells, are needed. In this study, we define a novel nanoscale surface coating composed of collagen/alginate polyelectrolyte multilayers and cross-linked for stability with genipin. This buildup follows an exponential growth regime versus the number of deposition cycles with a distinct nanofibrillar structure that is not damaged by the cross-linking step. Stability and cell compatibility of the cross-linked coatings were studied with human umbilical vein endothelial cells. The surface coating can be covered by a monolayer of vascular endothelial cells within 5 days. Genipin cross-linking renders the surface more suitable for cell attachment and proliferation compared to glutaraldehyde (more conventional cross-linker) cross-linked surfaces, where cell clumps in dispersed areas were observed. In summary, it is possible with the defined system to build fibrillar structures with a nanoscale control of film thickness, which would be useful for in vivo applications such as inner lining of lumens for vascular and tracheal implants.

- Cross-Linking and Degradation of Step-Growth Hydrogels Formed by Thiol–Ene Photoclick Chemistry
  Shih, H.; Lin, C. C. *Biomacromolecules* **2012**, *13*, 2003–2012.
  Abstract:



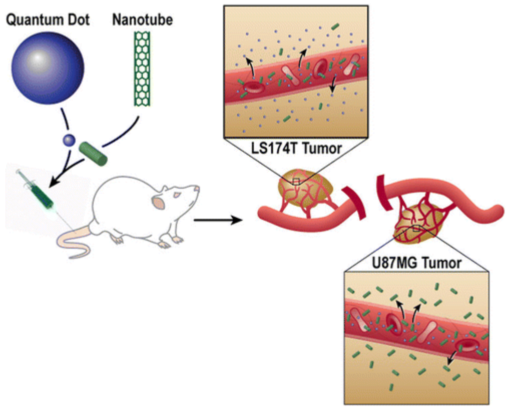
Thiol–ene photoclick hydrogels have been used for a variety of tissue engineering and controlled release applications. In this step-growth photopolymerization scheme, four-arm poly(ethylene glycol) norbornene (PEG4NB) was cross-linked with dithiol containing cross-linkers to form chemically cross-linked hydrogels. While the mechanism of thiol–ene gelation was well described in the literature, its network ideality and degradation behaviors are not well-characterized. Here, we compared the network cross-linking of thiol–ene hydrogels to Michael-type addition hydrogels and found thiol–ene hydrogels formed with faster gel points and higher degree of cross-linking. However, thiol–ene hydrogels still contained significant network nonideality, demonstrated by a high dependency of hydrogel swelling on macromer contents. In addition, the presence of ester bonds within the PEG-norbornene macromer rendered thiol–ene hydrogels hydrolytically degradable. Through validating model predictions with experimental results, we found that the hydrolytic degradation of thiol–ene hydrogels was not only governed by ester bond hydrolysis, but also affected by the degree of network cross-linking. In an attempt to manipulate network cross-linking and degradation of thiol–ene hydrogels, we incorporated peptide cross-linkers with different sequences and characterized the hydrolytic degradation of these PEG-peptide hydrogels. In addition, we incorporated a chymotrypsin-sensitive peptide as part of the cross-linkers to tune the mode of gel degradation from bulk degradation to surface erosion.

- Phase Behavior of Elastin-Like Synthetic Recombinamers in Deep Eutectic Solvents
  Nardecchia, S.; Gutiérrez, M. C.; Ferrer, L.; Alonso, M.; López, I. M.; Rodríguez-Cabello, J. C.; del Monte, F. *Biomacromolecules* **2012**, *13*, 2029–2036.
  Abstract:



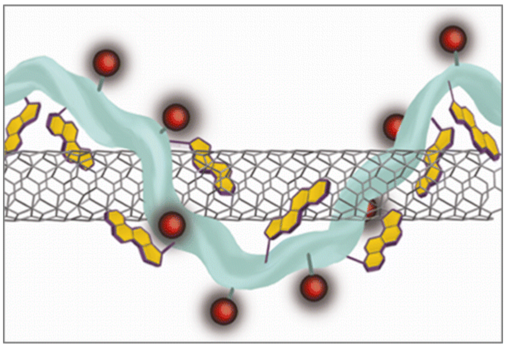
Deep eutectic solvents promoted the stabilization of the collapsed state of elastin-like recombinamers – and the subsequent formation of aggregates – upon the loss of the structural water molecules involved in hydrophobic hydration. Cryo-etch scanning electron microscopy allowed the observation of these aggregates in neat deep eutectic solvents. The suppression of the lower critical solution temperature transition, observed by differential scanning calorimetry and dynamic light scattering, confirmed the presence of the elastin-like recombinamers in their collapsed state. Actually, the transition from the collapsed to the expanded state was suppressed even after moderate aqueous dilution – for water contents ranging from nil to ca. 45 wt % – and it was only recovered upon further addition of water – above 50 wt %. These features revealed the preferred stabilization of the collapsed state in not only neat deep eutectic solvents but also partially hydrated deep eutectic solvents. We consider that the capability to trigger the lower critical solution temperature transition by partial hydration of deep eutectic solvent may open interesting perspectives for nano(bio)technological applications of elastin-like recombinamers.

- Shape Matters: Intravital Microscopy Reveals Surprising Geometrical Dependence for Nanoparticles in Tumor Models of Extravasation
  Smith, B. R.; Kempen, P.; Bouley, D.; Xu, A.; Liu, Z.; Melosh, N.; Dai, H.; Sinclair, R.; Gambhir, S. S. *Nano Letters* **2012**, *12*, 3369-3377.
  Abstract:



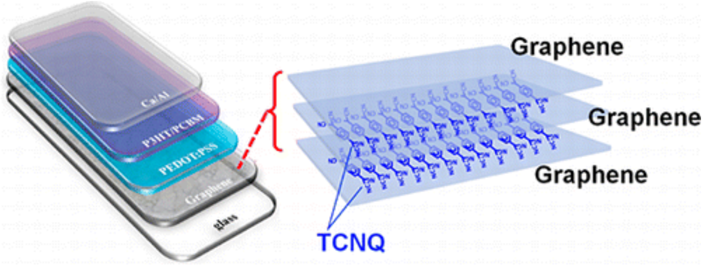
Delivery is one of the most critical obstacles confronting nanoparticle use in cancer diagnosis and therapy. For most oncological applications, nanoparticles must extravasate in order to reach tumor cells and perform their designated task. However, little understanding exists regarding the effect of nanoparticle shape on extravasation. Herein we use real-time intravital microscopic imaging to meticulously examine how two different nanoparticles behave across three different murine tumor models. The study quantitatively demonstrates that high-aspect ratio single-walled carbon nanotubes (SWNTs) display extravasational behavior surprisingly different from, and counterintuitive to, spherical nanoparticles although the nanoparticles have similar surface coatings, area, and charge. This work quantitatively indicates that nanoscale extravasational competence is highly dependent on nanoparticle geometry and is heterogeneous.

- A Facile, One-Step Nanocarbon Functionalization for Biomedical Applications
  Swierczewska, M.; Choi, K. Y.; Mertz, E. L.; Huang, X.; Zhang, F.; Zhu, L.; Yoon, H. Y.; Park, J. H.; Bhirde, A.; Lee, S.; Chen, X. *Nano Letters* **2012**, *12*, 3613-3620.
  Abstract:



Despite their immense potential in biomedicine, carbon nanomaterials suffer from inefficient dispersion and biological activity in vivo. Here we utilize a single, yet multifunctional, hyaluronic acid-based biosurfactant to simultaneously disperse nanocarbons and target single-walled carbon nanotubes (SWCNTs) to CD44 receptor positive tumor cells with prompt uptake. Cellular uptake was monitored by intracellular enzyme-activated fluorescence, and localization of SWCNTs within cells was further confirmed by Raman mapping. In vivo photoacoustic, fluorescence, and positron emission tomography imaging of coated SWCNTs display high tumor targeting capability while providing long-term, fluorescence molecular imaging of targeted enzyme events. By utilizing a single biomaterial surfactant for SWCNT dispersion without additional bioconjugation, we designed a facile technique that brings nanocarbons closer to their biomedical potential.

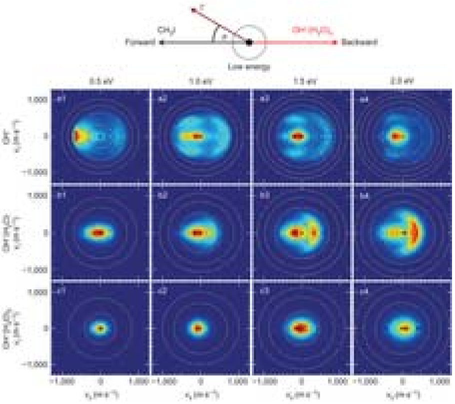
- Layer-by-Layer Graphene/TCNQ Stacked Films as Conducting Anodes for Organic Solar Cells
  Hsu, C.-L.; Lin, C.-T.; Huang, J.-H.; Chu, C.-W.; Wei, K.-H.; Li, L.-J. *ACS Nano* **2012,** *6*, 5031-5039.
  Abstract:



Large-area graphene grown by chemical vapor deposition (CVD) is a promising candidate for transparent conducting electrode applications in flexible optoelectronic devices such as light-emitting diodes or organic solar cells. However, the power conversion efficiency (PCE) of the polymer photovoltaic devices using a pristine CVD graphene anode is still not appealing due to its much lower conductivity than that of conventional indium tin oxide. We report a layer-by-layer molecular doping process on graphene for forming sandwiched graphene/tetracyanoquinodimethane (TCNQ)/graphene stacked films for polymer solar cell anodes, where the TCNQ molecules (as p-dopants) were securely embedded between two graphene layers. Poly(3-hexylthiophene)/phenyl-

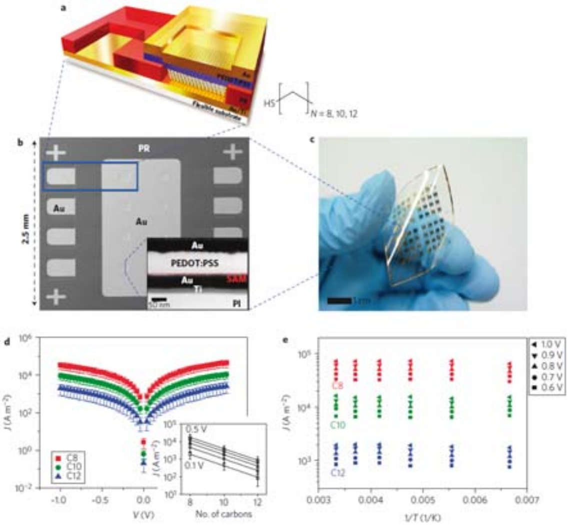
C61-butyric acid methyl ester (P3HT/PCBM) bulk heterojunction polymer solar cells based on these multilayered graphene/TCNQ anodes are fabricated and characterized. The P3HT/PCBM device with an anode structure composed of two TCNQ layers sandwiched by three CVD graphene layers shows optimum PCE (~2.58%), which makes the proposed anode film quite attractive for next-generation flexible devices demanding high conductivity and transparency.

- Single solvent molecules can affect the dynamics of substitution reactions
  Otto, R.; Brox, J.; Trippel, S.; Stei, M.; Best, T.; Wester, R. *Nature Chemistry* **2012**, *4,* 534–538.
  Abstract:



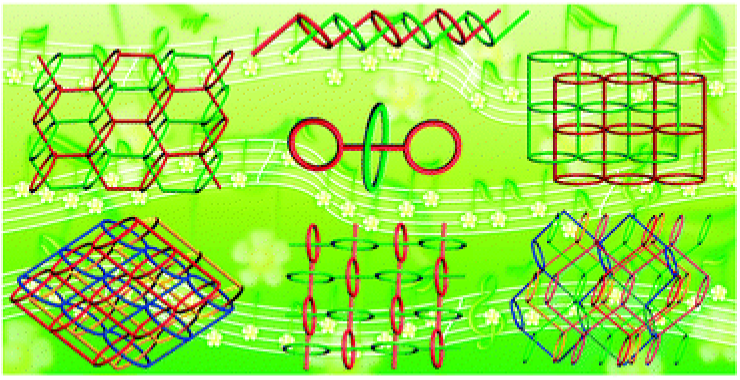
Solvents have a profound influence on chemical reactions in solution and have long been used to control their outcome. Such effects are generally considered to be governed by thermodynamics; however, little is known about the steric effects of solvent molecules. Here, we probe the influence of individual solvent molecules on reaction dynamics and present results on the atomistic dynamics of a microsolvated chemical reaction—the fundamentally important nucleophilic substitution reaction. We study the reaction of OH− with CH_3I using a technique that combines crossed-beam imaging with a cold source of microsolvated reactants. Our results reveal several distinct reaction mechanisms for different degrees of solvation; surprisingly, the classical co-linear substitution mechanism only dominates the dynamics for mono-solvated reactants. We analyse the relative importance of the different mechanisms using ab initio calculations and show that the steric characteristics are at least as relevant as the energetics in understanding the influence of solvent molecules in such microsolvated reactions.

- Flexible molecular-scale electronic devices
  Park, S.; Wang, G.; Cho, B.; Kim, Y.; Song, S.; Ji, Y.; Yoon, M-H.; Lee, T. *Nature Nanotechnology* **2012**, *7*, 438–442.
  Abstract:



Flexible materials and devices could be exploited in light-emitting diodes, electronic circuits, memory devices, sensors, displays, solar cells and bioelectronic devices. Nanoscale elements such as thin films, nanowires, nanotubes and nanoparticles can also be incorporated into the active films of mechanically flexible devices. Large-area devices containing extremely thin films of molecular materials represent the ultimate scaling of flexible devices based on organic materials, but the influence of bending and twisting on the electrical and mechanical stability of such devices has never been examined. Here, we report the fabrication and characterization of two-terminal electronic devices based on self-assembled monolayers of alkyl or aromatic thiol molecules on flexible substrates. We find that the charge transport characteristics of the devices remain stable under severe bending conditions (radius ≤ 1 mm) and a large number of repetitive bending cycles (≥1,000). The devices also remain reliable in various bending configurations, including twisted and helical structures.

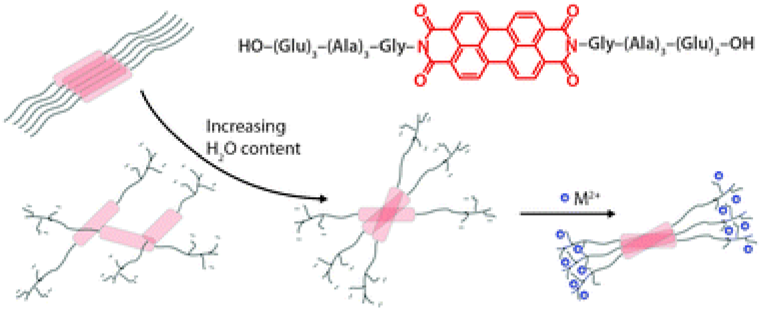
- Polyrotaxane metal–organic frameworks (PMOFs)
  Yang, J.; Ma, J. F.; Batten, S. R. *Chem. Commun.* **2012**, *48*, 7899-7912.
  Abstract:



In this feature article, we make some generalizations about the various classes of polyrotaxane metal–organic frameworks (PMOFs), and develop the definitions and nomenclature of these entanglements, including classification into trivial and nontrivial polyrotaxanes, and limits on what constitutes a (nontrivial) polyrotaxane.

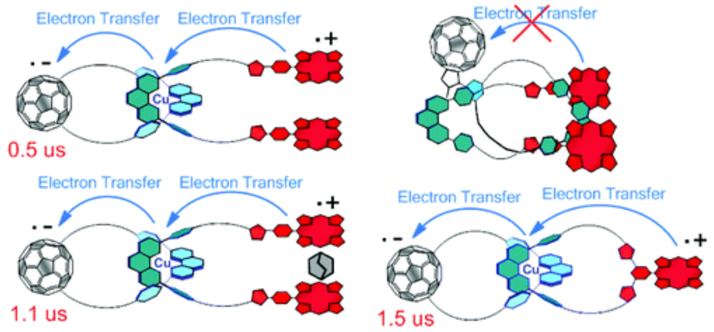
- Controlled aggregation of peptide-substituted perylene-bisimides

Gallaher, J. K.; Aitken, E. J.; Keyzers, R. A.; Hodgkiss, J. M. *Chem. Commun.* **2012**, *48*, 7961-7963.
Abstract:



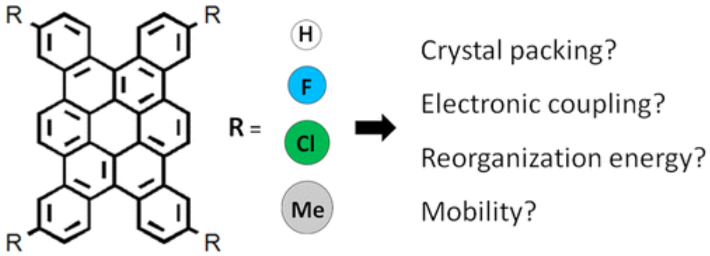
Controlled aggregation of perylene bisimides in multiple modes has been achieved via symmetric substitution with peptides.

- Topological and Conformational Effects on Electron Transfer Dynamics in Porphyrin-[60]Fullerene Interlocked Systems
  Megiatto, Jr., J. D.; Schuster, D. I.; de Miguel, G.; Wolfrum, S.; Guldi, D. M. *Chem. Mater.* **2012**, *24*, 2472–2485.
  Abstract:



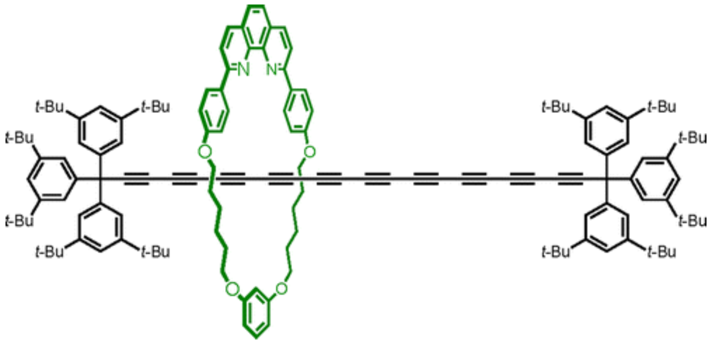
The effect of molecular topology and conformation on the dynamics of photoinduced electron transfer (ET) processes has been studied in interlocked electron donor–acceptor systems, specifically rotaxanes with zinc(II)-tetraphenylporphyrin (ZnP) as the electron donor and [60]fullerene (C60) as the electron acceptor. Formation or cleavage of coordinative bonds was used to induce major topological and conformational changes in the interlocked architecture. In the first approach, the tweezer-like structure created by the two ZnP stopper groups on the thread was used as a recognition site for complexation of 1,4-diazabicyclo[2.2.2]octane (DABCO), which creates a bridge between the two ZnP moieties of the rotaxane, generating a catenane structure. The photoinduced processes in the DABCO-complexed (ZnP)2-[2]catenate-C60 system were compared with those of the (ZnP)2-rotaxane-C60 precursor and the previously reported ZnP-[2]catenate-C60. Steady-state emission and transient absorption studies showed that a similar multistep ET pathway emerged for rotaxanes and catenanes upon photoexcitation at various wavelengths, ultimately resulting in a long-lived ZnP•+/C60•– charge-separated radical pair (CSRP) state. However, the decay kinetics of the CSRP states clearly reflect the topological differences between the rotaxane, the catenate, and DABCO-complexed-catenate architectures. The lifetime of the long-distance ZnP•+–[Cu(I)phen2]+–C60•– CSRP state is more than four times longer in 3 (1.03 μs) than in 1 (0.24 μs) and approaches that in catenate 2 (1.1 μs). The results clearly showed that creation of a catenane from a rotaxane topology inhibits the charge recombination process. In a second approach, when the Cu(I) ion used as the template to assemble the (ZnP)2–[Cu(I)phen2]+–C60 rotaxane was removed, it was evident that a major structural change had occurred. since charge separation between the chromophores was no longer observed upon photoexcitation in nonpolar as well as in polar solvents. Only ZnP and C60 triplet excited states were observed upon laser excitation of the Cu-free rotaxane. These results highlight the critical importance of the central Cu(I) ion for long-range ET processes in these nanoscale interlocked electron donor–acceptor systems.

- Contorted Tetrabenzocoronene Derivatives for Single Crystal Field Effect Transistors: Correlation between Packing and Mobility
  Pola, S.; Kuo, C.-H.; Peng, W.-T.; Islam, Md. M.; Chao, I.; Tao, Y.-T *Chem. Mater.* **2012**, *24*, 2566–2571.
  Abstract:



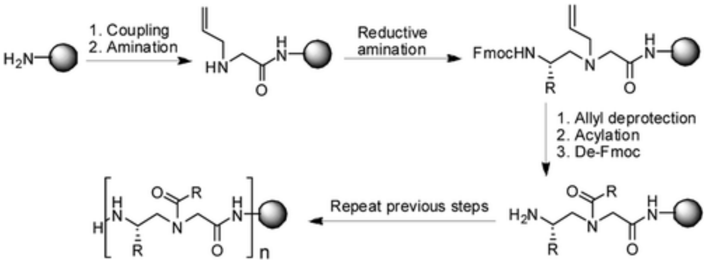
A series of contorted tetrabenzo[a,d,j,m]coronenes (TBCs) substituted with four fluoro-, chloro-, or methyl groups at 2,7,12,17-positions were synthesized and characterized. Except for the one with methyl substituents, which exhibits a shifted π–π stacking, the rest all show cofacial π–π stacking with small parallel displacements. One-dimensional growth along the stacking direction was observed in the single crystals for all derivatives. A systematic comparison of the crystal packing and the calculated electronic coupling/mobility with the measured field-effect mobility for single-crystal field-effect transistors shows a good correlation.

- Synthesis of Polyyne Rotaxanes
  Movsisyan, L. D.; Kondratuk, D. V.; Franz, M.; Thompson, A. L.; Tykwinski, R. R.; Anderson, H. L. *Org. Lett.* **2012**, *14*, 3424-3426.
  Abstract:



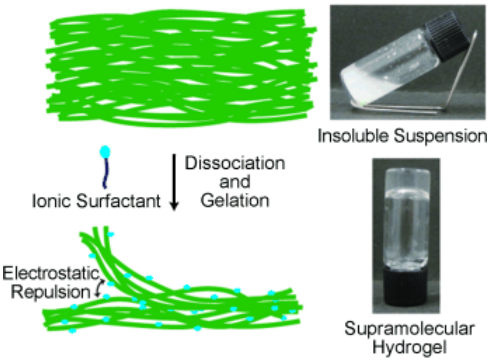
Active-metal templating has been used to synthesize rotaxanes consisting of a phenanthroline-based macrocycle threaded around a C8, C12, or C20 polyyne chain. The crystal structure of the C12 rotaxane has been determined. In the rhenium(I) carbonyl complex of this rotaxane, with $Re(CO)_3Cl$ coordinated to the phenanthroline macrocycle, the proximity of the polyyne chain quenches the luminescence of the rhenium. These rotaxanes offer a new approach to controlling the environment and interactions of a polyyne chain.

- Solid-Phase Synthesis of γ-AApeptides Using a Submonomeric Approach
  Wu, H.; Nassir Amin, M.; Niu, Y.; Qiao, Q.; Harfouch, N.; Nimer, A.; Cai, J. *Org. Lett.* **2012**, *14*, 3446-3449.
  Abstract:



The solid-phase synthesis of γ-AApeptides using a novel submonomeric approach that utilizes an allyl protection is reported. The strategy successfully circumvents the necessity of preparing γ-AApeptide building blocks in order to prepare γ-AApeptide sequences. This method will maximize the potential of developing chemically diverse γ-AApeptide libraries and thereby facilitate the biological applications of γ-AApeptides in the future.

- Ionic Surfactants Induce Amphiphilic Tris(Urea) Hydrogel Formation
  Jinno, Y.; Yamanaka, M. *Chem. Asian J.* **2012**, *7*, 1768–1771.
  Abstract:



All bundled up: A tris(urea)benzene hydrogelator first self-assembles into fibrous aggregates, which come together to form bundles (see scheme). The bundling process can be controlled by the concentration of ionic surfactant additive. The right concentration leads to supramolecular hydrogel formation.