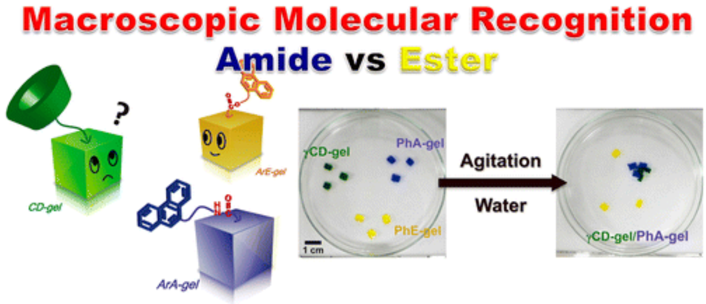
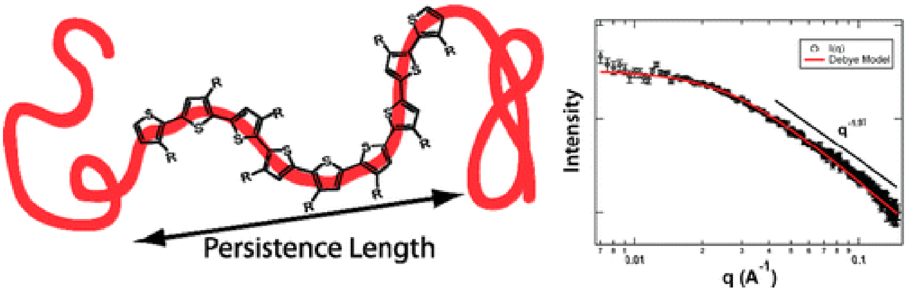
- Macroscopic Self-Assembly Based on Molecular Recognition: Effect of Linkage between Aromatics and the Polyacrylamide Gel Scaffold, Amide versus Ester
  Hashidzume, A.; Zheng, Y.; Takashima, Y.; Yamaguchi, H.; Harada, A. *Macromolecules* **2013**, *46*, 1939-1947.
  Abstract:



The interactions of polyacrylamide- (pAAm-) based gels possessing cyclodextrin (CD) residues (CD-gels) with pAAm-based gels modified with aromatic residues through amide and ester linkages (ArA-gels and ArE-gels, respectively) were investigated to examine the effect of linkage (i.e., amide and ester) between aromatic residues and the pAAm gel scaffold. In the present study, benzyl (Bz), 2-naphthylmethyl (Np), 9-phenanthrylmethyl (Ph), and 1-pyrenylmethyl (Py) residues were chosen as a series of aromatic residues. αCD-gel did not interact notably with the ArA-gels and ArE-gels in water. βCD-gel interacted with the ArA-gels and ArE-gels possessing smaller aromatic residues (i.e., Bz and Np residues) in water to form gel assemblies. γCD-gel showed different tendencies of its interactions with the ArA-gels and with the ArE-gels; γCD-gel interacted with the ArA-gels carrying larger aromatic residues (i.e., Ph and Py residues), while γCD-gel formed stable gel assemblies only with NpE-gel among the ArE-gels examined. This is because γCD residues in γCD-gel included favorably dimeric aromatic residues in the ArA-gels and ArE-gels. Reflection fluorescence spectra for the ArA-gels and ArE-gels possessing fluorescent aromatic residues (i.e., Np, Ph, and Py residues) in the presence of 10 mM γCD were indicative of weak selectivities of γCD toward NpE, PhA, and PyA residues. Such weak selectivities may be largely enhanced in the macroscopic observation of interaction of CD-gels with the ArA-gels and ArE-gels presumably because of multivalency.

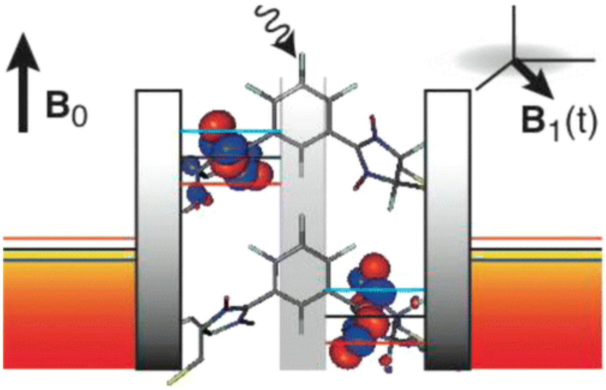
- Polymer Chain Shape of Poly(3-alkylthiophenes) in Solution Using Small-Angle Neutron Scattering
  McCulloch, B.; Ho, V.; Hoarfrost, M.; Stanley, C.; Do, C.; Heller, W. T.; Segalman, R. A. *Macromolecules* **2013**, *46*, 1899-1907.
  Abstract:



The chain shape of polymers affects many aspects of their behavior and is governed by their intramolecular interactions. Delocalization of electrons along the backbone of conjugated polymers has been shown to lead to increased chain rigidity by encouraging a planar conformation. Poly(3-

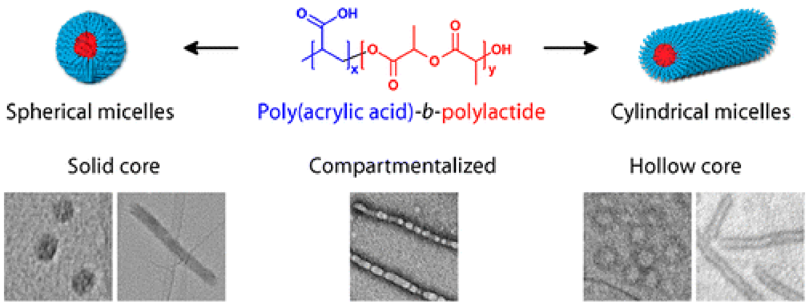
hexylthiophene) and other poly(3-alkylthiophenes) (P3ATs) are interesting for organic electronics applications, and it is clear that a hierarchy of structural features in these polymers controls charge transport. While other conjugated polymers are very rigid, the molecular structure of P3AT allows for two different planar conformations and a significant degree of torsion at room temperature. It is unclear, however, how their chain shape depends on variables such as side chain chemistry or regioregularity, both of which are key aspects in the molecular design of organic electronics. Small-angle neutron scattering from dilute polymer solutions indicates that the chains adopt a random coil geometry with a semiflexible backbone. The measured persistence length is shorter than the estimated conjugation length due to the two planar conformations that preserve conjugation but not backbone correlations. The persistence length of regioregular P3HT has been measured to be 3 nm at room temperature and decreases at higher temperatures. Changes in the regioregularity, side chain chemistry, or synthetic defects decrease the persistence length by 60-70%.

- Organic Single Molecular Structures for Light Induced Spin-Pump Devices
  Jahn, B. O.; Ottosson, H.; Galperin, M.; Fransson, J. *ACS Nano* **2013**, *7*, 1064-1071.
  Abstract:



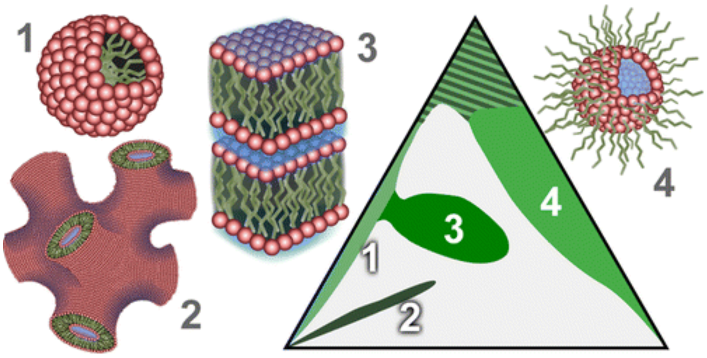
We present theoretical results on molecular structures for realistic spin-pump applications. Taking advantage of the electron spin resonance concept, we find that interesting candidates constitute triplet biradicals with two strongly spatially and energetically separated singly occupied molecular orbitals (SOMOs). Building on earlier reported stable biradicals, particularly bis(nitronyl nitroxide) based biradicals, we employ density functional theory to design a selection of potential molecular spin-pumps which should be persistent at ambient conditions. We estimate that our proposed molecular structures will operate as spin-pumps using harmonic magnetic fields in the MHz regime and optical fields in the infrared to visible light regime.

- Hollow Block Copolymer Nanoparticles through a Spontaneous One-step Structural Reorganization
  Petzetakis, N.; Robin, M. P.; Patterson, J. P.; Kelley, E. G.; Cotanda, P.; Bomans, P. H. H.; Sommerdijk, N. A. J. M.; Dove, A. P.; Epps, T. H.; O'Reilly, R. K. *ACS Nano* **2013**, *7*, 1120-1128.
  Abstract:



The spontaneous one-step synthesis of hollow nanocages and nanotubes from spherical and cylindrical micelles based on poly(acrylic acid)-b-polylactide (P(AA)-b-P(LA)) block copolymers (BCPs) has been achieved. This structural reorganization, which occurs simply upon drying of the samples, was elucidated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). We show that it was necessary to use stain-free imaging to examine these nanoscale assemblies, as the hollow nature of the particles was obscured by application of a heavy metal stain. Additionally, the internal topology of the P(AA)-b-P(LA) particles could be tuned by manipulating the drying conditions to give solid or compartmentalized structures. Upon resuspension, these reorganized nanoparticles retain their hollow structure and display significantly enhanced loading of a hydrophobic dye compared to the original solid cylinders.

- Phase Behavior, Small-Angle Neutron Scattering and Rheology of Ternary Nonionic Surfactant–Oil–Water Systems: A Comparison of Oils
  Tabor, R. F.; Zaveer, M. I.; Dagastine, R. R.; Grillo, I.; Garvey, C. J. *Langmuir* **2013**, *29*, 3575–3582.
  Abstract:

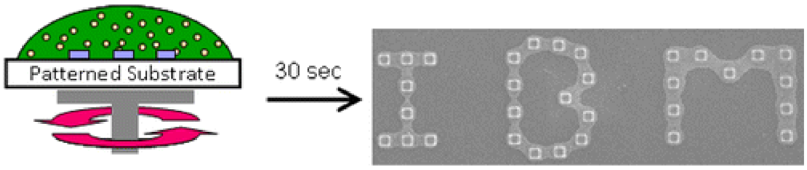


The phase behavior of the nonionic surfactant Triton X-100 (polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether) was studied in two three-component systems: Triton–water–p-xylene and Triton–water–trichloroethylene. It was found that the aromatic solvent was able to produce monophasic soft matter systems at a significantly greater range of compositions. The structural characteristics of the phases generated were analyzed by small-angle neutron scattering, showing evidence for microemulsion, lamellar, and reverse-microemulsion phases. In addition, for the Triton–water–p-xylene system, an L3 "sponge" phase was found in a water-rich region of the phase diagram and the properties of this were examined using rheological measurements. The differences in phase behavior are discussed in light of the solvation properties of the surfactant in the different solvents studied. Most notably, xylene appears to favor phases with low-curvature interfaces, suggesting preferential solvation of the central phenyl group of Triton.

- Programmable Nanoparticle Ensembles via High-Throughput Directed Self-Assembly

Dai, Q.; Chen, Y.; Liu, C-C.; Rettner, C. T.; Holmdahl, B.; Gleixner, S.; Chung, R.; Pitera, J. W.; Cheng, J.; Nelson, A. *Langmuir* **2013**, *29*, 3567–3574.

Abstract:

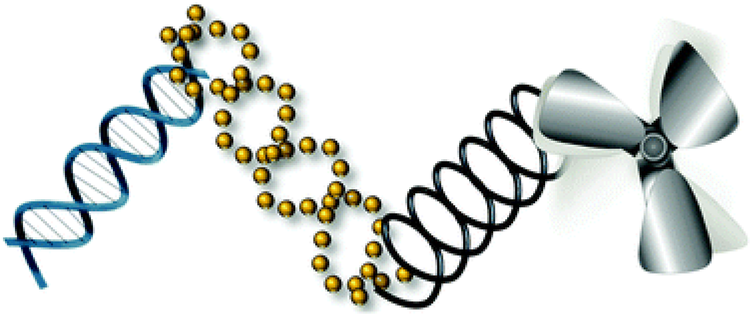


We present a simple and facile strategy for the directed self-assembly of nanoparticles into complex geometries using a minimal set of post guiding features patterned on a substrate. This understanding is based on extensive studies of nanoparticle self-assembly into linear, dense-packed, circular, and star-shaped ensembles when coated onto patterned substrates of predefined post arrays. We determined the conditions under which nanoparticles assemble and “connect” two adjacent post features, thereby forming the desired shapes. We demonstrate that with rational design of the post patterns to enforce the required pairwise interactions with posts, we can create arbitrary arrangements of nanoparticles—for example, to write “IBM” in a deterministic manner. This demonstration of programmable, high-throughput directed self-assembly of nanoparticles shows an alternative route to generate functional nanoparticle assemblies.

- Emerging chirality in nanoscience

  Wang, Y.; Xu, J.; Wang, Y.; Chen, H. *Chem. Soc. Rev.* **2013**, *42*, 2930-2962.

  Abstract:

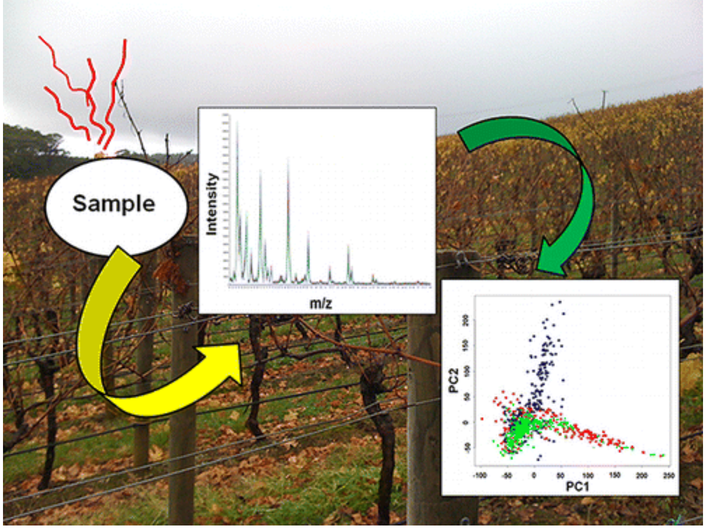


Chirality in nanoscience may offer new opportunities for applications beyond the traditional fields of chirality, such as the asymmetric catalysts in the molecular world and the chiral propellers in the macroscopic world. In the last two decades, there has been an amazing array of chiral nanostructures reported in the literature. This review aims to explore and categorize the common mechanisms underlying these systems. We start by analyzing the origin of chirality in simple systems such as the helical spring and hair vortex. Then, the chiral nanostructures in the literature were categorized according to their material composition and underlying mechanism. Special attention is paid to highlight systems with original discoveries, exceptional structural characteristics, or unique mechanisms.

- Instrumental Methods (Spectroscopy, Electronic Nose, and Tongue) As Tools To Predict Taste and Aroma in Beverages: Advantages and Limitations

  Smyth, H.; Cozzolino, D. *Chem. Rev.* **2013**, *113*, 1429–1440.

  Abstract:



The human senses have always been used to assess food quality. Although the senses of sight, hearing, taste, smell, and touch are used daily in all aspects of our lives, their analytical applications to evaluate food properties are relatively recent. The sensory systems of Homo sapiens are the product of millions of years of evolution where natural selection has resulted in our capacity to detect a wide range of compounds present in the environment, advantageous to our survival, allowing hedonistic evaluation of our environment.

Many features of food can be studied analytically using sensory methods and techniques (e.g., taste, aroma, texture, and color), and they can be integrated to provide the overall sensory evaluation of food. Additionally, the human senses have the ability to “focus” or concentrate on specific attributes (e.g., sweetness or bitterness of a beverage). It is only recently (compared to the evolutionary time scale) that instrumental methods have reached a level of sophistication which enables investigation of the properties of food. For example, recent advances in chromatographic separation, coupled with sensitive detection systems, can be used to obtain qualitative and quantitative data to assess food composition.

Overall two main types of methods for evaluation of the quality of beverages and foods can be used, namely, subjective and objective. Subjective methods are those based on human assessment of the quality characteristics of the food. These methods involve perception of texture, flavor, odor, color, and touch by a panel of experts or consumers. However, even though human evaluators can be highly trained, their opinions might vary due to psychological and physical variability. Subjective sensory methods are also time consuming and susceptible to large sources of variation. By nature, such assessments can be biased by individual preferences and may be subject to day-to-day variations.

In contrast, objective methods for assessment of quality include instrumental analysis and could be very beneficial for numerous reasons as they are nonsubjective, highly repeatable, and reproducible and, most of all, the fact that instruments do not suffer from fatigue or adaptation.

Given the complex nature of alcoholic beverages, there are many advantages to developing instrumental methods to describe their quality or sensory profile. However, to be of practical use by the beverage industry, instrumental methods must be cost effective and provide rapid, reproducible results with continuous operation.

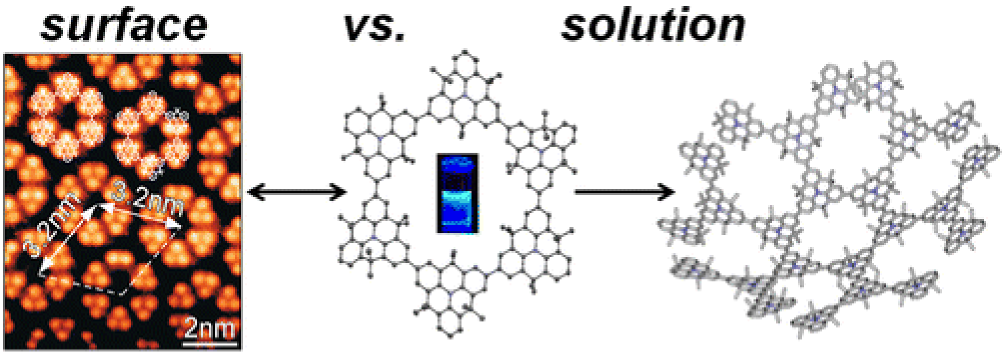
To date, instrumental methods for sensory analysis have lacked the ability to consistently perceive all of the key sensory attributes of interest and have been inconsistent in predicting relationships between sensory and instrumental measurements, depending on the attribute and food matrix analyzed.

Existing analytical methods used to measure wine and alcoholic beverages composition and quality are not adequate for the demands of production in a global market due to their high cost and slow turnaround time. Factors like promptness and low cost of analysis, minimal sample preparation, and environmentally friendly methods are of paramount importance in the modern and sustainable wine and alcoholic beverage industries.

In order to enable the beverage (and other food applications) industry to rapidly respond to the changing demands of both consumers and the market, it is important to have a quantitative means for assessing sensory properties by means of objective measurements (e.g., analysis of volatile compounds) which can provide reliable information about the quality of the food. However, many of these methods are unsuitable to be used or adopted by the industry for rapid analysis of quality. For example, analysis of volatile compounds in wine to assess wine aroma by gas chromatography–mass spectrometry (GC-MS) involves expensive instrumentation and time-consuming sample preparation using solvents as well as analysis (from a few to several minutes).

In the last 20 years increasing interest on the use of rapid screening techniques or instrumental methods to determine quality characteristics of foods and beverages has been of great interest to the food industry. These techniques are relatively inexpensive and easy to operate, often require little or no sample preparation, and can be used in-line or at-line to obtain results quickly. Such techniques or sensors can be grouped into electronic noses (EN), optical methods based in vibrational spectroscopy (e.g., infrared, UV), and more recently the so-called electronic tongue instruments that were developed to characterize complex food or beverage samples in order to replace or reduce the use of sensory analysis using human subjects.

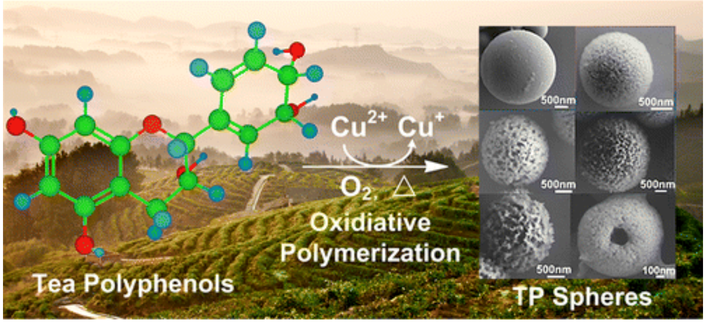
- π-Conjugated Heterotriangulene Macrocycles by Solution and Surface-supported Synthesis toward Honeycomb Networks
  Schlütter, F.; Rossel, F.; Kivala, M.; Enkelmann, V.; Gisselbrecht, J.-P.; Ruffieux, P.; Fasel, R.; Müllen, K. *J. Am. Chem. Soc.* **2013**, *135,* 4550–4557.
  Abstract:



A comparative analysis between a solution and a surface-mediated synthesis of heterotriangulene macrocycles is reported. The results show a preferential formation of the π-conjugated macrocycles on surface due to two-dimensional confinement. The macrocycle prepared on a several hundred milligram scale by solution chemistry was characterized by single-crystal X-ray analysis and was furthermore extended toward next generation honeycomb species. Investigation of the photophysical and electronic properties together with the good thermal stability revealed the potential of MC6 as hole-transport material for organic electronics.

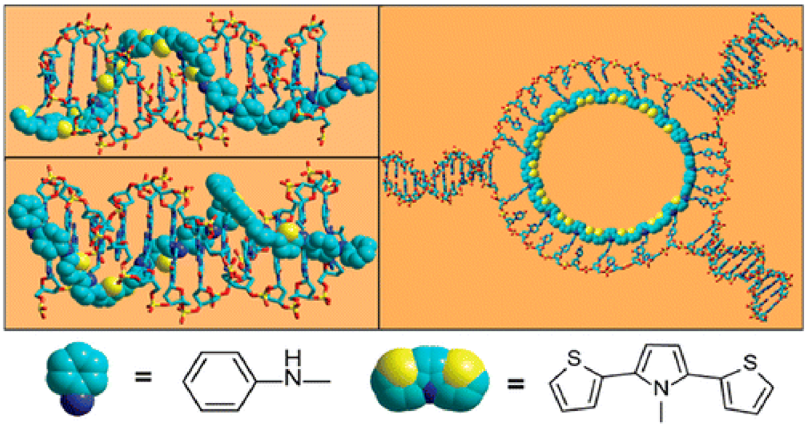
- Biocompatible, Functional Spheres Based on Oxidative Coupling Assembly of Green Tea

Polyphenols
Chen, Z.; Wang, C.; Chen, J.; Li, X. *J. Am. Chem. Soc.*, **2013**, *135*, 4179–4182.
Abstract:



Green luminescent, monodisperse, smooth, porous and hollow spheres were simply prepared by Cu^{2+} and temperature mediated oxidative coupling assembly of green tea polyphenols in water. These polymeric tea polyphenol spheres are GSH responsive, acid resistant but alkali-responsive, ideally used as platform for controlled delivery of functional guests.

- Precise Sequence Control in Linear and Cyclic Copolymers of 2,5-Bis(2-thienyl)pyrrole and Aniline by DNA-Programmed Assembly
  Chen, W.; Schuster, G. B. *J. Am. Chem. Soc.* **2013**, *135,* 4438–4449.
  Abstract:

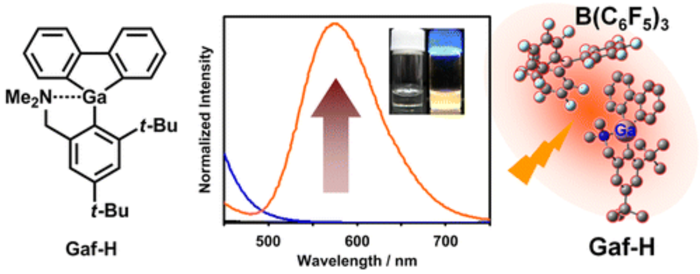


DNA-Programmed Sequence Control of Copolymers

A series of linear and cyclic, sequence controlled, DNA-conjoined copolymers of aniline (ANi) and 2,5-bis(2-thienyl)pyrrole (SNS) were synthesized. In one approach, linear copolymers were prepared from complementary DNA oligomers containing covalently attached SNS and ANi monomers. Hybridization of the oligomers aligns the monomers in the major groove of the DNA. Treatment of the SNS- and ANi-containing duplexes with horseradish peroxidase (HRP) and H2O2 causes rapid and efficient polymerization. In this way, linear copolymers (SNS)4(ANi)6 and (ANi)2(SNS)2(ANi)2(SNS)2(ANi)2 were prepared and analyzed. A second approach to the preparation of linear and cyclic copolymers of ANi and SNS employed a DNA encoded module strategy. In this approach, single-stranded DNA oligomers composed of a central region containing (SNS)6 or (ANi)5 covalently attached monomer blocks and flanking 5′- and 3′-single-strand DNA recognition sequences were combined in buffer solution. Self-assembly of these oligomers by Watson–Crick base pairing of the recognition sequences creates linear or cyclic arrays of SNS and ANi monomer blocks. Treatment of these arrays with HRP/H2O2 causes rapid and efficient polymerization to form copolymers having patterns such as cyclic BBA and linear ABA, where B stands for an (SNS)6 block and A stands for an (ANi)5 block. These

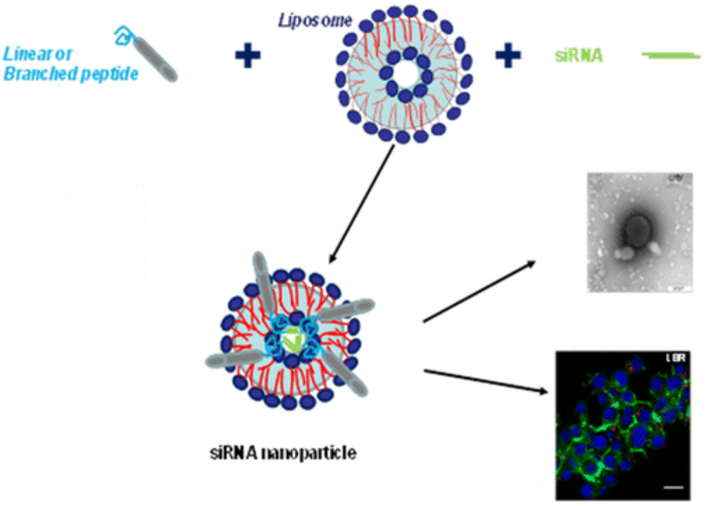
DNA-conjoined copolymers were characterized by melting temperature analysis, circular dichroism spectroscopy, native and denaturing polyacrylamide gel electrophoresis, and UV–visible–near-IR optical spectroscopy. The optical spectra of these copolymers are typical of those of conducting polymers and are uniquely dependent on the specific order of monomers in the copolymer.

- Synthesis and Optical Properties of Stable Gallafluorene Derivatives: Investigation of Their Emission via Triplet States
  Matsumoto, T.; Tanaka, K.; Chujo, Y. J. *Am. Chem. Soc.* **2013**, *135*, 4211–4214.
  Abstract:



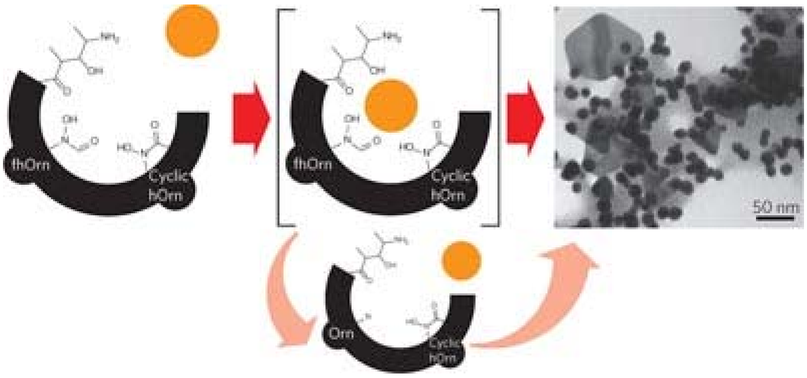
We designed and synthesized air- and moisture-stable gallafluorenes in which two benzene rings were bridged by the four-coordinate gallium atoms. The series of gallafluorenes were prepared by introducing electron-donating and -withdrawing groups through Suzuki–Miyaura coupling reactions. The gallafluorenes showed unique emissions via their triplet states in the presence of B(C_6F_5)$_3$. These emissions were obtained via the triplet exciplex of gallafluorene and B(C_6F_5)$_3$.

- Comparison of Nanocomplexes with Branched and Linear Peptides for SiRNA Delivery
  Tagalakis, A. D.; Saraiva, L.; McCarthy, D.; Gustafsson, K. T.; Hart, S. L. *Biomacromolecules* **2013**, *14*, 761-770.
  Abstract:



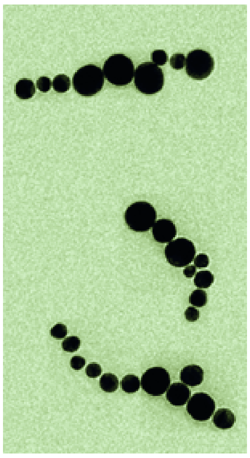
Efficient delivery of small interfering RNA (siRNA) remains the greatest technological barrier to the clinical implementation of RNA interference strategies. We are investigating the relationship between the biophysical properties of siRNA nanocomplexes and their transfection efficiency as an approach to the generation of improved formulations. Peptide-based formulations are of great interest, and so in this study we have compared nanocomplex formulations for siRNA delivery containing linear and branched oligolysine or oligoarginine peptides. Peptides were combined with cationic liposomes in siRNA formulations and compared for transfection efficiency, siRNA packaging efficiency, biophysical properties, and particle stability. Nanocomplexes containing linear peptides were more condensed and stable than branched peptide formulations; however, their silencing activity was lower, suggesting that their greater stability might limit siRNA release within the cell. Thus, differences in transfection appeared to be associated with differences in packaging and stability, indicating the importance of optimizing this feature in siRNA nanocomplexes.

- Gold biomineralization by a metallophore from a gold-associated microbe
  Johnston, C. W.; Wyatt, M. A.; Li, X.; Ibrahim, A.; Shuster, J.; Southam, G.; Magarvey, N. A. *Nature Chem. Biol.* **2013**, *9*, 241–243.
  Abstract:



Microorganisms produce and secrete secondary metabolites to assist in their survival. We report that the gold resident bacterium *Delftia acidovorans* produces a secondary metabolite that protects from soluble gold through the generation of solid gold forms. This finding is the first demonstration that a secreted metabolite can protect against toxic gold and cause gold biomineralization.

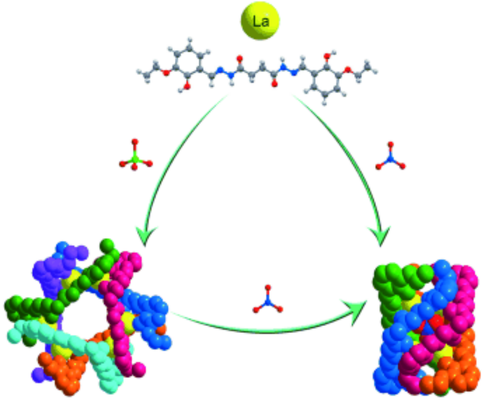
- Size-Dependent Electrostatic Chain Growth of pH-Sensitive Hairy Nanoparticles
  Xia, H.; Su, G.; Wang, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 3726 –3730.
  Abstract:



Big and small, short and tall: Nanoparticles (NPs) coated with pH-sensitive polymers underwent reversible chain growth as a result of varying electrostatic interparticle repulsion as determined by the pH value. Tuning of the pH value also enabled the coupling of differently sized NPs to form linear composite chains reminiscent of block copolymers (see picture).

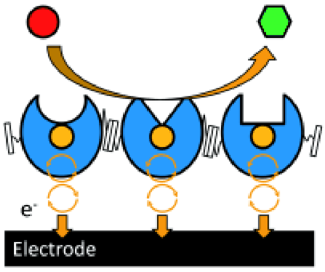
- Multiple Lanthanide Helicate Clusters and the Effects of Anions on Their Configuration
  Wang, B.; Zang, Z.; Wang, H.; Dou, W.; Tang, X.; Liu, W.; Shao, Y.; Ma, J.; Li, Y.; Zhou, J. *Angew.*

Chem. Int. Ed. **2013**, *52*, 3756 –3759.
Abstract:



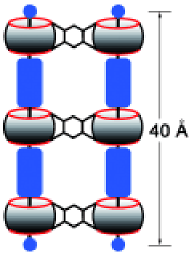
Shaping up your clusters: Two supramolecular clusters of multiple lanthanide helicates have been synthesized. Cluster structure is controlled by the choice of anion, with tetrahedral ClO4− producing larger circular helicates, and trigonal-planar NO3− leading to a compact quadruple-stranded helicate (see picture).

- Self-Assembling Enzyme Networks—A New Path towards Multistep Bioelectrocatalytic Systems
  Schröder, U. *Angew. Chem. Int. Ed.* **2013**, *13*, 3568-3569.
  Abstract:



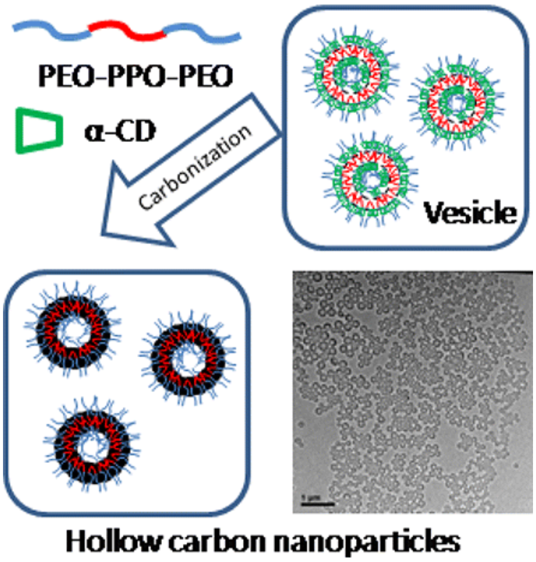
Enzymes for energy: Recently, an elegant and efficient protein-engineering approach was proposed to create self-assembling enzyme arrays. This approach paves the way for efficient biofuel cells and for complex bioelectrocatalytic processes (general scheme shown; blue: enzyme, red: substrate, green: product).

- Supramolecular Ladders from Dimeric Cucurbit[6]uril
  Wittenberg, J. B.; Zavalij, P. Y.; Isaacs, L. *Angew. Chem. Int. Ed.* **2013**, *13*, 3690-3694.
  Abstract:



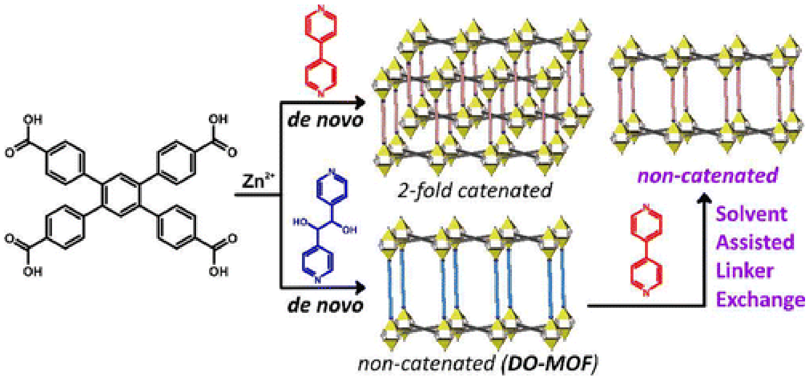
Climbing the cucurbit ladder: Cucurbit[6]uril dimers (connected gray cylinders; see scheme) were prepared by condensation of glycoluril hexamer with the appropriate tetraaldehydes. The self-assembly process between these dimers and oligoviologen compounds (blue) in water leads to a supramolecular ladder with the dimensions and molecular weight typical of small proteins.

- Hollow Carbon Nanoparticles of Tunable Size and Wall Thickness by Hydrothermal Treatment of α-Cyclodextrin Templated by F127 Block Copolymers
  Yang, Z.-C.; Zhang, Y.; Kong, J.-H.; Wong, S. Y.; Li, X.; Wang, J. *Chem. Mater.* **2013**, *25*, 704-710**.**
  Abstract:



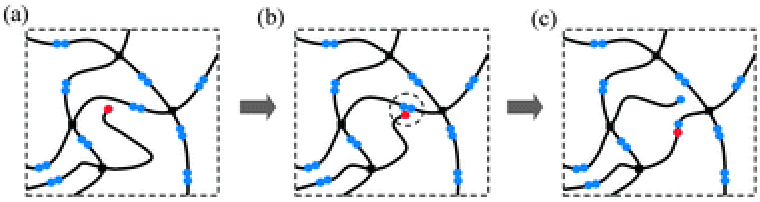
On the basis of the strategy of forming supermolecular structure between α-cyclodextrin and poly(ethylene oxide), a facile synthesis process has been successfully developed for producing hollow carbon nanoparticles of controllable size and morphology by hydrothermal treatment of α-cyclodextrin in the presence of Pluronic F127 as a soft template. The hollow carbon nanoparticles thus derived are demonstrated to exhibit excellent hydrophilic behavior. Their sizes and wall thicknesses can be tuned by adjusting the ratio of α-cyclodextrin to F127. After pyrolysis at 900 °C in argon gas, the hollow carbon nanoparticles exhibit a meso-/microporous carbon wall with specific surface area of >400 m^2/g and a high specific charge capacity of >450 mAh/g when employed as an anode in a lithium ion battery.

- Control over Catenation in Pillared Paddlewheel Metal–Organic Framework Materials via Solvent-Assisted Linker Exchange
  Bury, W.; Fairen-Jimenez, D.; Lalonde, M. B.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. *Chem. Mater.* **2013**, *25*, 739-744.
  Abstract:



Control over catenation in a pillared paddlewheel metal–organic framework was achieved via solvent-assisted linker exchange. The linker exchange was demonstrated on the noncatenated structure of **DO-MOF**, by using 4,4′-bipyridine (**L4**) and 4,4′-azobis(pyridine) (**L5**) as linkers, leading to noncatenated materials **SALEM-3** and **SALEM-4**. The *de novo* synthesized analogues of **SALEM-3** and **SALEM-4** can only be obtained as 2-fold interpenetrated frameworks. The reaction progress of the linker exchange was monitored by NMR spectroscopy, and structure and framework catenation were characterized by powder X-ray diffraction and thermogravimetric methods.

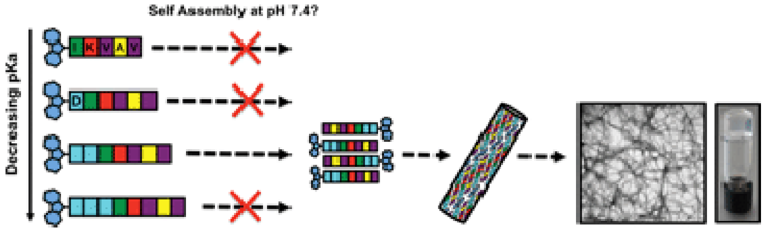
- Modeling the mechanics of covalently adaptable polymer networks with temperature-dependent bond exchange reactions
  Long, R.; Qi, H. J.; Dunn, M. L. *Soft Matter* **2013**, *9*, 4083-4096.
  Abstract:



We study a class of polymers with bond exchange reactions that can rearrange the polymer network topology while maintaining the network integrity. Examples include the recently developed epoxy-acid network with transesterification reaction and polybutadiene polymer with olefin metathesis reaction. This class of polymers, although covalently crosslinked and thus insoluble, are rendered malleable through viscoelastic flow caused by the bond exchange reactions. The reaction also facilitates unique and technologically important behavior such as self-healing, thermoforming, and recyclability. Here we develop a thermodynamically consistent continuum model to describe the coupling between the macroscopic thermo-mechanics and the microscopic network-altering chemical reactions. Our basic approach is to decompose the network into groups of chains that are reformed at different times during the loading history; at any instant the network strain energy is obtained by summing the contributions from all chains. Evolution of the chain composition, determined by the temperature-dependent chemical reaction kinetics, changes the total strain energy and leads to macroscopic relaxation. Our model is applicable to general three-dimensional finite deformation with arbitrary thermal and mechanical boundary conditions. In the case of isothermal processes, only four material parameters are required: two describing the mechanical behavior and two describing the chemical kinetics. Using the epoxy-acid network as an example, we show that our model captures the key features of recently reported experiments. An important feature of these materials is that they can be processed like a thermoplastic, while retaining the appealing properties of a thermoset. Specifically, one can deform the material and then heat it to relax stresses, after which it will maintain its deformed shape, although there may be some elastic springback. To this end, we use our model to derive simple analytical estimates for a *fixity parameter*, defined as the ratio of the permanent deformation after the thermomechanical process to the prescribed deformation. We also implement our model in a 3D nonlinear finite element code and use it to study two representative thermoforming examples: twisting of a strip and indentation of a substrate. We extract the fixity parameter from the finite element results and show that our analytical estimates provide a reasonable approximation.

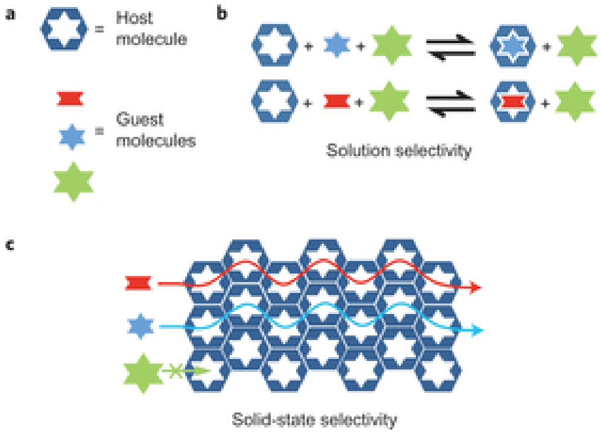
- Tuning the amino acid sequence of minimalist peptides to present biological signals via

charge neutralised self assembly
Rodriguez, L.; Parish, C. L.; Nisbet, D. R.; Williams, R. J. *Soft Matter* **2013**, *9*, 3915-3919.
Abstract:



Nanofibrous materials yielded by the self-assembly of peptides are rich in potential; particularly for the formation of scaffolds that mimic the landscape of the host environment of the cell. Here, we report a novel methodology to direct the formation of supramolecular structures presenting desirable amino acid sequences by the self-assembly of minimalist peptides which cannot otherwise yield the desired scaffold structures under biologically relevant conditions. Through the rational modification of the pK_a, we were able to optimise ordered charge neutralised assembly towards *in vivo* conditions.

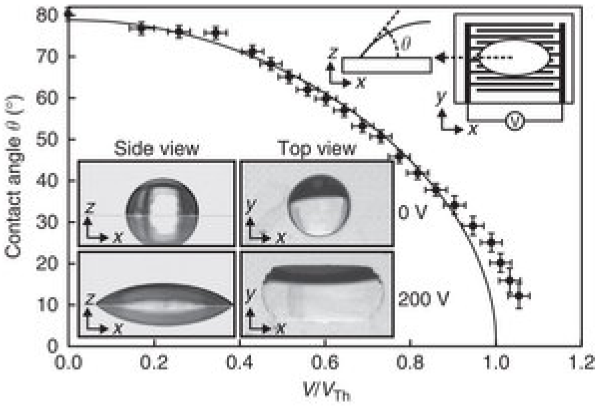
- Molecular shape sorting using molecular organic cages
  Mitra, T.; Jelfs, K. E.; Schmidtmann, M.; Ahmed, A.; Chong, S. Y.; Adams, D. J.; Cooper, A. I. *Nature Chem.* **2013**, *5*, 276–281.
  Abstract:



The energy-efficient separation of chemical feedstocks is a major sustainability challenge. Porous extended frameworks such as zeolites or metal–organic frameworks are one potential solution to this problem. Here, we show that organic molecules, rather than frameworks, can separate other organic molecules by size and shape. A molecular organic cage is shown to separate a common aromatic feedstock (mesitylene) from its structural isomer (4-ethyltoluene) with an unprecedented perfect specificity for the latter. This specificity stems from the structure of the intrinsically porous cage molecule, which is itself synthesized from a derivative of mesitylene. In other words, crystalline organic molecules are used to separate other organic molecules. The specificity is defined by the cage structure alone, so this solid-state ‘shape sorting’ is, uniquely, mirrored for cage molecules in solution. The behaviour can be understood from a combination of atomistic simulations for individual cage molecules and solid-state molecular dynamics simulations.

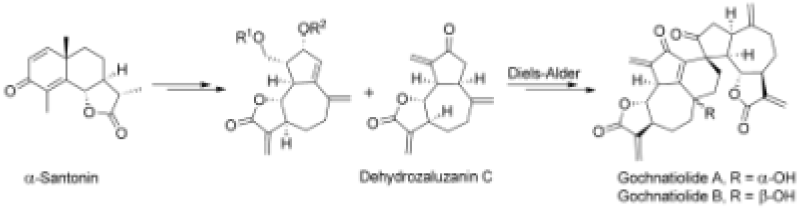
- Voltage-induced spreading and superspreading of liquids
  McHale, G.; Brown, C. V.; Sampara, N. *Nature Commun.* **2013**, *4*, 1605.

Abstract:



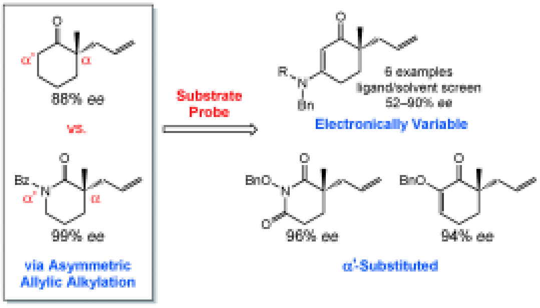
The ability to quickly spread a liquid across a surface and form a film is fundamental for a diverse range of technological processes, including printing, painting and spraying. Here we show that liquid dielectrophoresis or electrowetting can produce wetting on normally non-wetting surfaces, without needing modification of the surface topography or chemistry. Additionally, superspreading can be achieved without needing surfactants in the liquid. Here we use a modified Hoffman-de Gennes law to predict three distinct spreading regimes: exponential approach to an equilibrium shape, spreading to complete wetting obeying a Tanner's law-type relationship and superspreading towards a complete wetting film. We demonstrate quantitative experimental agreement with these predictions using dielectrophoresis-induced spreading of stripes of 1,2 propylene glycol. Our findings show how the rate of spreading of a partial wetting system can be controlled using uniform and non-uniform electric fields and how to induce more rapid superspreading using voltage control.

- Total Syntheses of Ainsliadimer B and Gochnatiolides A and B
  Xia, D.; Du, Y.; Yi, Z.; Song, H. *Chem. Eur. J.* **2013**, *19*, 4423-4427.
  Abstract:



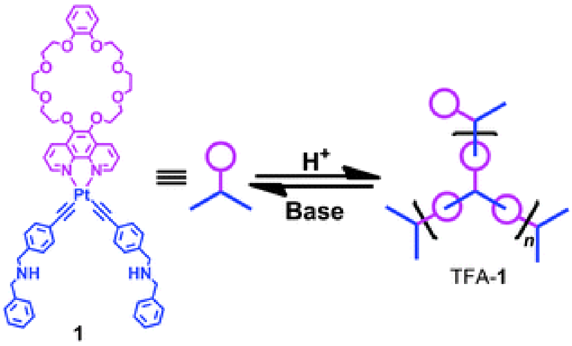
Oh my goch: The total syntheses of ainsliadimer B and gochnatiolides A and B from α-santonin have been accomplished in 25 steps with approximately 1% overall yield. A Diels–Alder reaction of natural dehydrozaluzanin C with a monomeric guaianolide derivative allows stereoselective assembly of a dimeric gochnatiolide-type skeleton with the required stereochemistry and preinstalled functionalities for the synthesis of dimeric ainsliadimer B and gochnatiolides A and B (see scheme).

- Expanding Insight into Asymmetric Palladium-Catalyzed Allylic Alkylation of N-Heterocyclic Molecules and Cyclic Ketones
  Bennett, N. B.; Duquette, D. C.; Kim, J.; Liu, W.-B.; Marziale, A. N.; Behenna, D. C.; Virgil, S. C.; Stoltz, B. M. *Chem. Eur. J.* **2013**, *19*, 4414-4418.
  Abstract:



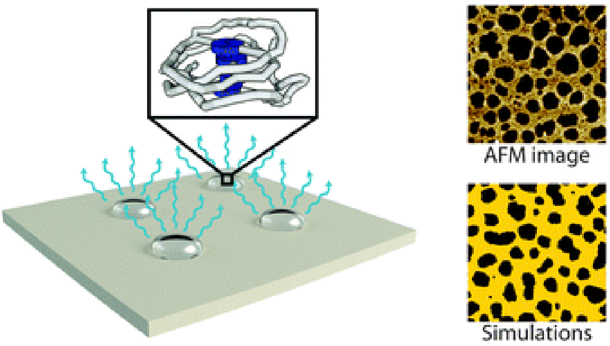
Eeny, meeny, miny … enaminones! Lactams and imides have been shown to consistently provide enantioselectivities substantially higher than other substrate classes previously investigated in the palladium-catalyzed asymmetric decarboxylative allylic alkylation. Several new substrates have been designed to probe the contributions of electronic, steric, and stereoelectronic factors that distinguish the lactam/imide series as superior alkylation substrates (see scheme). These studies culminated in marked improvements on carbocyclic allylic alkylation substrates.

- Synthesis and characterization of a luminescence metallosupramolecular hyperbranched polymer
  Yu, B.; Guo, S.; He, L.; Bu, W. *Chem. Commun.* **2013**, *49*, 3333-3335.
  Abstract:



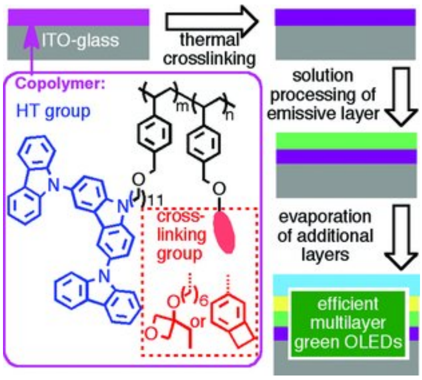
A luminescence supramolecular hyperbranched polymer is reversibly fabricated by successively adding acid and base to a solution of an AB2 platinum(II) monomer in dichloromethane on the basis of acid–base controllable host–guest recognition of dibenzo[24]crown-8 moieties with dialkylammonium ion centers.

- Evaporative self-assembly of single-chain, polymeric nanoparticles
  van Roekel, H. W. H.; Stals, P. J. M.; Gillissen, M. A. J.; Hilbers, P. A. J.; Markvoort, A. J.; de Greef, T. F. A. *Chem. Commun.* **2013**, *49*, 3122-3124.
  Abstract:



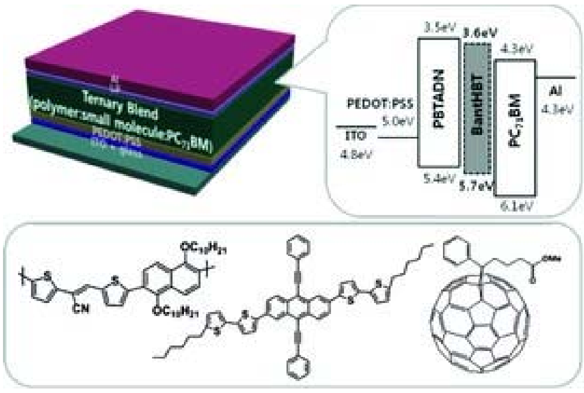
Evaporative self-assembly of dilute solutions containing single-chain polymeric nanoparticles results in characteristic morphologies imaged using atomic force microscopy. Quantitative comparison of experimental data to morphologies obtained by lattice-gas simulations shows that the nonequilibrium patterns emerge from a complex interplay between dewetting, solvent evaporation and nanoparticle diffusion.

- Crosslinking Using Rapid Thermal Processing for the Fabrication of Efficient Solution-Processed Phosphorescent Organic Light-Emitting Diodes
  Zuniga, C. A.; Abdallah, J.; Haske, W.; Zhang, Y.; Coropceanu, I.; Barlow, S.; Kippelen, B.; Marder, S. R. *Adv. Mater.* **2013**, *25*, 1739–1744.
  Abstract:



Copolymers with a triscarbazole hole-transport group and an oxetane or benzocyclobutene crosslinkable group can be readily thermally crosslinked on timescales of 30 min or less, with rapid thermal processing (RTP) being highly effective for this purpose. Devices with RTP-crosslinked hole-transport layers and spin-coated emissive layers exhibit high external quantum efficiencies of up to 15%.

- Complementary Absorbing Star-Shaped Small Molecules for the Preparation of Ternary Cascade Energy Structures in Organic Photovoltaic Cells
  Cha, H.; Chung, D. S.; Bae, S. Y.; Lee, M.-J.; An, T. K.; Hwang, J.; Kim, K. H.; Kim, Y.-H.; Choi, D. H.; Park, C. E. *Adv. Funct. Mater.* **2013**, *23*, 1556–1565.
  Abstract:



Two anthracene-based star-shaped conjugated small molecules, 5′,5′-(9,10-bis((4-hexylphenyl)ethynyl)anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene), HBantHBT, and 5′,5′-(9,10-bis(phenylethynyl)anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene), BantHBT, are used as electron-cascade donor materials by incorporating them into organic photovoltaic cells prepared using a poly((5,5-E-alpha-((2-thienyl)methylene)-2-thiopheneacetonitrile)-alt-2,6-[(1,5-

didecyloxy)naphthalene])) (PBTADN):[6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) blend. The small molecules penetrate the PBTADN:$PC_{71}BM$ blend layer to yield complementary absorption spectra through appropriate energy level alignment and optimal domain sizes for charge carrier transfer. A high short-circuit current (J_{SC}) and fill factor (FF) are obtained using solar cells prepared with the ternary blend. The highest photovoltaic performance of the PBTADN:BantHBT:$PC_{71}BM$ blend solar cells is characterized by a J_{SC} of 11.0 mA cm^{-2}, an open circuit voltage (V_{OC}) of 0.91 V, a FF of 56.4%, and a power conversion efficiency (PCE) of 5.6% under AM1.5G illumination (with a high intensity of 100 mW^{-2}). The effects of the small molecules on the ternary blend are investigated by comparison with the traditional poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) system.