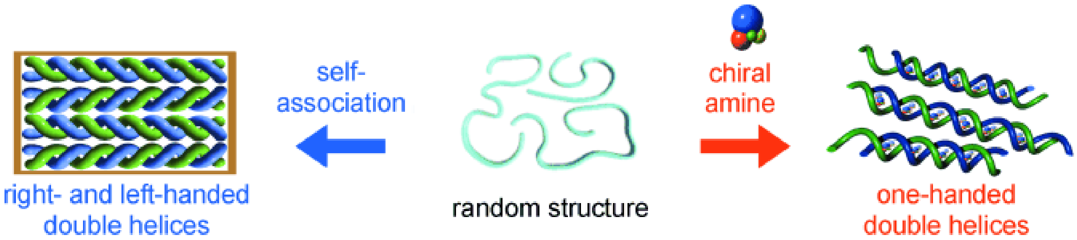
- Formation of a Homo Double Helix of a Conjugated Polymer with Carboxy Groups and Amplification of the Macromolecular Helicity by Chiral Amines Sandwiched between the Strands

  Makiguchi, W.; Kobayashi, S.; Furusho, Y.; Yashima, E. *Angew. Chem. Int. Ed.* **2013**, *52*, 5275 – 5279.

  Abstract:

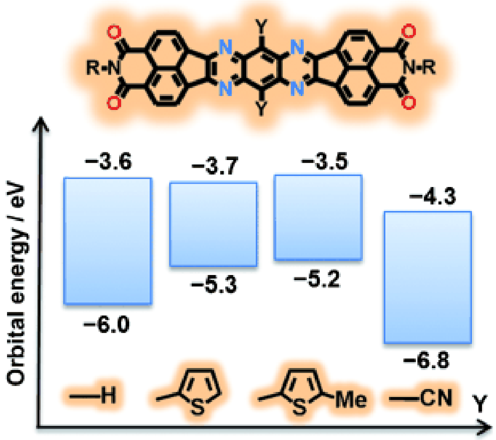


Sandwiched amines: A π-conjugated polymer with carboxy groups self-associates to form a racemic double helix. In contrast, with chiral amines it forms a unique one-handed double helix, in which the strands sandwich pairs of chiral amines through cyclic hydrogen-bonding networks (see picture). The chiral information of the amines is transferred to the polymer backbones with remarkable amplification of the helical chirality.

- Tetraazabenzodifluoranthene Diimides: Building Blocks for Solution-Processable n-Type Organic Semiconductors

  Li, H.; Kim, F. S.; Ren, G.; Hollenbeck, E. C.; Subramaniyan, S.; Jenekhe, S. A. *Angew. Chem. Int. Ed.* **2013**, *52*, 5513 –5517.

  Abstract:

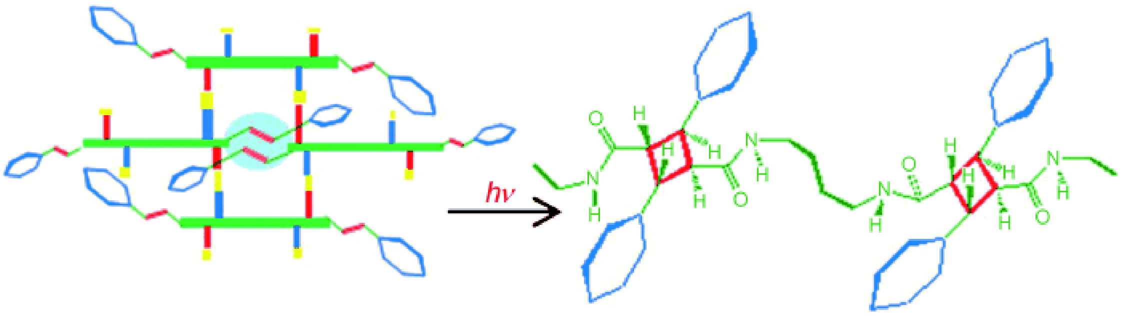


11-Ring heterocyclic diimides were synthesized and found to be planar and to exhibit a slipped face-to-face π stacking. Variation of the substituents tunes the electronic structure and properties. In n-channel organic field-effect transistors, the new organic semiconductors have a high electron mobility. When they were used as acceptor material in polymer solar cells, a power conversion efficiency of 1.8 % was obtained.

- Tunable Plastic Films of a Crystalline Polymer by Single-Crystal-to-Single-Crystal Photopolymerization of a Diene: Self-Templating and Shock-Absorbing Two-Dimensional Hydrogen-Bonding Layers

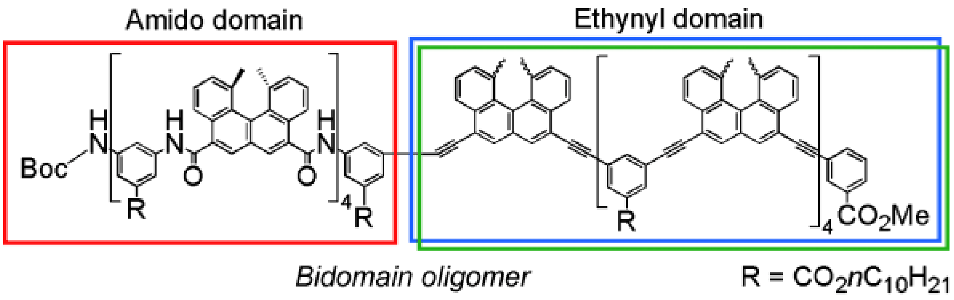
  Garai, M.; Santra, R.; Biradha, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 5548 –5551.

  Abstract:



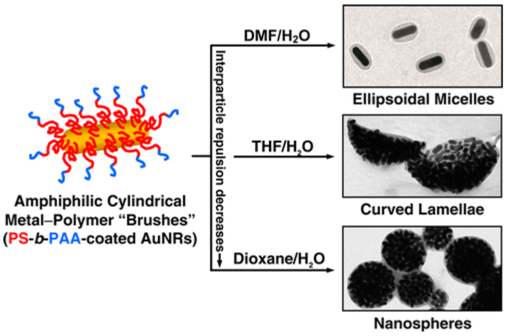
Film review: Two amide-containing bisolefin monomers undergo solid-state polymerization (see example) through a [2+2] reaction in a single-crystal-to-single-crystal fashion. The transformation was favored by the self-templating and shock-absorbing nature of hydrogen-bonding layers. The pyridine-containing polymers were soluble and useful for making plastic films with considerable tensile strengths.

- Tetrameric ααββ Aggregate Formation by Stereoisomeric Bidomain Helicene Oligomers
  Ichinose, W.; Ito, J.; Yamaguchi, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 5290 –5294.
  <u>Abstract:</u>



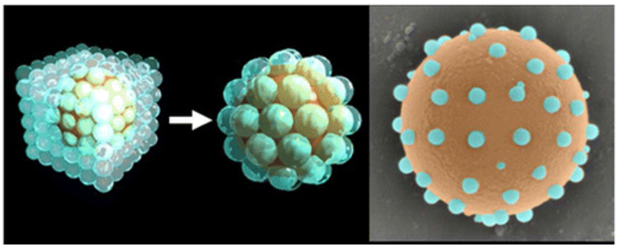
How to aggregate your domains: A method of forming tetrameric aggregates with an ααββ structure has been developed using stereoisomeric bidomain oligomers. Upon mixing the oligomers, a tetrameric ααββ aggregate was obtained by heteroaggregation at the ethynyl domain. The tetrameric aggregate reversibly changed its structure between the dimeric homoaggregates on heating and cooling, whereas gelation by polymerization occurred in toluene.

- Morphological Control in Aggregates of Amphiphilic Cylindrical Metal-Polymer "Brushes"
  Mai, Y.; Xiao, L.; Eisenberg, A. *Macromolecules* **2013**, *46*, 3183-3189.
  <u>Abstract:</u>



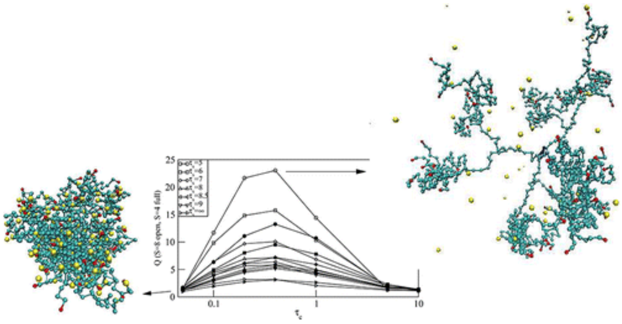
Controlled self-assembly of gold nanorods (AuNRs) into nanostructures of various morphologies has attracted considerable interest because it provides a high degree of freedom in tailoring the properties of the nanostructures by the coupling of the optical and electronic properties of the individual AuNRs. This paper presents a new strategy for making AuNR aggregates of tunable morphologies. In this approach, the surface of AuNRs is chemically coated with an amphiphilic diblock copolymer. The coating gives the AuNRs a cylindrical brush structure. By varying the nature of the common solvent or the interparticle electrostatic repulsion, the self-assembly of the amphiphilic cylindrical AuNR–polymer "brushes" can produce water-soluble aggregates of controllable morphologies, including single-rod ellipsoidal micelles, curved circular lamellae, and nanospheres. The AuNRs in the various aggregates generate different surface plasmon resonance (SPR) absorption patterns, with the longitudinal SPR band in the near-infrared spectral window shifting as the aggregate morphology changes.

- Packed Colloidal Phases Mediate the Synthesis of Raspberry-Structured Microgel Heteroaggregates
  Gaulding, J. C.; Saxena, S.; Montanari, D. E.; Lyon, A. L. *ACS Macro Lett.* **2013**, *2*, 337-340.
  Abstract:



Hybrid nanoparticles with complex architectures combine the properties of two distinct materials and integrate them to synergistically provide new characteristics to the assembly. In this work we demonstrate the ability to decorate the surface of a variety of micrometer-sized "core" particles with responsive microgels, forming raspberry-like particles. We use a templating technique wherein the microgel coating is applied from a high-volume-fraction colloidal phase, leading to high surface coverage and enhanced colloidal stability of the resultant particles. Concentrated colloidal dispersions enable microgel/core combinations driven by both specific and nonspecific interactions and offer improved coverage relative to dilute heteroaggregation. This approach is versatile and allows both the core material and microgel phase to be altered while still remaining effective. Though the recovered particles are highly diluted, recycling the unincorporated microgels following raspberry-like particle isolation and reforming the packed colloidal assembly allow multiple cycles of particle synthesis, which improves overall yield.

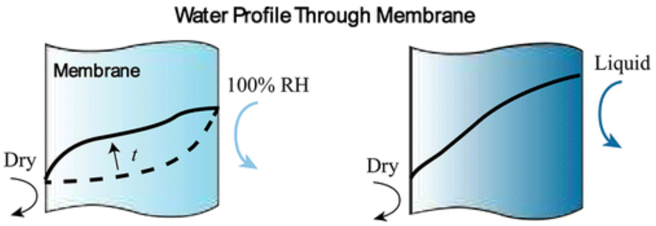
- Simulations of Neutral and Charged Dendrimers in Solvents of Varying Quality
  Klos, J. S.; Sommer, J.-U. *Macromolecules* **2013**, *46*, 3107-3117.
  Abstract:



We study neutral and charged dendrimers of various generations G, spacer length S, and molecular weight N under systematic variation of the solvent quality ranging from athermal to poor solvents.

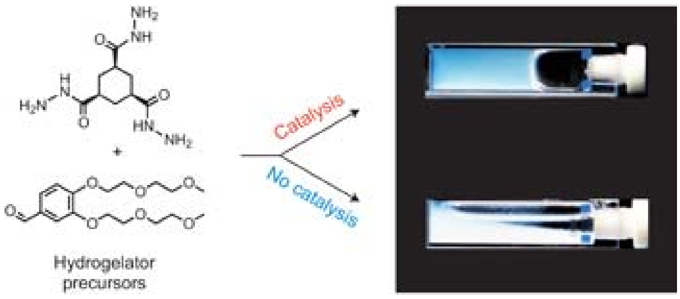
We use Monte Carlo simulations based on the bond fluctuation model and we take into account explicitly counterions, the full Coulomb and excluded volume interactions. The effect of solvent is accounted for implicitly by a short-range attraction between the monomers. The range of attraction is chosen in order to avoid unphysical freezing effects at temperatures well below the Θ-point. Our simulations support the Flory-type scaling prediction of the dendrimers' size under all solvent conditions for neutral dendrimers. Neutral dendrimers also display universal scaling properties with respect to the spacer length and spacer self-density. The maximum of electrostatically driven swelling, controlled by osmotically active residual counterions, is found to be nearly independent of solvent quality. Under poor solvent conditions the electrostatically driven volume degree of swelling reaches values up to Q=23, which indicates potential applications for those molecules as stimuli-responsive nanoparticles.

- Understanding Water Uptake and Transport in Nafion Using X-ray Microtomography
  Hwang, G. S.; Parkinson, D. Y.; Kusoglu, A.; MacDowell, A. A.; Weber, A. Z. *ACS Macro Lett.* **2013**, *2*, 288-291.
  Abstract:



To develop new ionomers and optimize existing ones, there is a need to understand their structure/function relationships experimentally. In this letter, synchrotron X-ray microtomography is used to examine water distributions within Nafion, the most commonly used ionomer. Simultaneous high spatial (~1 µm) and temporal (~10 min) resolutions, previously unattained by other techniques, clearly show the nonlinear water profile across the membrane thickness, with a continuous transition from dynamic to steady-state transport coefficients with the requisite water-content dependence. The data also demonstrate the importance of the interfacial condition in controlling the water profile and help to answer some long-standing debates in the literature.

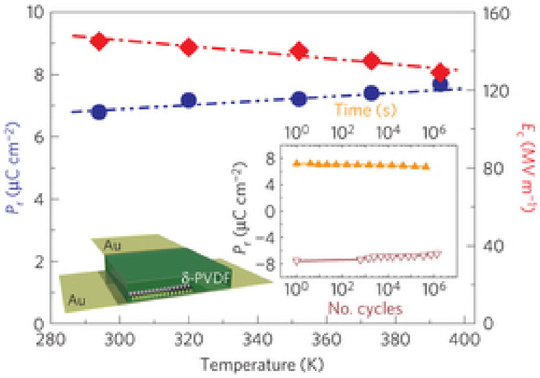
- Catalytic control over supramolecular gel formation
  Boekhoven, J.; Poolman, J. M.; Maity, C.; Li, F.; van der Mee, L.; Minkenberg, C. B.; Mendes, E.; van Esch, J. H.; Eelkema, R. *Nature Chem.* **2013**, *5*, 433–437.
  Abstract:



Low-molecular-weight gels show great potential for application in fields ranging from the petrochemical industry to healthcare and tissue engineering. These supramolecular gels are often metastable materials, which implies that their properties are, at least partially, kinetically controlled.

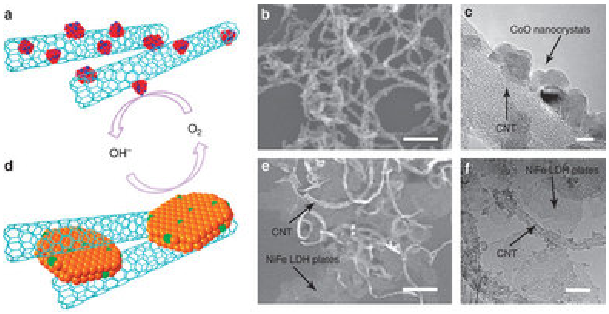
Here we show how the mechanical properties and structure of these materials can be controlled directly by catalytic action. We show how in situ catalysis of the formation of gelator molecules can be used to accelerate the formation of supramolecular hydrogels, which drastically enhances their resulting mechanical properties. Using acid or nucleophilic aniline catalysis, it is possible to make supramolecular hydrogels with tunable gel-strength in a matter of minutes, under ambient conditions, starting from simple soluble building blocks. By changing the rate of formation of the gelator molecules using a catalyst, the overall rate of gelation and the resulting gel morphology are affected, which provides access to metastable gel states with improved mechanical strength and appearance despite an identical gelator composition.

- Revisiting the δ-phase of poly(vinylidene fluoride) for solution-processed ferroelectric thin films
  Li, M.; Wondergem, H. J.; Spijkman, M.-J.; Asadi, K.; Katsouras, I.; Blom, P. W. M.; de Leeuw, D. M. *Nature Mater.* **2013**, *12*, 433–438.
  Abstract:



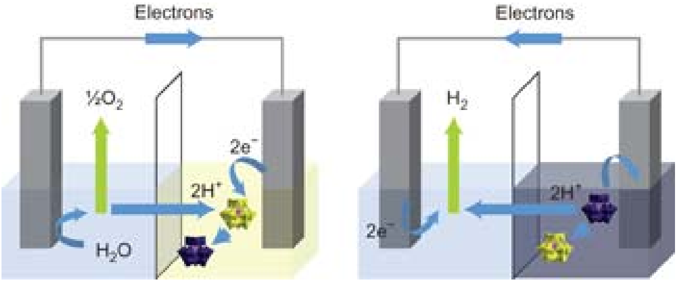
Ferroelectric poly(vinylidene-fluoride) (PVDF) has, in the past, been proposed as an ideal candidate for data storage applications as it exhibits a bistable, remanent, polarization that can repeatedly be switched by an electric field. However, fabrication of smooth ferroelectric PVDF thin films, as required for microelectronic applications, is a long-standing problem. At present, the copolymer of PVDF with trifluoroethylene P(VDF–TrFE) is used, but the stack integrity and the limited thermal stability of its remanent polarization hamper large-scale integration. Here we show that smooth neat PVDF films can be made at elevated substrate temperature. On applying a short electrical pulse the ferroelectric polar δ-phase is formed, an overlooked polymorph of PVDF proposed 30 years ago, but never experimentally verified. The remanent polarization and coercive field are comparable to those of the copolymer. The enhanced thermal stability of the polarization is directly related to the high Curie temperature, whereas the ferroelectric properties are related to the molecular packing as derived from the refined crystal structure. The replacement of P(VDF–TrFE) by the commodity polymer PVDF may boost large-scale industrial applications.

- Advanced zinc-air batteries based on high-performance hybrid electrocatalysts
  Li, Y.; Gong, M.; Liang, Y.; Feng, J.; Kim, J.-E.; Wang, H.; Hong, G.; Zhang, B.; Dai, H. *Nature Commun.* **2013**, *4*, 1805.
  Abstract:



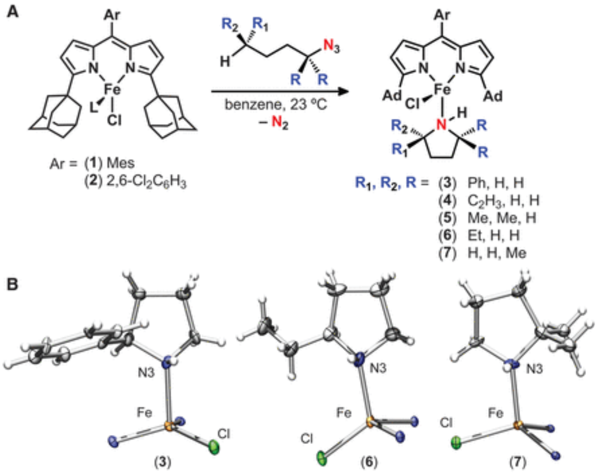
Primary and rechargeable Zn-air batteries could be ideal energy storage devices with high energy and power density, high safety and economic viability. Active and durable electrocatalysts on the cathode side are required to catalyse oxygen reduction reaction during discharge and oxygen evolution reaction during charge for rechargeable batteries. Here we developed advanced primary and rechargeable Zn-air batteries with novel CoO/carbon nanotube hybrid oxygen reduction catalyst and Ni-Fe-layered double hydroxide oxygen evolution catalyst for the cathode. These catalysts exhibited higher catalytic activity and durability in concentrated alkaline electrolytes than precious metal Pt and Ir catalysts. The resulting primary Zn-air battery showed high discharge peak power density ~265 mW cm^{-2}, current density ~200 mA cm^{-2} at 1 V and energy density >700 Wh kg^{-1}. Rechargeable Zn-air batteries in a tri-electrode configuration exhibited an unprecedented small charge–discharge voltage polarization of ~0.70 V at 20 mA cm^{-2}, high reversibility and stability over long charge and discharge cycles.

- Decoupling hydrogen and oxygen evolution during electrolytic water splitting using an electron-coupled-proton buffer
  Symes, M. D.; Cronin, L. *Nature Chem.* **2013**, *5*, 403–409.
  Abstract:



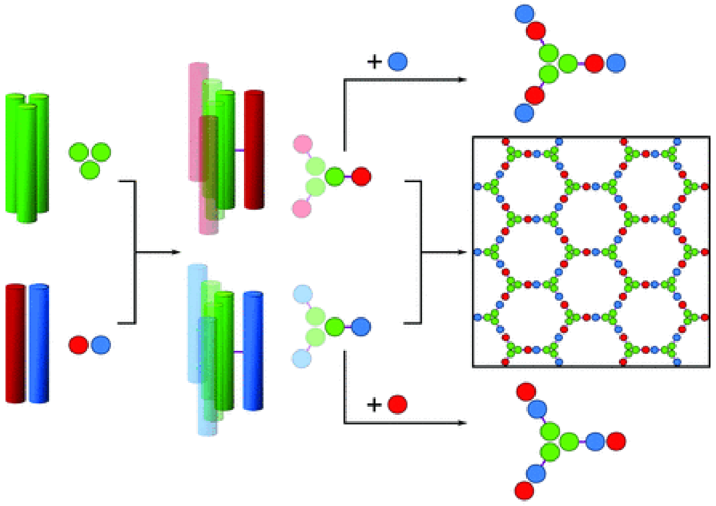
Hydrogen is essential to several key industrial processes and could play a major role as an energy carrier in a future ‘hydrogen economy’. Although the majority of the world's hydrogen supply currently comes from the reformation of fossil fuels, its generation from water using renewables-generated power could provide a hydrogen source without increasing atmospheric CO_2 levels. Conventional water electrolysis produces H_2 and O_2 simultaneously, such that these gases must be generated in separate spaces to prevent their mixing. Herein, using the polyoxometalate $H_3PMo_{12}O_{40}$, we introduce the concept of the electron-coupled-proton buffer (ECPB), whereby O_2 and H_2 can be produced at separate times during water electrolysis. This could have advantages in preventing gas mixing in the headspaces of high-pressure electrolysis cells, with implications for safety and electrolyser degradation. Furthermore, we demonstrate that temporally separated O_2 and H_2 production allows greater flexibility regarding the membranes and electrodes that can be used in water-splitting cells.

- Complex N-Heterocycle Synthesis via Iron-Catalyzed, Direct C–H Bond Amination
  Hennessy, E. T.; Betley, T. A. *Science* **2013**, *340*, 591-595.
  Abstract:



The manipulation of traditionally unreactive functional groups is of paramount importance in modern chemical synthesis. We have developed an iron-dipyrrinato catalyst that leverages the reactivity of iron-borne metal-ligand multiple bonds to promote the direct amination of aliphatic C–H bonds. Exposure of organic azides to the iron dipyrrinato catalyst furnishes saturated, cyclic amine products (N-heterocycles) bearing complex core-substitution patterns. This study highlights the development of C–H bond functionalization chemistry for the formation of saturated, cyclic amine products and should find broad application in the context of both pharmaceuticals and natural product synthesis.

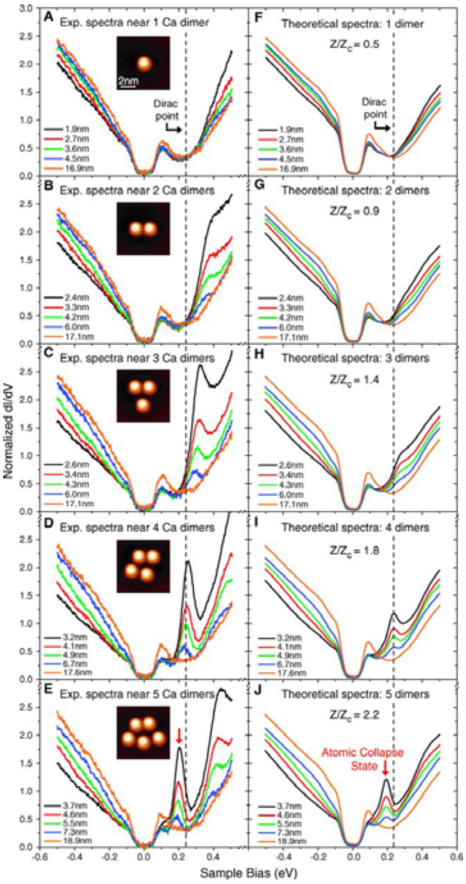
- Self-Assembling Cages from Coiled-Coil Peptide Modules
  Fletcher, J. M.; Harniman, R. L.; Barnes, F. R. H.; Boyle, A. L.; Collins, A.; Mantell, J.; Sharp, T. H.; Antognozzi, M.; Booth, P. J.; Linden, N.; Miles, M. J.; Sessions, R. B.; Verkade, P.; Woolfson, D. N. *Science* **2013**, *340*, 595-599.
  Abstract:



An ability to mimic the boundaries of biological compartments would improve our understanding of self-assembly and provide routes to new materials for the delivery of drugs and biologicals and the development of protocells. We show that short designed peptides can be combined to form unilamellar spheres approximately 100 nanometers in diameter. The design comprises two, noncovalent, heterodimeric and homotrimeric coiled-coil bundles. These are joined back to back to

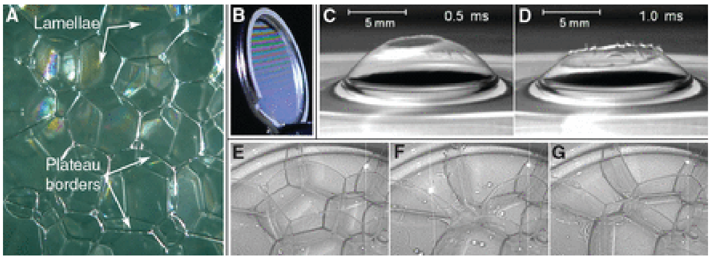
render two complementary hubs, which when mixed form hexagonal networks that close to form cages. This design strategy offers control over chemistry, self-assembly, reversibility, and size of such particles.

- Observing Atomic Collapse Resonances in Artificial Nuclei on Graphene
  Wang Y.; Wong, D.; Shyton, A. V.; Brar, V. W.; Choi, S.; Wu, Q.; Tsai, H.-Z.; Regan, W.; Zettl, A.; Kawakami, R.; Louie, S. G.; Levitov, L. S.; Crommie, M. F. *Science* **2013**, *340*, 734-737.
  Abstract:



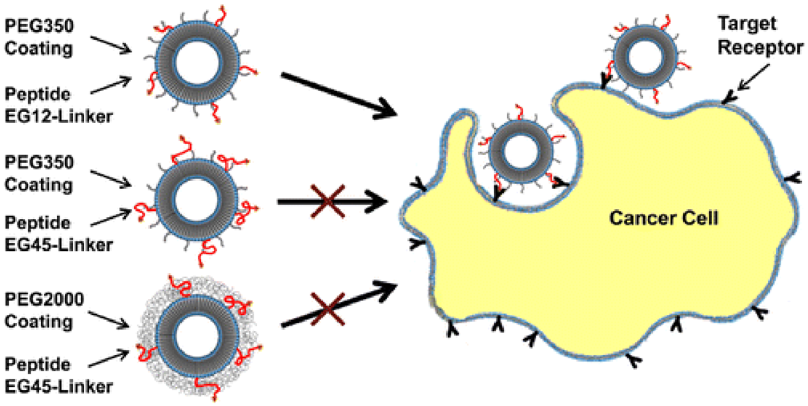
Relativistic quantum mechanics predicts that when the charge of a superheavy atomic nucleus surpasses a certain threshold, the resulting strong Coulomb field causes an unusual atomic collapse state; this state exhibits an electron wave function component that falls toward the nucleus, as well as a positron component that escapes to infinity. In graphene, where charge carriers behave as massless relativistic particles, it has been predicted that highly charged impurities should exhibit resonances corresponding to these atomic collapse states. We have observed the formation of such resonances around artificial nuclei (clusters of charged calcium dimers) fabricated on gated graphene devices via atomic manipulation with a scanning tunneling microscope. The energy and spatial dependence of the atomic collapse state measured with scanning tunneling microscopy revealed unexpected behavior when occupied by electrons.

- Multiscale Modeling of Membrane Rearrangement, Drainage, and Rupture in Evolving Foams
  Saye, R. I.; Sethian, J. A. *Science* **2013**, *340*, 720-724.
  Abstract:



Modeling the physics of foams and foamlike materials, such as soapy froths, fire retardants, and lightweight crash-absorbent structures, presents challenges, because of the vastly different time and space scales involved. By separating and coupling these disparate scales, we have designed a multiscale framework to model dry foam dynamics. This leads to a predictive and flexible computational methodology linking, with a few simplifying assumptions, foam drainage, rupture, and topological rearrangement, to coupled interface-fluid motion under surface tension, gravity, and incompressible fluid dynamics. Our computed results match theoretical analyses and experimentally observed physical effects, including thin-film drainage and interference, and are used to study bubble rupture cascades and macroscopic rearrangement. The developed multiscale model allows quantitative computation of complex foam evolution phenomena.

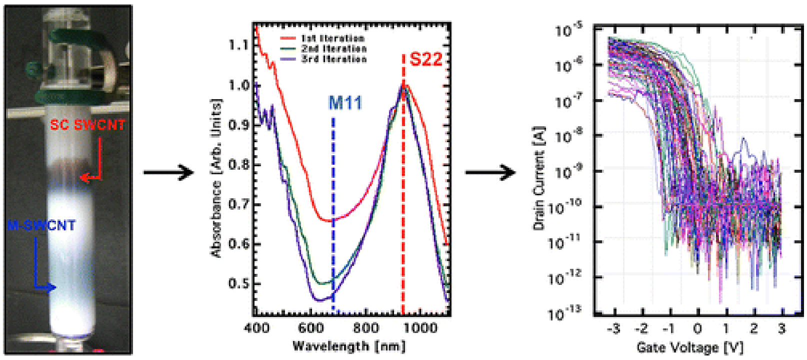
- A Systematic Analysis of Peptide Linker Length and Liposomal Polyethylene Glycol Coating on Cellular Uptake of Peptide-Targeted Liposomes
  Stefanick, J. F.; Ashley, J. D.; Kiziltepe, T.; Bilgicer, B. *ACS Nano* **2013**, *7*, 2935-2947.
  Abstract:



PEGylated liposomes are attractive pharmaceutical nanocarriers; however, literature reports of ligand-targeted nanoparticles have not consistently shown successful results. Here, we employed a multifaceted synthetic strategy to prepare peptide-targeted liposomal nanoparticles with high purity, reproducibility, and precisely controlled stoichiometry of functionalities to evaluate the role of liposomal PEG coating, peptide EG-linker length, and peptide valency on cellular uptake in a systematic manner. We analyzed these parameters in two distinct disease models where the liposomes were functionalized with either HER2- or VLA-4-antagonistic peptides to target HER2-overexpressing breast cancer cells or VLA-4-overexpressing myeloma cells, respectively. When targeting peptides were tethered to nanoparticles with an EG45 (PEG2000) linker in a manner similar to a more traditional formulation, their cellular uptake was not enhanced compared to non-targeted versions regardless of the liposomal PEG coating used. Conversely, reduction of the liposomal PEG to PEG350 and the peptide linker to EG12 dramatically enhanced cellular uptake by 9 fold and 100 fold in the breast cancer and multiple myeloma cells, respectively. Uptake efficiency reached a maximum and a plateau with 2% peptide density in both disease models. Taken together, these results

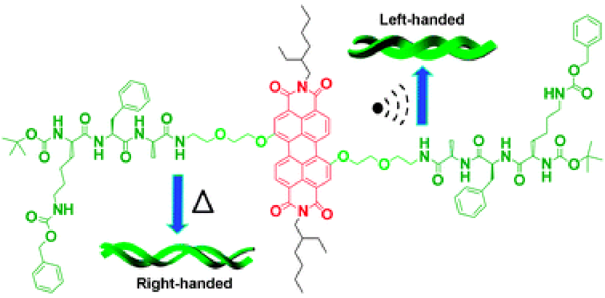
demonstrate the significance of using the right design elements such as the appropriate peptide EG-linker length in coordination with the appropriate liposomal PEG coating and optimal ligand density in efficient cellular uptake of liposomal nanoparticles.

- High Purity Isolation and Quantification of Semiconducting Carbon Nanotubes via Column Chromatography
  Tulevski, G. S.; Franklin, A. D.; Afzali, A. *ACS Nano* **2013**, *7*, 2971-2976.
  Abstract:



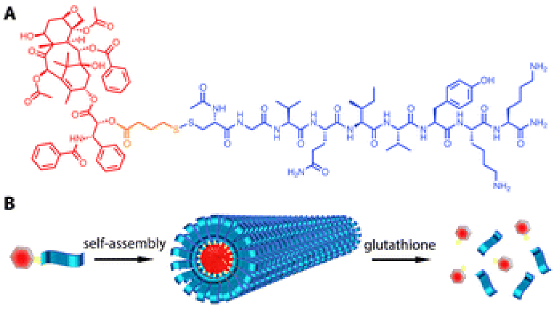
The isolation of semiconducting carbon nanotubes (CNTs) to ultrahigh (ppb) purity is a prerequisite for their integration into high-performance electronic devices. Here, a method employing column chromatography is used to isolate semiconducting nanotubes to 99.9% purity. The study finds that by modifying the solution preparation step, both the metallic and semiconducting fraction are resolved and elute using a single surfactant system, allowing for multiple iterations. Iterative processing enables a far more rapid path to achieving the level of purities needed for high performance computing. After a single iteration, the metallic peak in the absorption spectra is completely attenuated. Although absorption spectroscopy is typically used to characterize CNT purity, it is found to be insufficient in quantifying solutions of high purity (>98 to 99%) due to low signal-to-noise in the metallic region of ultrahigh purity solutions. Therefore, a high throughput electrical testing method was developed to quantify the degree of separation by characterizing 4000 field-effect transistors fabricated from the separated nanotubes after multiple iterations of the process. The separation and characterization methods described here provide a path to produce the ultrahigh purity semiconducting CNT solutions needed for high performance electronics.

- Conformation-variable PDI@β-sheet nanohelices show stimulus-responsive supramolecular chirality
  Ke, D.; Tang, A.; Zhan, C.; Yao, J. *Chem. Commun.*, **2013**, *49*, 4914-4916.
  Abstract:



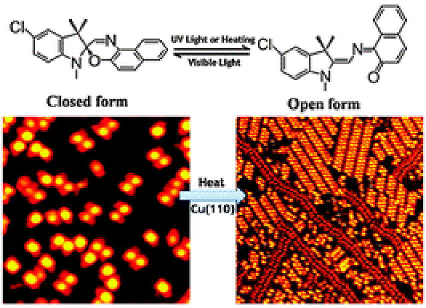
A tripeptide–perylene diimide (PDI) conjugate self-assembles into PDI@β-sheet nanohelices, whose local conformations are sensitive to the external stimuli of concentration, heating and ultrasound, showing stimulus-responsive supramolecular chirality.

- Supramolecular filaments containing a fixed 41% paclitaxel loading
  Lin, R.; Cheetham, A. G.; Zhang, P.; Lina, Y.; Cui, H. *Chem. Commun*. **2013**, *49*, 4968-4970.
  Abstract:



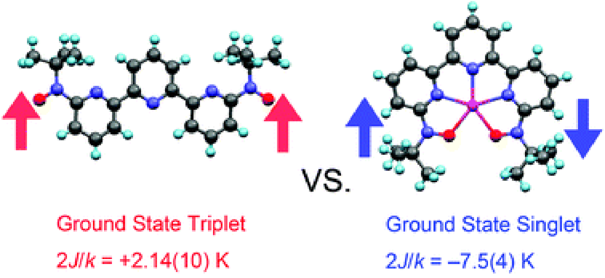
We report here the self-assembly of a rationally designed paclitaxel drug amphiphile into well-defined supramolecular filaments that possess a fixed 41% paclitaxel loading. These filaments can exert effective cytotoxicity against a number of cell lines comparable to that of free paclitaxel.

- A molecular conformational change induced self-assembly: from randomness to order
  Xu, W.; Chang, C.; Gersen, H.; Sun, Q.; Kong, H.; Dong, L.; Sheng, K.; Tan, Q.; Lægsgaard, E.; Besenbacher, F. *Chem. Commun*. **2013**, *49*, 5207-5209.
  Abstract:



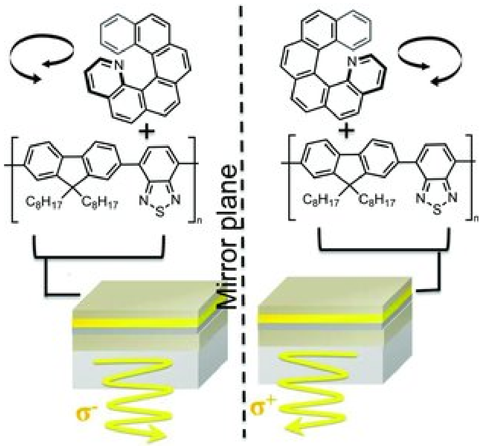
From an interplay of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations we reveal how a molecular conformational change induced self-assembly process can result in the conversion from a random molecular phase to the formation of two types of ordered surface nanostructures with different apparent heights.

- A supramolecular switch between ground high- and low-spin states using 2,2′:6′,2″-terpyridine-6,6″-diyl bis(tert-butyl nitroxide)
  Konno, T.; Koide, K.; Ishida, T. *Chem. Commun*. **2013**, *49*, 5156-5158.
  Abstract:



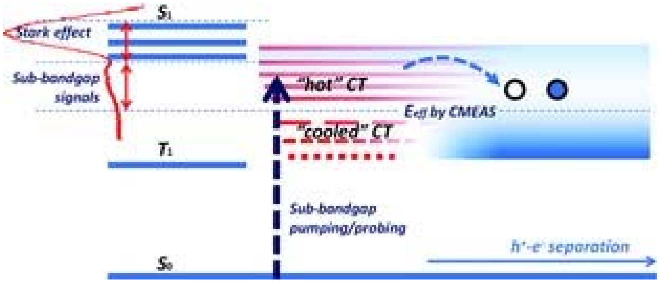
Biradical 2,2′:6′,2″-terpyridine-6,6″-diyl bis(tert-butyl nitroxide) (tpybNO) showed intramolecular ferromagnetic coupling with 2J/kB = +2.14(10) K and its complex [Zn(tpybNO)(MeOH)2](BF4)2 exhibited intramolecular antiferromagnetic coupling with 2J/kB = −7.5(4) K, suggesting exchange coupling switchable by means of supramolecular chemistry.

- Induction of Circularly Polarized Electroluminescence from an Achiral Light-Emitting Polymer via a Chiral Small-Molecule Dopant
  Yang, Y. ; da Costa, R. C.; Smilgies, D.-M.; Campbell, A. J.; Fuchter, M. J. *Adv. Mater.* **2013**, *25*, 2624–2628.
  Abstract:



By simply doping the conventional light-emitting polymer F8BT with a helically chiral aromatic molecule, it is shown that substantial levels of CP-electroluminescence can be generated directly. Both photoluminescent and electroluminescent emission from the polymer are observed to become circularly polarized, with the sign of the CP emission directly determined by the handedness of the dopant.

- Energy Level Alignment and Sub-Bandgap Charge Generation in Polymer:Fullerene Bulk Heterojunction Solar Cells
  Tsang, S.-W.; Chen, S.; So, F. *Adv. Mater.* **2013**, *25*, 2434–2439.
  Abstract:

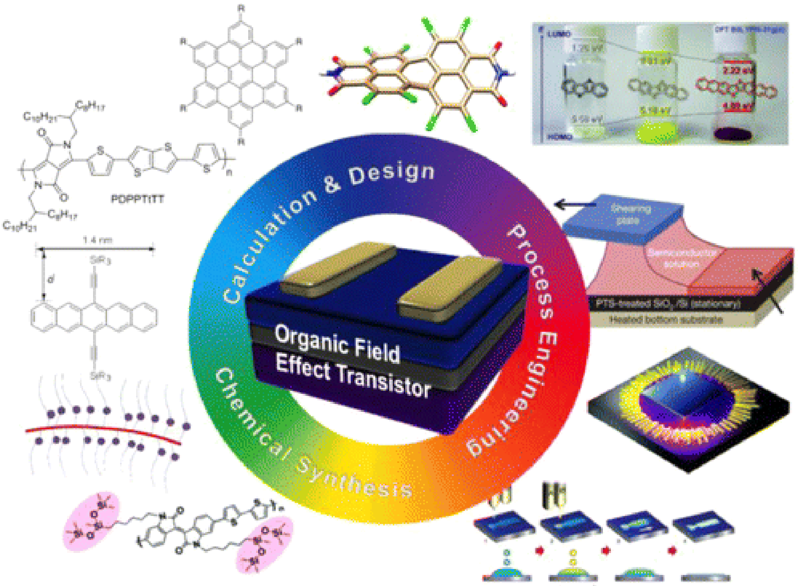


Using charge modulated electroabsorption spectroscopy (CMEAS), for the first time, the energy level alignment of a polymer:fullerene bulk heterojunction photovoltaic cell is directly measured. The charge-transfer excitons generated by the sub-bandgap optical pumping are coupled with the modulating electric field and introduce subtle changes in optical absorption in the sub-bandgap region. This minimum required energy for sub-bandgap charge genreation is defined as the effective bandgap.

- Integrated Materials Design of Organic Semiconductors for Field-Effect Transistors

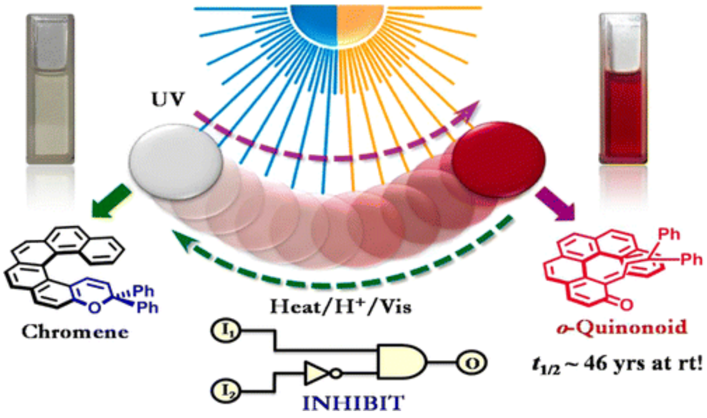
Mei, J.; Diao, Y.; Appleton, A.L.; Fang, L.; Bao, Z. *J. Am. Chem. Soc.* **2013**, *135,* 6724–6746.

Abstract:



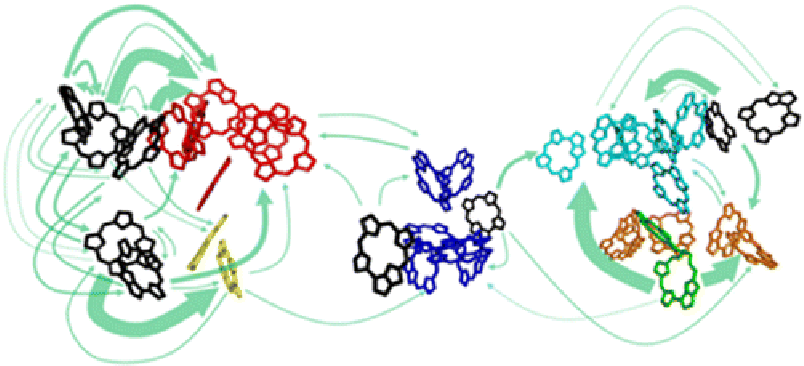
The past couple of years have witnessed a remarkable burst in the development of organic field-effect transistors (OFETs), with a number of organic semiconductors surpassing the benchmark mobility of 10 cm^2/(V s). In this perspective, we highlight some of the major milestones along the way to provide a historical view of OFET development, introduce the integrated molecular design concepts and process engineering approaches that lead to the current success, and identify the challenges ahead to make OFETs applicable in real applications.

- Helicity as a Steric Force: Stabilization and Helicity-Dependent Reversion of Colored o-Quinonoid Intermediates of Helical Chromenes
  Moorthy, J. N.; Mandal, S.; Mukhopadhyay, A.; Samanta, S. *J. Am. Chem. Soc.* **2013**, *135,* 6872–6884.
  Abstract:



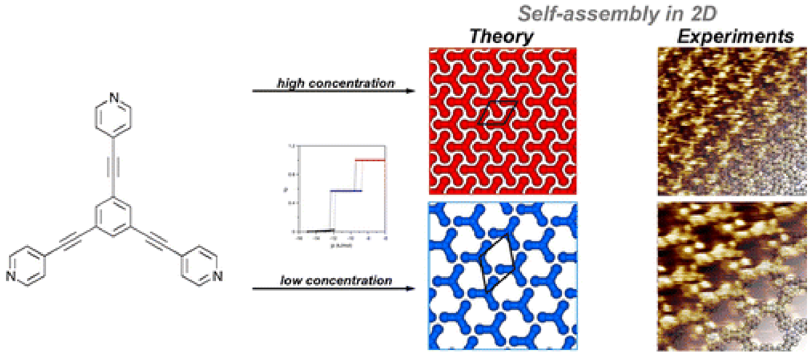
Photolysis of regioisomeric helical chromenes 1 and 2 leads to colored reactive intermediates. While the latter generally decay quite rapidly, they are found to be longer lived in 1 and highly persistent in 2. The remarkable stability of the otherwise fleeting transient in 2 allowed isolation and structural characterization by X-ray crystallography. The structural analyses revealed that steric force inherent to the helical scaffold is the origin of stability as well as differentiation in the persistence of the intermediates of 1 and 2 (1Q and 2Q). The structure further shows that diphenylvinyl moiety in the TT isomer of 2Q gets splayed over the helical scaffold such that it is fraught with a huge steric strain to undergo required bond rotations to regenerate the precursor chromene. Otherwise, reversion of 2Q was found to occur at higher temperatures. Aazahelical chromenes 3 and 4 with varying magnitudes of helicity were designed in pursuit of o-quinonoid intermediates with graded activation barriers. Their photogenerated intermediates 3Q and 4Q were also isolated and structurally characterized. The activation barriers for thermal reversion of 2Q–4Q, as determined from Arrhenius and Eyring plots, are found to correlate nicely with the helical turn, which decisively determines the steric force. The exploitation of helicity is thus demonstrated to develop a novel set of photoresponsive helicenes 2–4 that lead to colored intermediates exhibiting graded stability. It is further shown that the photochromism of 2–4 in conjunction with response of 2Q–4Q to external stimuli (acid, heat, and visible radiation) permits development of molecular logic gates with INHIBIT function.

- Photosystem II Does Not Possess a Simple Excitation Energy Funnel: Time-Resolved Fluorescence Spectroscopy Meets Theory
  Shibata, Y.; Nishi, S.; Kawakami, K.; Shen, J.-R.; Renger, T. *J. Am. Chem. Soc.* **2013***, 135,* 6903–6914.
  Abstract:



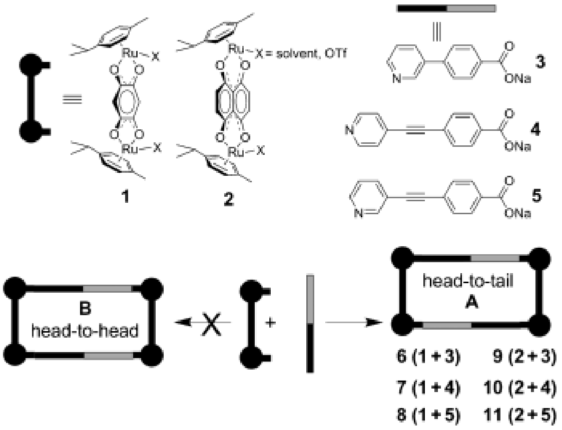
The experimentally obtained time-resolved fluorescence spectra of photosystem II (PS II) core complexes, purified from a thermophilic cyanobacterium Thermosynechococcus vulcanus, at 5–180 K are compared with simulations. Dynamic localization effects of excitons are treated implicitly by introducing exciton domains of strongly coupled pigments. Exciton relaxations within a domain and exciton transfers between domains are treated on the basis of Redfield theory and generalized Förster theory, respectively. The excitonic couplings between the pigments are calculated by a quantum chemical/electrostatic method (Poisson-TrEsp). Starting with previously published values, a refined set of site energies of the pigments is obtained through optimization cycles of the fits of stationary optical spectra of PS II. Satisfactorily agreement between the experimental and simulated spectra is obtained for the absorption spectrum including its temperature dependence and the linear dichroism spectrum of PS II core complexes (PS II-CC). Furthermore, the refined site energies well reproduce the temperature dependence of the time-resolved fluorescence spectrum of PS II-CC, which is characterized by the emergence of a 695 nm fluorescence peak upon cooling down to 77 K and the decrease of its relative intensity upon further cooling below 77 K. The blue shift of the fluorescence band upon cooling below 77 K is explained by the existence of two red-shifted chlorophyll pools emitting at around 685 and 695 nm. The former pool is assigned to Chl45 or Chl43 in CP43 (Chl numbering according to the nomenclature of Loll et al. Nature2005, 438, 1040) while the latter is assigned to Chl29 in CP47. The 695 nm emitting chlorophyll is suggested to attract excitations from the peripheral light-harvesting complexes and might also be involved in photoprotection.

- Concentration-Dependent Supramolecular Engineering of Hydrogen-Bonded Nanostructures at Surfaces: Predicting Self-Assembly in 2D
  Ciesielski, A.; Szabelski, P. J.; Rżysko, W.; Cadeddu, A.; Cook, T. R.; Stang, P. J.; Samorì, P. *J. Am. Chem. Soc.* **2013***, 135,* 6942–6950.
  Abstract:



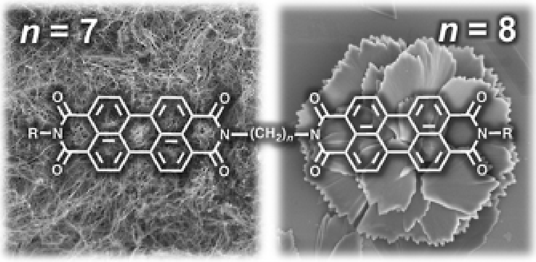
We report a joint computational and experimental study on the concentration-dependent self-assembly of a flat C3-symmetric molecule at surfaces. As a model system we have chosen a rigid molecular module, 1,3,5-tris(pyridine-4-ylethynyl)benzene, which can undergo self-association via hydrogen bonding (H-bonding) to form ordered 2D nanostructures. In particular, the lattice Monte Carlo method, combined with density functional calculations, was employed to explore the spontaneous supramolecular organization of this tripod-shaped molecule under surface confinement. We analyzed the stability of different weak H-bonded patterns and the influence of the concentration of the starting molecule on the 2D supramolecular packing. We found that ordered, densely packed monolayers and 2D porous networks are obtained at high and low concentrations, respectively. A concentration-dependent scanning tunneling microscopy investigation of the molecular self-assembly at a graphite–solution interface revealed supramolecular motifs, which are in perfect agreement with those obtained by simulations. Therefore, our computational approach represents a step forward toward the deterministic prediction of molecular self-assembly at surfaces and interfaces.

- Self-Assembly of Ambidentate Pyridyl-Carboxylate Ligands with Octahedral Ruthenium Metal Centers: Self-Selection for a Single-Linkage Isomer and Anticancer-Potency Studies
  Jung, H.; Dubey, A.; Koo, H. J.; Vajpayee, V.; Cook, T. R.; Kim, H.; Kang, S. C.; Stang, P. J.; Chi, K.-W. *Chem. Eur. J.* **2013**, *21*, 6709-6717.
  Abstract:



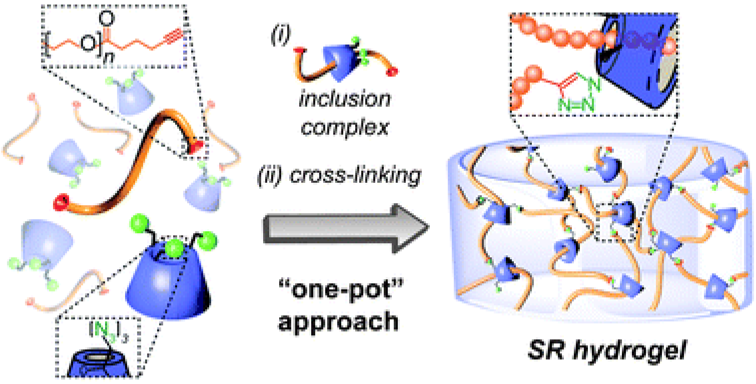
The synthesis of six new [2+2] metallarectangles through the coordination-driven self-assembly of octahedral Ru^{II}-based acceptors with ambidentate pyridyl-carboxylate donors is described. These molecular rectangles are fully characterized by ^{1}H NMR spectroscopy, high-resolution electrospray mass spectrometry, and single-crystal X-ray diffraction. In each case, despite the possible formation of multiple isomers, based on the relative orientation of the pyridyl and carboxylate groups (head-to-head versus head-to-tail), evidence for the formation of a single preferred ensemble (head-to-tail) was found in the ^{1}H NMR spectra. Furthermore, the cytotoxicities of all of the rectangles were established against A549 (lung), AGS (gastric), HCT-15 (colon), and SK hep 1 (liver) human cancer cell lines. The cytotoxicities of rectangles that contained the 5,8-dihydroxy-1,4-naphthaquinonato bridging moiety between the Ru centers (**9**–**11**) were particularly high against AGS cancer cells, with IC_{50} values that were comparable to that of reference drug cisplatin.

- Covalent Modular Approach for Dimension-Controlled Self-Organization of Perylene Bisimide Dyes
  Lin, X.; Hirono, M.; Seki, T.; Kurata, H.; Karatsu, T.; Kitamura, A.; Kuzuhara, D.; Yamada, H.; Ohba, T.; Saeki, S. ; Yagai, S. *Chem. Eur. J.* **2013**, *21*, 6561-6565.
  Abstract:



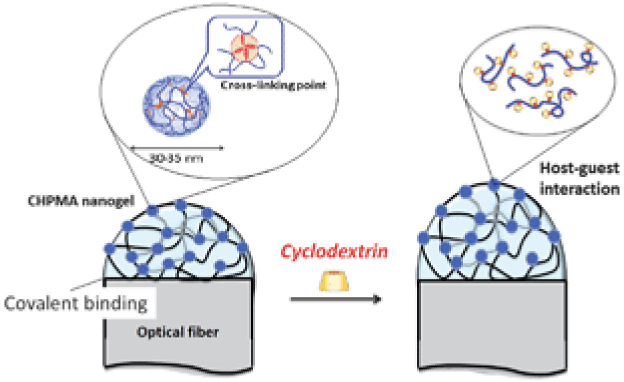
Organogels: Dimerization of perylene bisimide dyes through an oligomethylene linker enabled the facile control over columnar and lamellar self-organized architectures by an odd/even effect with respect to the number of methylene groups. The difference in the self-organized architectures was shown to have an impact on their material morphologies, as well as charge-carrier mobilities (see scheme).

- A novel one-pot approach towards dynamically cross-linked hydrogels
  Tan, S.; Blencowe, A.; Ladewig, K.; Qiao, G. G. *Soft Matter* **2013,** *9*, 5239-5250.
  Abstract:



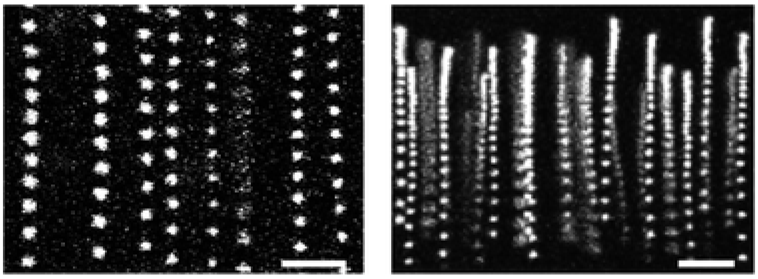
Herein, we report the synthesis of sliding-ring (SR) hydrogel networks in a one-pot click-mediated approach using α,ω-dialkyne poly(ethylene glycol) (PEG) and azido-functionalised cyclodextrin, which acts as both sliding cross-link and end-capping agent. This novel approach resulted in polymeric networks that possess a combination of both SR and covalent (CV) cross-link points. The extent of inclusion complexation and the ratio of SR to CV cross-links in the hydrogels was found to be dependent on both the concentration of the precursors and the curing temperature. Based upon model studies where rotaxanes were synthesised from the same precursors, it was observed that an increase in the precursor concentration led to an increase in click efficiency and inclusion ratio, which in turn affects the overall hydrogel rigidity and elasticity. Hydrogels synthesised at higher curing temperatures led to more homogeneous networks that were significantly tougher as a result of the overall increase in cross-linking density and the extent of CV cross-links. We therefore present a facile one-pot method for the synthesis of SR networks with tunable physicochemical properties. Additionally, the resultant hydrogel networks are potentially capable of supporting post-modification with various (bio)molecules or therapeutics utilizing the remaining azide groups on the cyclodextrin cross-links. Preliminary cytotoxicity studies revealed that the hydrogels did not impede cell growth and demonstrate negligible toxicity. Thus, these networks may have potential for soft-tissue engineering or biomedical applications, including sustained release and drug-delivery systems.

- Cyclodextrin triggered dimensional changes of polysaccharide nanogel integrated hydrogels at nanometer resolution
  Gao, M.; Toita, S.; Sawada, S.-I.; Akiyoshi, K.; Stokke, B. T. *Soft Matter* **2013,** *9*, 5178-5185.
  Abstract:



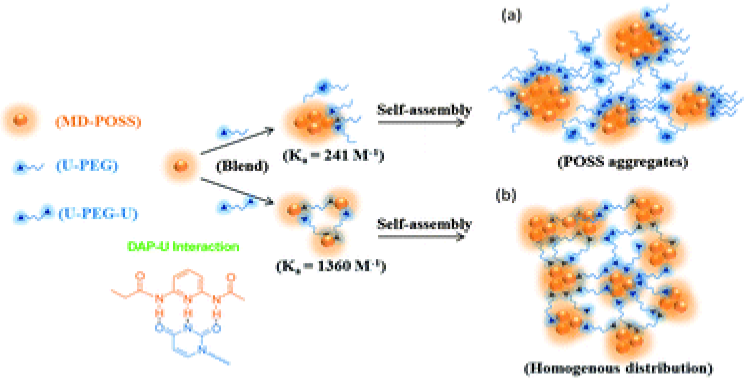
High resolution monitoring of dimensional changes of cholesterol bearing pullulan (CHP) hydrogels was performed as a model for materials' dimensional changes associated with drug delivery. Hydrogels consisting of methacryloyl group-modified cholesterol bearing pullulan (CHPMA) were covalently attached at the end of an optical fibre for interferometric monitoring of dimensional changes. Hydrogels polymerized by CHPMA self-assembled nanogels with different methacryloyl groups (4 and 7 methacryloyl groups per 100 glucose units) at different original CHP concentrations (35, 45 and 55 mg ml^{-1}) were employed to prepare soft materials with various swelling properties. The substituted cholesteryl groups in CHP gels affect the hydrogel swelling by forming association domains by hydrophobic interaction that can also be destabilized by host–guest interactions with cyclodextrins. The swelling properties were determined with 2 nm resolution in optical length and sampled at a frequency of approximately 1 Hz for the 50 µm radius hemispherical hydrogels. The results show that the equilibrium swelling and swelling kinetics of the CHP depend on its composition and the exposure to cyclodextrin types and concentrations. CHP hydrogels with the least number of methacryloyl groups and the lowest CHP concentration yielded the largest swelling changes on exposure to methyl-β-cyclodextrin. The swelling rate induced by cyclodextrin was independent of CHP concentration and type of cyclodextrin. The interferometric investigation of CHP hydrogel swelling associated with the disassociation of cholesterol group aggregates has proved its potential in providing information on hydrogel swelling relevant to materials' dimensional changes associated with controlled drug delivery.

- Transport of charged colloids in a nonpolar solvent
  Lin, T.; Kodger, T. E.; Weitz, D. A. *Soft Matter* **2013,** *9*, 5173-5177.
  Abstract:



In nonpolar solvents, surfactants stabilize charge through the formation of reverse micelles; this enables the dissociation of charge from the surfaces of particles, thereby charge-stabilizing particle suspensions. We investigate the dynamics of such charged particles by directly visualizing their motion across a microfluidic channel in response to an external electric field. The presence of the reverse micelles has a significant effect on particle motion: in a constant field, the particles initially move, then slow down exponentially, and eventually stop. This is due to the accumulation of reverse micelles at the channel walls, which screens the applied field, leading to the subsequent decay of the internal electric field. The time constant of decay depends on the electrical conductivity of the particle suspension and the width of the channel; this behavior is modeled as an equivalent RC circuit.

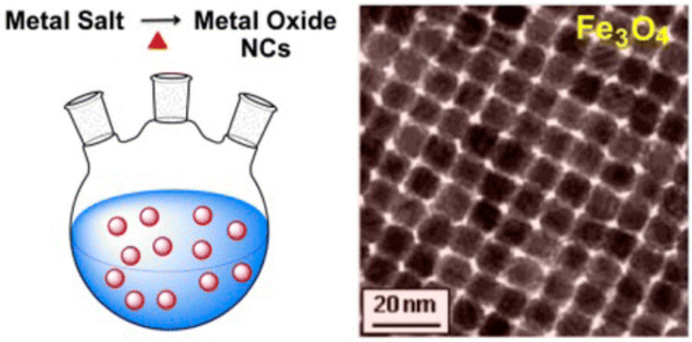
- Supramolecular structures of uracil-functionalized PEG with multi-diamidopyridine POSS through complementary hydrogen bonding interactions
  Wang, J.-H.; Altukhov, O.; Cheng, C.-C.; Chang, F.-C.; Kuo, S.-W. *Soft Matter* **2013,** *9*, 5196-5206.
  Abstract:



In this study, we synthesized (i) a multi-diamidopyridine-functionalized polyhedral oligomeric silsesquioxane (MD-POSS) through nucleophilic substitution and click 1,3-cycloaddition reactions and (ii) both mono- and bis-uracil (U)-functionalized poly(ethylene glycol) derivatives (U–PEG and U–PEG–U, respectively) through Michael additions of U to acryloyl-functionalized PEG oligomers. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) revealed that supramolecular structures self-assembled from mixtures of MD-POSS and U–PEG and from MD-POSS and U–PEG–U. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy confirmed the presence of multiple hydrogen bonding interactions between the diaminopyridine

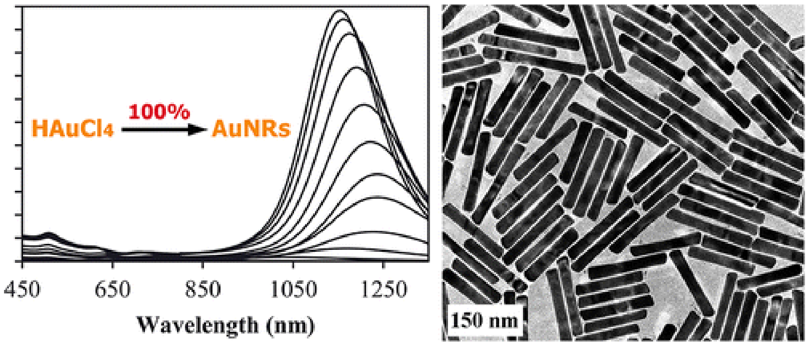
groups of MD-POSS and the U groups of U–PEG and U–PEG–U. Because of these strong reversible intermolecular multiple hydrogen bonds, the POSS-based polymer-like supramolecular materials exhibited improved thermal properties upon increasing the MD-POSS content.

- High-Temperature Solution-Phase Syntheses of Metal-Oxide Nanocrystals
  Lee, J.; Zhang, S.; Sun, S. *Chem. Mater.* **2013**, *25*, 1293-1304.
  Abstract:



This review highlights the recent progress in synthesizing some representative metal-oxide nanocrystals (MONCs) with controlled magnetic, electronic, and optical properties for potentially important technological applications. It first introduces the synthesis of MONCs of magnetite (Fe_3O_4), ferrite (MFe_2O_4), and hollow Fe_3O_4 with controlled magnetic properties. It then highlights the potentials of these nanocrystals (NCs) as highly effective contrast enhancement agents for magnetic resonance imaging (MRI) and as efficient nanoplatforms for target specific drug delivery. The review further surveys some typical high-temperature solution-phase approaches to the common semiconductive MONCs of indium tin oxide (ITO, $In_2O_3 \cdot xSnO_2$)/tin oxide (SnO_2), zinc oxide (ZnO), titanium oxide (TiO_2), and copper oxide (Cu_2O or CuO) with controlled band-gap energies and optical properties for optoelectronics, photocatalysis, and sensor applications.

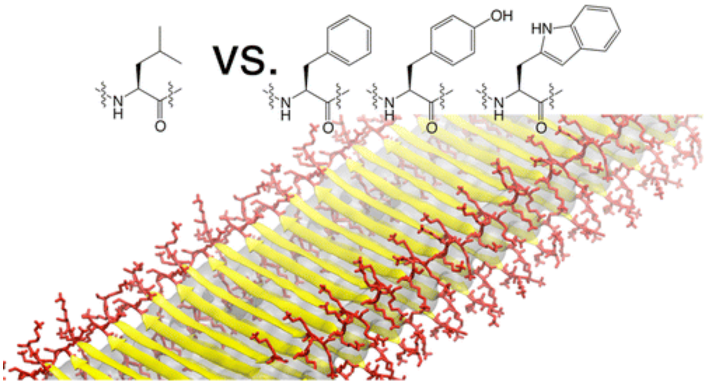
- High-Yield Synthesis of Gold Nanorods with Longitudinal SPR Peak Greater than 1200 nm Using Hydroquinone as a Reducing Agent
  Vigderman, L.; Zubarev, E. R. *Chem. Mater.* **2013**, *25*, 1450-1457.
  Abstract:



While gold nanorods have been extensively studied and used in many biological, plasmonics, and sensing applications, their conventional seed-mediated synthesis still presents a number of limitations. Its high sensitivity to the concentration of the reducing agent (ascorbic acid) leads to problems with reliability as well as extremely poor yield of ionic-to-metallic gold conversion, which is only ~15%. In addition, the synthesis of high purity nanorods with longitudinal surface plasmon resonance (LSPR) peak higher than 1000 nm is particularly difficult utilizing this technique. This report

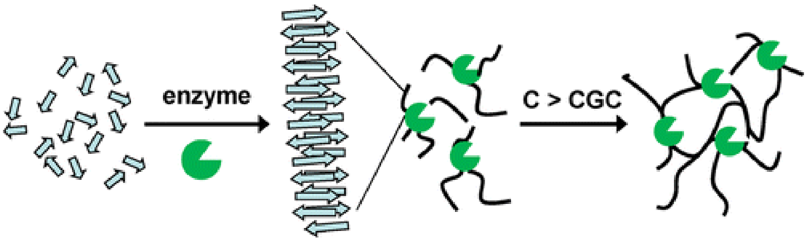
demonstrates the use of hydroquinone for the synthesis of gold nanorods which addresses these two major limitations. By replacing ascorbic acid with a large excess of hydroquinone, rods with LSPR up to 1230 nm can be synthesized with a high degree of purity, reliability, and near quantitative conversion of gold ions to metallic gold. The growth of the rods is tracked by TEM utilizing a thiolation reaction to halt their growth. Finally, the effect of changing various parameters including hydroquinone, seed, gold, and silver concentration is examined, demonstrating the tunability of the procedure over the broad range of attainable LSRPs from 770 to 1230 nm.

- Self-Assembling Multidomain Peptide Fibers with Aromatic Cores
  Bakota, E. L.; Sensoy, O.; Ozgur, B.; Sayar, M.; Hartgerink, J. D. *Biomacromolecules* **2013**, *14*, 1370-1378.
  Abstract:



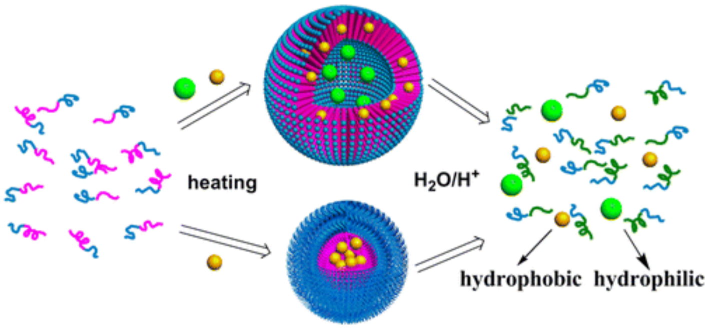
Self-assembling multidomain peptides have been shown to have desirable properties, such as the ability to form hydrogels that rapidly recover following shear-thinning and the potential to be tailored by amino acid selection to vary their elasticity and encapsulate and deliver proteins and cells. Here we describe the effects of substitution of aliphatic hydrophobic amino acids in the central domain of the peptide for the aromatic amino acids phenylalanine, tyrosine, and tryptophan. While the basic nanofibrous morphology is retained in all cases, selection of the particular core residues results in switching from antiparallel hydrogen bonding to parallel hydrogen bonding in addition to changes in nanofiber morphology and in hydrogel rheological properties. Peptide nanofiber assemblies are investigated by circular dichroism polarimetry, infrared spectroscopy, atomic force microscopy, transmission and scanning electron microscopy, oscillatory rheology, and molecular dynamics simulations. Results from this study will aid in designing next generation cell scaffolding materials.

- Effect of Enzyme Concentration of the Morphology and Properties of Enzymatically Triggered Peptide Hydrogels
  Guilbaud, J.-B.; Rochas, C.; Miller, A. F.; Saiani, A. *Biomacromolecules* **2013**, *14*, 1403-1411.
  Abstract:



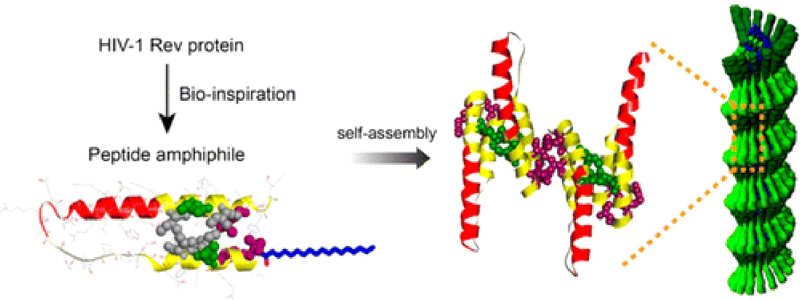
We have recently shown that thermolysine, a protease enzyme obtained from *Bacillus thermoproteolyticus rokko*, can be used to trigger the gelation of FEFK (F, phenylalanine; E, glutamic acid; K, lysine) tetrapeptides through reverse hydrolysis and formation of longer peptide sequences, mainly octapeptides, that self-assemble readily. In this article we investigate the effect of enzyme concentration on the morphology and properties of enzymatically triggered peptide hydrogels using HPLC, FTIR, real-time SAXS, TEM, and shear rheology. We have shown that the enzyme concentration, C_{enz}, does not affect the final composition of the samples. Instead, this is dictated by the initial tetrapeptide concentration, C_0, suggesting the existence of a chemical equilibrium. We went on to show that C_{enz} does not affect the self-assembly of these peptides at a molecular level either nor the structure of the fibrillar network formed at the nanometer scale. Interestingly, the mechanical properties were found to be affected by C_{enz}, where the shear moduli of the hydrogels were found to increase with increasing C_{enz}. These results suggest that morphological differences between the hydrogels at the microscale are at the origin of their difference in mechanical properties. In this paper, we propose a morphological model in which denser network regions are found around the enzymes, resulting in the creation of heterogeneous networks. These were confirmed by TEM measurements. The existence of these denser network regions will result in the reinforcement of the hydrogels, thus, explaining the high shear moduli obtained increasing C_{enz}.

- Polymersomes from Dual Responsive Block Copolymers: Drug Encapsulation by Heating and Acid-Triggered Release
  Qiao, Z.-Y.; Ji, R.; Huang, X.-N.; Du, F.-S.; Zhang, R.; Liang, D.-H.; Li, Z.-C. *Biomacromolecules* **2013**, *14*, 1555-1563.
  Abstract:



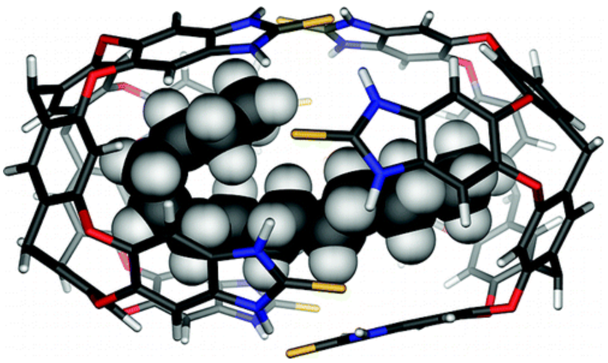
A series of well-defined thermoresponsive diblock copolymers (PEO$_{45}$-*b*-P*t*NEA$_n$, n = 22, 44, 63, 91, 172) were prepared by the atom transfer radical polymerization of *trans-N*-(2-ethoxy-1,3-dioxan-5-yl) acrylamide (*t*NEA) using a poly(ethylene oxide) (PEO$_{45}$) macroinitiator. All copolymers are water-soluble at low temperature, but upon quickly heating to 37 °C, laser light scattering (LLS) and transmission electron microscopy (TEM) characterizations indicate that these copolymers self-assemble into aggregates with different morphologies depending on the chain length of P*t*NEA and the polymer concentration; the morphologies gradually evolved from spherical solid nanoparticles to a polymersome as the degree of polymerization ("*n*") of P*t*NEA block increased from 22 to 172, with the formation of clusters with rod-like structure at the intermediate P*t*NEA length. Both the spherical nanoparticle and the polymersome are stable at physiological pH but susceptible to the mildly acidic medium. Acid-triggered hydrolysis behaviors of the aggregates were investigated by LLS, Nile red fluorescence, TEM, and ^{1}H NMR spectroscopy. The results revealed that the spherical nanoparticles formed from PEO$_{45}$-*b*-P*t*NEA$_{44}$ dissociated faster than the polymersomes of PEO$_{45}$-*b*-P*t*NEA$_{172}$, and both aggregates showed an enhanced hydrolysis under acidic conditions. Both the spherical nanoparticle and polymersome are able to efficiently load the hydrophobic doxorubicin (DOX), and water-soluble fluorescein isothiocyanate-lysozyme (FITC-Lys) can be conveniently encapsulated into the polymersome without using any organic solvent. Moreover, FITC-Lys and DOX could be coloaded in the polymersome. The drugs loaded either in the polymersome or in the spherical nanoparticle could be released by acid triggering. Finally, the DOX-loaded assemblies display concentration-dependent cytotoxicity to HepG2 cells, while the copolymers themselves are nontoxic.

- Bioinspired Self-Assembled Peptide Nanofibers with Thermostable Multivalent α-Helices
  Han, S.-H.; Lee, M.-K.; Lim, Y.-B. *Biomacromolecules* **2013**, *14*, 1594-1599.
  Abstract:



The stabilization of peptide's active conformation is a critical determinant of its target binding efficiency. Here we present a structure-based self-assembly strategy for the design of nanostructures with multiple and thermostable α-helices using bioinspired peptide amphiphiles. The design principle was inspired by the oligomerization of the human immunodeficiency virus type-1 (HIV-1) Rev protein. Our goal was to find a strategy to modify the Rev protein into a chemically manageable self-assembling peptide while stabilizing its α-helical structure. Instead of using cyclic peptides for structure stabilization, this strategy utilizes the pseudocyclization for helix stabilization. The self-assembly induced stabilization of α-helical conformation could be observed, and the α-helices were found to be stable even at high temperature (at least up to 74 °C). Conjugation of a hydrophobic alkyl chain to the Rev peptide was crucial for forming the self-assembled nanostructures, and no nanostructures could be obtained without this modification. Because chemical modifications to the α-helical peptide domain can be avoided, potentially any α-helical peptide fragment can be grafted into this self-assembling peptide scaffold.

- More Chemistry in Small Spaces
  Ajami, D.; Rebek , J. Jr. *Acc. Chem. Res.* **2013**, *46*, 990–999.
  Abstract:



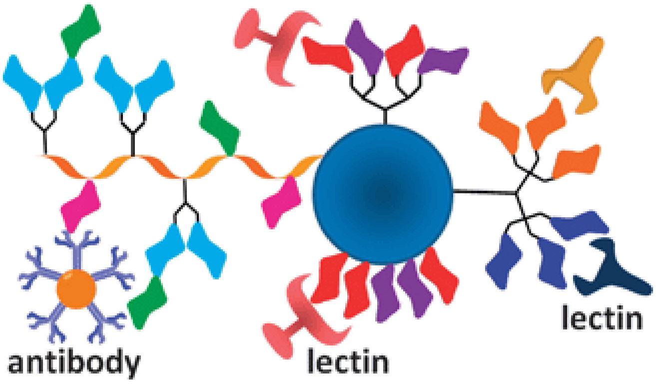
This Account is about coaxing molecules into spaces barely big enough to contain them: encapsulation complexes. In capsules, synthetic modules assemble to fold around their molecular targets, isolate them from the medium for relatively long times, place them in a hydrophobic environment, and present them with functional groups. These arrangements also exist in the interior spaces of biology, and the consequences include the familiar features of enzymes: rapid reactions, stabilization of reactive intermediates, and catalysis. But inside capsules there are phenomena unknown to biology or historical chemistry, including new structures, new stereochemical relationships, and new reaction pathways.

In encapsulation complexes, as in architecture, the space that is created by a structure determines what goes on inside. There are constant interactions between the container and contained molecules: encounters are not left to chance; they are prearranged, prolonged, and intense. Unlike architecture, these reversibly formed containers emerge only when a suitable guest is present. The components exist, but they cannot assemble without anything inside. Modifications of the capsule components give rise to the results of the present Account. The focus will be on how seemingly small changes in the encapsulation complexes, exchanging a C=S for a C=O, reducing an angle here and there, or replacing a hydrogen with a methyl, can lead to unexpectedly large differences in behavior.

- Multivalency in heterogeneous glycoenvironments: hetero-glycoclusters, -glycopolymers and -glycoassemblies

  Jiménez Blanco, J. L.; Ortiz Melleta, C.; García Fernández, J. M. *Chem. Soc. Rev.* **2013**, *42*, 4518–4531.

  Abstract:



Despite efficiently imitating functional ligand presentations in terms of valency and density, most of the reported multivalent carbohydrate prototypes barely reflect the inherent heterogeneity of biological systems, therefore underestimating the potential contribution of synergistic or antagonistic effects to molecular recognition events. To address this question, the design of novel molecular and supramolecular entities displaying different saccharide motifs in a controlled manner is of critical importance. In this review we highlight the current efforts made to synthesize heteromultivalent glycosystems on different platforms (peptides, dendrimers, polymers, oligonucleotides, calixarenes, cyclodextrins, microarrays, vesicles) and to evaluate the influence of heterogeneity in carbohydrate–protein (lectin, antibody) recognition phenomena. Although the number of publications on this topic is limited as compared to the huge volume of reports on homomultivalent sugar displays, the current body of results has already unravelled the existence of new binding mechanisms that operate in heterogeneous environments whose exact biological significance remains to be unveiled.