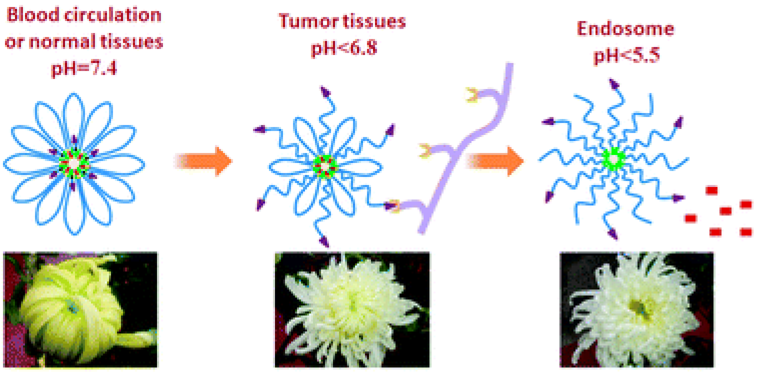
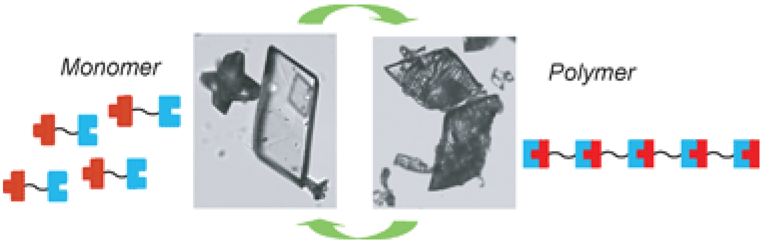
- pH-triggered blooming of ‘nano-flowers’ for tumor intracellular drug delivery
  Yuan, Z.; Que, Z.; Cheng, S.; Zhuo, R.; Li, F. *Chem. Commun.* **2012**, *48*, 8129-8131.
  Abstract:



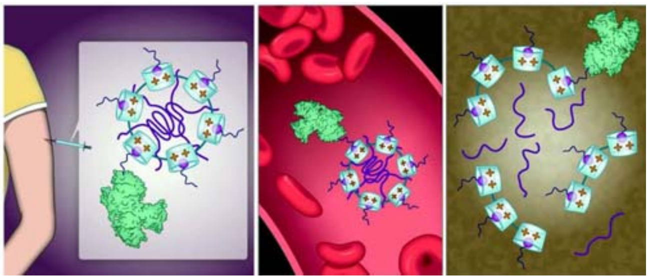
A novel polymeric ‘nano-flower’ showed a pH-triggered blooming behavior in two stages for specific tumor-targeting and drug-release, respectively.

- Topochemical photo-reversible polymerization of a bioinspired monomer and its recovery and repolymerization after photo-depolymerization
  Johnston, P.; Braybrook, C.; Saito, K. *Chem. Sci.* **2012**, *3*, 2301-2306.
  Abstract:



Synthesis of a new cyclobutane polymer by solid-state topochemical polymerization and investigation of its reversible photo-depolymerization.

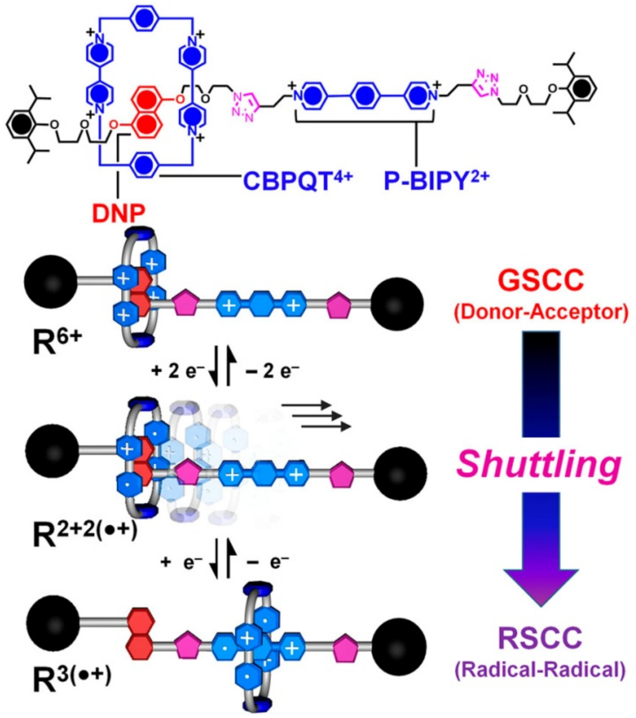
- Nanomaterials for Drug Delivery
  Hubbell, J. A.; Chilkoti, A. *Science* **2012**, *337*, 303-305.
  Abstract:



Nanometer-scale polymeric materials are increasingly used to surmount the barriers faced by drugs and vaccines on their way to their site of action.

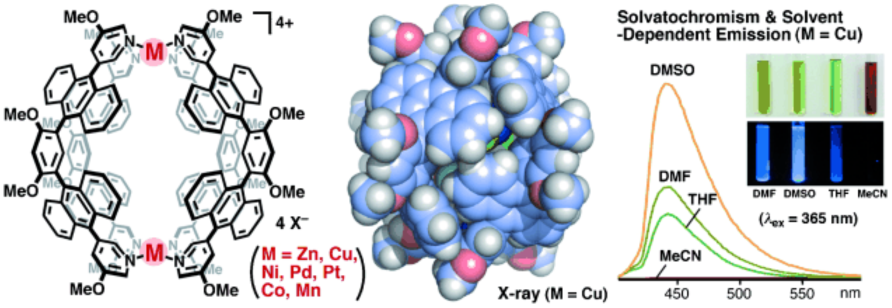
- Mechanically induced intramolecular electron transfer in a mixed-valence molecular shuttle
  Barnes, J. C.; Fahrenbach, A. C.; Dyar, S. M.; Frasconi, M.; Giesener, M. A.; Zhu, Z.; Liu, Z.; Hartlieb, K. J.; Carmieli, R.; Wasielewski, M. R.; Stoddart, J. F. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 11546-11551.

Abstract:



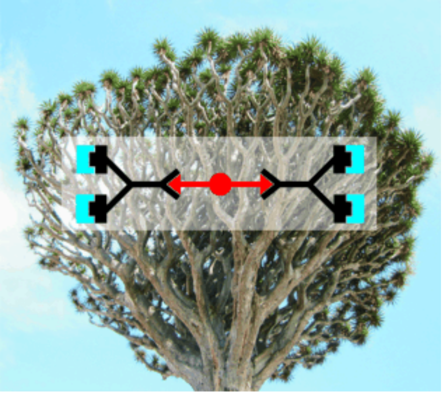
The kinetics and thermodynamics of intramolecular electron transfer (IET) can be subjected to redox control in a bistable [2]rotaxane comprised of a dumbbell component containing an electron-rich 1,5-dioxynaphthalene (DNP) unit and an electron-poor phenylenebridged bipyridinium (P-BIPY^{2+}) unit and a cyclobis (*p*-araquatp-phenylene) (CBPQT^{4+}) ring component. The [2]rotaxane exists in the ground-state co-conformation (GSCC) wherein the CBPQT^{4+} ring encircles the DNP unit. Reduction of the CBPQT^{4+} leads to the CBPQT2$^{(\bullet+)}$ diradical dication while the P-BIPY^{2+} unit is reduced to its P-BIPY$^{\bullet+}$ radical cation. A radical-state co-conformation (RSCC) results from movement of the CBPQT2$^{(\bullet+)}$ ring along the dumbbell to surround the P-BIPY$^{\bullet+}$ unit. This shuttling event induces IET to occur between the pyridinium redox centers of the P-BIPY$^{\bullet+}$ unit, a property which is absent between these redox centers in the free dumbbell and in the 1:1 complex formed between the CBPQT$^{2(\bullet+)}$ ring and the radical cation of methyl-phenylene-viologen (MPV$^{\bullet+}$). Using electron paramagnetic resonance (EPR) spectroscopy, the process of IET was investigated by monitoring the line broadening at varying temperatures and determining the rate constant (k_{ET}=1.33 × 10^{7} s^{-1}) and activation energy ($\Delta G^{\ddagger}$=1.01 kcal mol^{-1}) for electron transfer. These values were compared to the corresponding values predicted, using the optical absorption spectra and Marcus-Hush theory.

- Isostructural M2L4 Molecular Capsules with Anthracene Shells: Synthesis, Crystal Structures, and Fluorescent Properties
  Li, Z.; Kishi, N.; Yoza, K.; Akita, M.; Yoshizawa, M. *Chem. Eur. J.* **2012**, *18*, 8358–8365.
  Abstract:



An isostructural series of M_2L_4 molecular capsules quantitatively self-assembled from two M^{II} ions (M=Zn, Cu, Pt, Pd, Ni, Co, and Mn) and four bent ligands with embedded anthracene fluorophores. X-ray crystallographic analysis (for M=Zn, Cu, Ni, and Pd) confirmed the formation of closed-shell structures in which the large interior cavities inside the molecular capsules (about 1 nm) were shielded by eight anthracene panels. Analysis of the Zn^{II} and Cu^{II} structures showed the inclusion of an unusual triad guest cluster; four MeCN molecules, one water molecule, and one $CF_3SO_3^-$ ion were located inside the cavities. Full characterization by NMR spectroscopy and MS (ESI-TOF) demonstrated that the molecular capsules were quite stable and persist in solution. The fluorescence properties of the isostructural capsules were strongly dependent on the identity of the metal species: the Zn^{II} capsule emitted strong blue fluorescence with a high quantum yield (Φ=0.8), in sharp contrast to the weakly emissive Ni^{II} and Mn^{II} capsules and the completely non-emissive Pd^{II}, Pt^{II}, and Co^{II} capsules. On the other hand, the Cu^{II} capsule exhibited solvatochromism and solvent-dependent emission behavior; blue emission of the capsule was “on” in DMSO but “off” in MeCN.

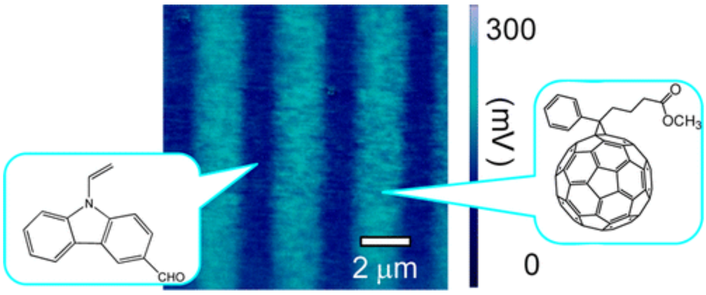
- Second-Generation Supramolecular Dendrimer with a Defined Structure due to Orthogonal Binding
  Eckelmann, J.; Dethlefs, C.; Brammer, S.; Doğan, A.; Uphoff, A.; Lüning, U. *Chem. Eur. J.* **2012**, *18*, 8498–8507.
  Abstract:



A second-generation supramolecular dendrimer has been prepared by orthogonal multiple hydrogen bonding. In the first (inner) recognition domain, the interaction of one bis-isocyanuric acid (**25**) with two branching units (**21**) that carry complementary Hamilton receptors has been exploited. In the second (outer) generation, the two ADDA (A=hydrogen-bond acceptor, D=donor) receptors of each branching unit (**21**) have bound complementary DAAD units (**4**). The problem of limited solubility of the building blocks has been overcome by the introduction of branched ethylhexyl residues and by the use of flexible alkylene or oligo(ethylene glycol) linking chains. The orthogonal binding of the two hydrogen-bonding pairs was elucidated by chemical induced shift NMR titrations, which proved that the two pairs, isocyanuric acid with the Hamilton receptor and ADDA with DAAD, bind preferentially.

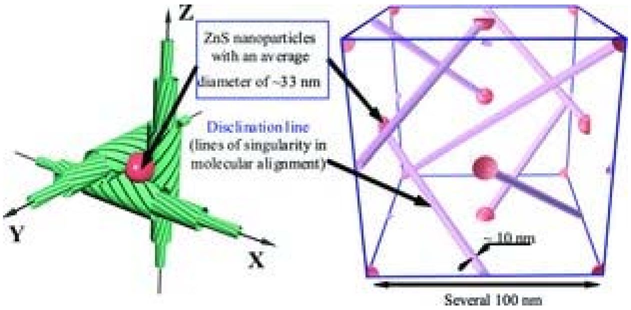
The formation of the supramolecular self-assembled 1:2:4 dendrimer with a molecular weight of 5065 g mol^{-1} was investigated by diffusion NMR spectroscopy.

- Electron Donor and Acceptor Spatial Distribution in Structured Bulk Heterojunction Photovoltaic Devices Induced by Periodic Photopolymerization
  Watanabe, S.; Fukuchi, Y.; Fukasawa, M.; Sassa, T.; Uchiyama, M.; Yamashita, T.; Matsumoto, M.; Aoyama, T. *Langmuir* **2012**, *28*, 10305-10309.
  Abstract:



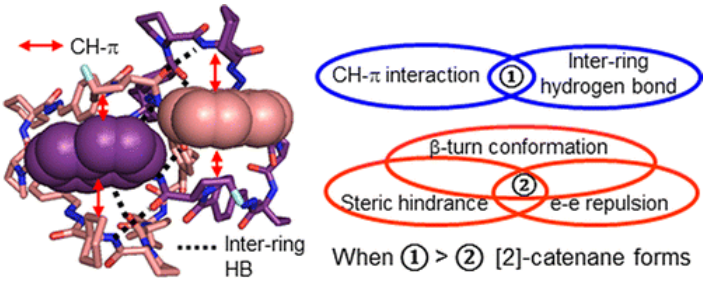
Donor and acceptor spatial distributions were directly formed in a surface relief grating of structured bulk heterojunction (BHJ) photovoltaic devices by simple periodic photopolymerization. Enhanced photocurrents were observed in the structured BHJ photovoltaic devices and formation of the D/A spatial distribution was confirmed by Kelvin probe force microscopy. This technique enables the fabrication of structured BHJ photovoltaic devices with solution-processable organic semiconductors, and has tremendous potential for controlling D/A spatial distribution in organic optoelectronics devices.

- Hysteresis-Free Blue Phase Liquid-Crystal-Stabilized by ZnS Nanoparticles
  Wang, L.; He, W.; Xiao, X.; Meng, F.; Zhang, Y.; Yang, P.; Wang, L.; Xiao, J.; Yang, H.; Lu, Y. *Small* **2012**, *8*, 2189–2193.
  Abstract:



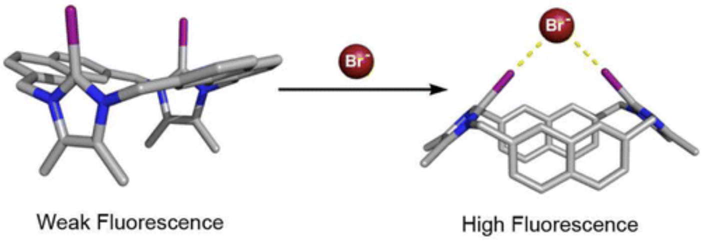
Reversible electro-optical switching is achieved in a facile manner by dispersing a small amount of ZnS nanoparticles into blue phase I (BPI). The hysteresis is so small that it can be considered as hysteresis-free at a 0.5–0.7 wt% doping level, and the on-state voltage is much lower than that of polymer-stabilized BPI.

- Self-Assembled Multi-Component Catenanes: The Effect of Multivalency and Cooperativity on Structure and Stability
  Chung, M.-K.; Lee, S. J.; Waters, M. L.; Gagné, M. R. *J. Am. Chem. Soc.* **2012**, *134*, 11430–11443.
  Abstract:



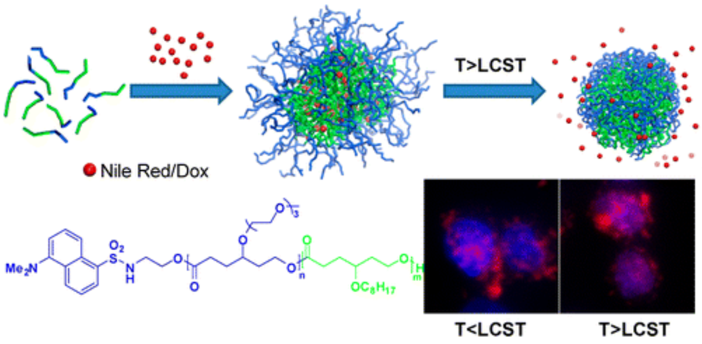
Using dynamic combinatorial chemistry, mixtures of dipeptide monomers were combined to probe how the structural elements of a family of self-assembled [2]-catenanes affect their equilibrium stability versus competing non-catenated structures. Of particular interest were experiments to target the effects of CH−π interactions, inter-ring hydrogen bonds, and β-turn types on [2]-catenane energetics. The non-variant core of the [2]-catenane was shown only to adopt type II′ and type VIII turns at the β-2 and β-4 positions, respectively. Monomers were designed to delineate how these factors contribute to [2]-catenane equilibrium speciation/stability. Dipeptide turn adaptation studies, including three-component dynamic self-assembly experiments, suggested that stability losses are localized to the mutated sites, and that the turn types for the core β-2 and β-4 positions, type II′ and type VIII, respectively, cannot be modified. Mutagenesis studies on the core Aib residue involved in a seemingly key CH−π–CH sandwich reported on how CH−π interactions and inter-ring hydrogen bonds affect stability. The interacting methyl group of Aib could be replaced with a range of alkyl and aryl substituents with monotonic affects on stability, though polar heteroatoms were disproportionately destabilizing. The importance of a key cross-ring H-bond was also probed by examining an Aib for l-Pro variant. Inductive affects and the effect of CH donor multiplicity on the core proline−π interaction also demonstrated that electronegative substituents and the number of CH donors can enhance the effectiveness of a CH−π interaction. These data were interpreted using a cooperative binding model wherein multiple non-covalent interactions create a web of interdependent interactions. In some cases, changes to a component of the web lead to compensating effects in the linked interactions, while in others, the perturbations create a cascade of destabilizing interactions that lead to disproportionate losses in stability.

- Fluorescent Charge-Assisted Halogen-Bonding Macrocyclic Halo-Imidazolium Receptors for Anion Recognition and Sensing in Aqueous Media
  Zapata, F.; Caballero, A.; White, N. G.; Claridge, T. D. W.; Costa, P. J.; Félix, V.; Beer, P. D. *J. Am. Chem. Soc.* **2012**, *134*, 11533–11541.
  Abstract:



The synthesis and anion binding properties of a new family of fluorescent halogen bonding (XB) macrocyclic halo-imidazolium receptors are described. The receptors contain chloro-, bromo-, and iodo-imidazolium motifs incorporated into a cyclic structure using naphthalene spacer groups. The large size of the iodine atom substituents resulted in the isolation of anti and syn conformers of the iodo-imidazoliophane, whereas the chloro- and bromo-imidazoliophane analogues exhibit solution dynamic conformational behavior. The syn iodo-imidazoliophane isomer forms novel dimeric isostructural XB complexes of 2:2 stoichiometry with bromide and iodide anions in the solid state. Solution phase DOSY NMR experiments indicate iodide recognition takes place via cooperative convergent XB–iodide 1:1 stoichiometric binding in aqueous solvent mixtures. ^{1}H NMR and fluorescence spectroscopic titration experiments with a variety of anions in the competitive CD_3OD/D_2O (9:1) aqueous solvent mixture demonstrated the bromo- and syn iodo-imidazoliophane XB receptors to bind selectively iodide and bromide respectively, and sense these halide anions exclusively via a fluorescence response. The protic-, chloro-, and anti iodo-imidazoliophane receptors proved to be ineffectual anion complexants in this aqueous methanolic solvent mixture. Computational DFT and molecular dynamics simulations corroborate the experimental observations that bromo- and syn iodo-imidazoliophane XB receptors form stable cooperative convergent XB associations with bromide and iodide.

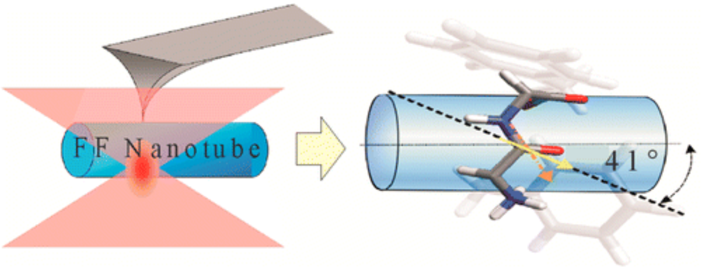
- Thermally Controlled Release of Anticancer Drug from Self-Assembled γ-Substituted Amphiphilic Poly(ε-caprolactone) Micellar Nanoparticles
  Cheng, Y.; Hao, J.; Lee, L. A.; Biewer, M. C.; Wang, Q.; Stefan, M. C. *Biomacromolecules* **2012**, *13*, 2163–2173.
  Abstract:



A thermo-responsive poly{γ-2-[2-(2-methoxyethoxy)ethoxy]ethoxy-ε-caprolactone}-*b*-poly(γ-octyloxy-ε-caprolactone) (**PMEEECL-*b*-POCTCL**) diblock copolymer was synthesized by ring-opening polymerization using tin octanoate ($Sn(Oct)_2$) catalyst and a fluorescent dansyl initiator. The **PMEEECL-*b*-POCTCL** had a lower critical solution temperature (LCST) of 38 °C, and it was employed to prepare thermally responsive micelles. Nile Red and Doxorubicin (DOX) were loaded into the micelles, and the micellar stability and drug carrying ability were investigated. The size and the morphology of the cargo-loaded micelles were determined by DLS, AFM, and TEM. The Nile-Red-loaded polymeric micelles were found to be stable in the presence of both fetal bovine serum and bovine serum albumin over a 72 h period and displayed thermo-responsive in vitro drug release. The blank micelles showed a low cytotoxicity. As comparison, the micelles loaded with DOX showed a much higher in vitro cytotoxicity against MCF-7 human breast cancer cell line when the incubation temperature was elevated above the LCST. Confocal laser scanning microscopy was used to study the cellular uptake and showed that the DOX-loaded micelles were internalized into the cells via an endocytosis pathway.

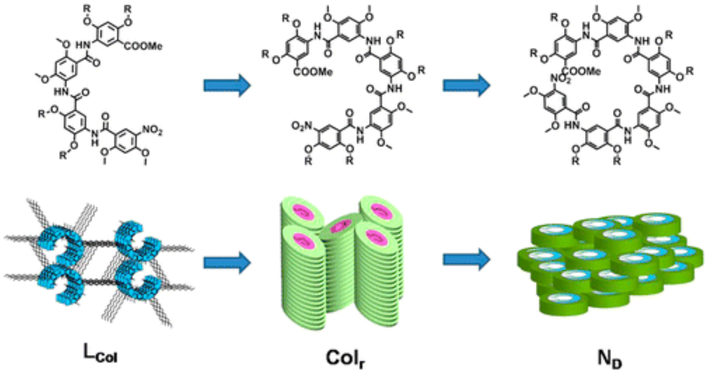
- Investigations of the Supramolecular Structure of Individual Diphenylalanine Nano- and Microtubes by Polarized Raman Microspectroscopy
  Lekprasert, B.; Korolkov, V.; Falamas, A.; Chis, V.; Roberts, C. J.; Tendler, S. J. B.; Notingher, I. *Biomacromolecules* **2012**, *13*, 2181–2187.

Abstract:



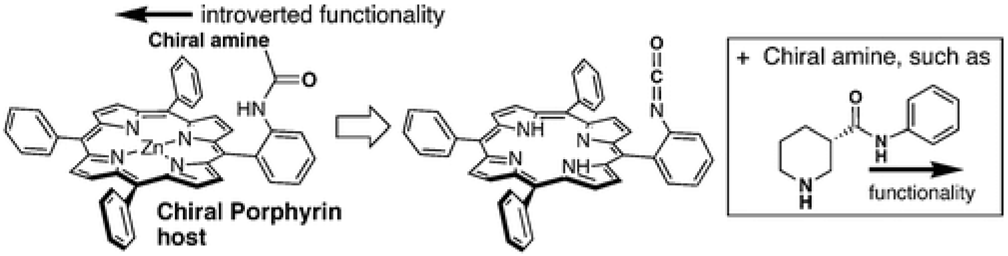
Polarized Raman microspectroscopy and atomic force microscopy were used to obtain quantitative information regarding the molecular structure of individual diphenylalanine (FF) nano- and microtubes. The frequencies of the Raman spectral bands corresponding to the amide I (1690 cm^{-1}) and amide III (1249 cm^{-1}) indicated that the FF-molecules interact by hydrogen bonding at the N–H and not at the C═O sites. The calculated mean orientation angles of the principal axes of the Raman tensors (PARTs) obtained from the polarized Raman spectral measurements were 41 ± 4° for the amide I and 59 ± 5° for amide III. On the basis of the orientation of the PART for the amide I mode, it was found that the C═O bond is oriented at an angle of 8 ± 4° to the tube axis. These values did not vary significantly with the diameter of the tubes (range 400–1700 nm) and were in agreement with the molecular structure proposed previously for larger crystalline specimens.

- Tunable Mesogens Based on Shape-Persistent Aromatic Oligoamides: From Lamellar, Columnar, to Nematic Liquid Crystalline Phase
  Zou, S.; He, L.; Zhang, J.; He, Y.; Yuan, L.; Wu, L.; Luo, J.; Wang, Y.; Feng, W. *Org. Lett.* **2012**, *14*, 3584-3587.
  Abstract:



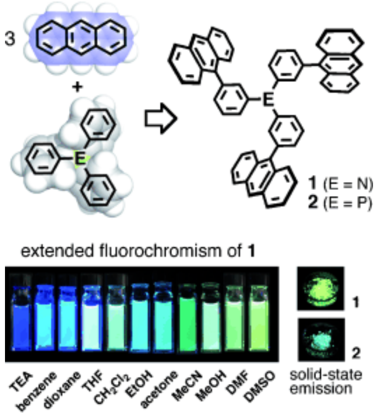
Crescent aromatic oligoamides are shown to form thermotropic lamellar columnar, rectangular columnar, and discotic nematic mesophases according to structural variation, demonstrating their capability to serve as a new class of diverse mesogens of liquid crystals.

- l-Nipecotic Acid-Porphyrin Derivative: A Chiral Host with Introverted Functionality for Chiral Recognition
  Wu, X.; Starnes, S. D. *Org. Lett.* **2012**, *14*, 3652-3655.
  Abstract:



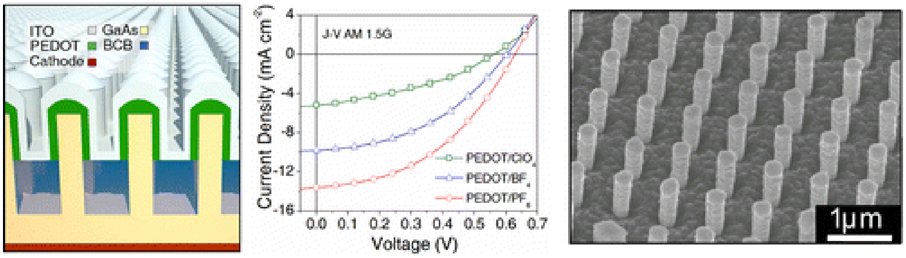
The synthesis and chiral recognition properties of a porphyrin host with introverted functionality is reported. The host is a hybrid of tetraphenyl zinc porphyrin and the *N*-phenylamide derivative of (*S*)-nipecotic acid. The chiral recognition properties of the porphyrin host with chiral carboxylate-containing guests is described. UV/vis and ^{1}H NMR spectroscopic results indicate the host shows enantioselectivity for (*S*)-mandelate tetrabutyl ammonium salt.

- Extended Fluorochromism of Anthracene Trimers with a *meta*-Substituted Triphenylamine or Triphenylphosphine Core
  Li, Z.; Ishizuka, H.; Sei, Y.; Akita, M.; Yoshizawa, M. *Chem. Asian J.* **2012**, *7*, 1789–1794.
  <u>Abstract:</u>



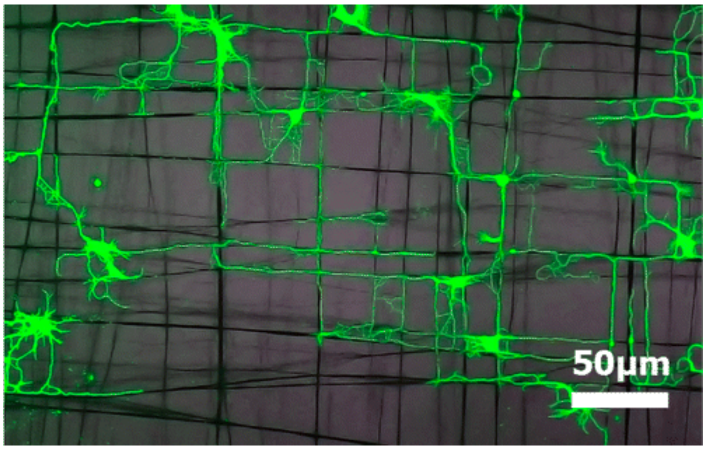
Combining *meta*-triphenylamine or triphenylphosphine with three anthracene fluorophores gives rise to fluorescent non-planar triskelions **1** and **2**. The emissive properties of **1** are highly solvatochromic, yielding blue to pale green and even pale yellow fluorescence, whereas the blue emission of **2** is solvent-insensitive. Anthracene trimers **1** and **2** are both emissive in the solid state, displaying yellow and pale green fluorescence, respectively, with moderate quantum yields.

- Three-Dimensional Core–Shell Hybrid Solar Cells via Controlled in Situ Materials Engineering
  Mariani, G.; Wang, Y.; Wong, P.-S.; Lech, A.; Hung, C.-H.; Shapiro, J.; Prikhodko, S.; El-Kady, M.; Kaner, R. B.; Huffaker, D. L. *Nano Letters* **2012**, *12*, 3581-3586.
  <u>Abstract:</u>



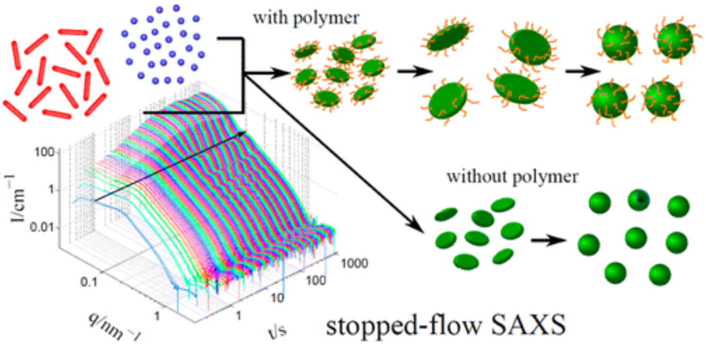
Three-dimensional core–shell organic–inorganic hybrid solar cells with tunable properties are demonstrated via electropolymerization. Air-stable poly(3,4-ethylenedioxythiophene) (PEDOT) shells with controlled thicknesses are rapidly coated onto periodic GaAs nanopillar arrays conformally, preserving the vertical 3D structure. The properties of the organic layer can be readily tuned in situ, allowing for (1) the lowering of the highest occupied molecular orbital level ($|\Delta E|$ ~0.28 eV), leading to the increase of open-circuit voltage (V_{OC}), and (2) an improvement in PEDOT conductivity that results in enhanced short-circuit current densities (J_{SC}). The incorporation of various anionic dopants in the polymer during the coating process also enables the tailoring of the polymer/semiconductor interface transport properties. Systematic tuning of the device properties results in a J_{SC} of 13.6 mA cm^{-2}, V_{OC} of 0.63 V, peak external quantum efficiency of 58.5%, leading to a power conversion efficiencies of 4.11%.

- Directional Neurite Outgrowth on Superaligned Carbon Nanotube Yarn Patterned Substrate
  Fan, L.; Feng, C.; Zhao, W.; Qian, L.; Wang, Y.; Li, Y. *Nano Letters* **2012**, *12*, 3668-3673.
  Abstract:



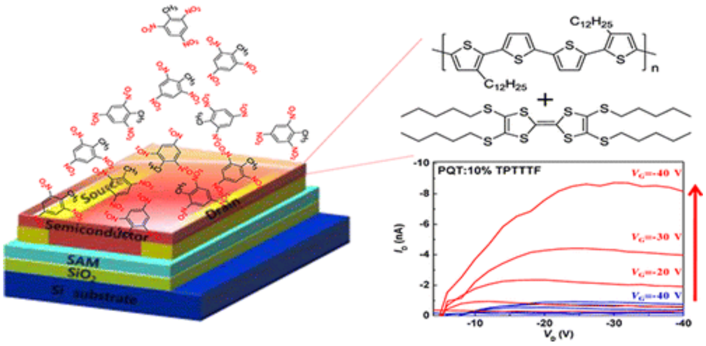
Superaligned carbon nanotube (CNT) yarn patterned substrates were developed as the topographic scaffold for guiding the neurite outgrowth. As-prepared patterned substrates were used for culturing rat hippocampal neurons, without purifying and functionalizing processes on the CNTs. The neurite outgrowth on the patterned substrate exhibited a strong tendency to being aligned along the CNT yarns long axes. The neurite grown along the CNT yarns had much less branching than the one on a uniform planar substrate typically used for neuron culture. These results indicate that the pure CNT yarns possess the main characteristics of a guidance scaffold for neurite outgrowth. Furthermore, the CNT yarns can be mass produced and be easily weaved into desired structures, which may make them attractive for neuronal regeneration and tissue engineering.

- Shaping Vesicles–Controlling Size and Stability by Admixture of Amphiphilic Copolymer
  Bressel, K.; Muthig, M.; Prevost, S.; Gummel, J.; Narayanan, T.; Gradzielski, M. *ACS Nano* **2012**, *6*, 5858-5865.
  Abstract:



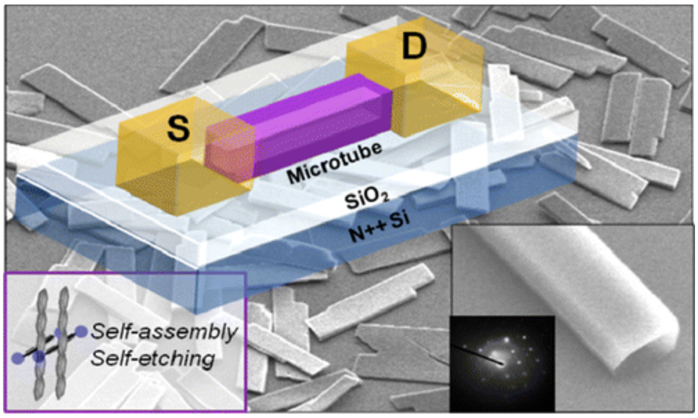
The production of structurally well-defined unilamellar vesicles and the control of their stability are of utmost importance for many of their applications but still a largely unresolved practical issue. In the present work we show that by admixing small amounts of amphiphilic copolymer to the original components of a spontaneously vesicle-forming surfactant mixture we are able to control the self-assembly process in a systematic way. For this purpose we employed a zwitanionic model system of zwitterionic TMDAO and anionic LiPFOS. As the copolymer reduces the line tension of the intermediately formed disks, this translates directly into a longer disk growth phase and formation of correspondingly larger vesicles. By this approach we are able to vary their size over a large range and produce vesicles of extremely low polydispersity. Furthermore, the temporal stability of the formed vesicles is enhanced by orders of magnitude in proportion to the concentration of copolymer added. This is achieved by exerting kinetic control that allows engineering the vesicle structure *via* a detailed knowledge of the formation pathway as obtained by highly time-resolved SAXS experiments. Synthesis of such very well-defined vesicles by the method shown should in general be applicable to catanionic or zwitanionic amphiphiles and will have far reaching consequences for controlled nanostructure formation and application of these self-assembled systems.

- Electrical "Turn-On" Response of Poly(3,3‴-didodecylquaterthiophene) and Electron Donor Blend Transistors to 2,4,6-Trinitrotoluene
  Kong, H.; Jung, B. J.; Sinha, J.; Katz, H. E. *Chem. Mater.* **2012**, *24*, 2621–2623.
  <u>Abstract:</u>



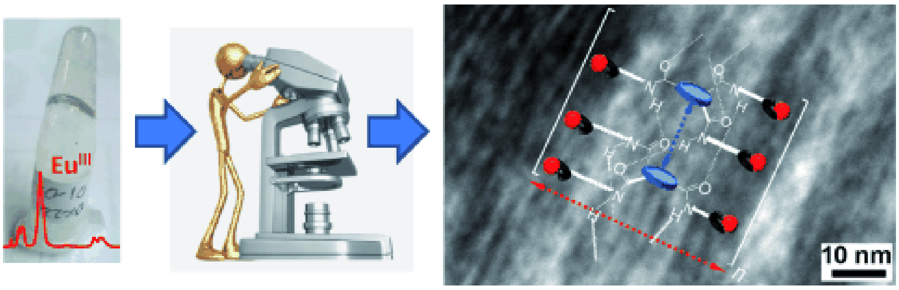
In recent years, research on chemical sensors for the detection of hazardous chemicals has been compelling to improve public safety. Organic field-effect transistor (OFET) based sensors have been proposed and investigated, as OFETs possess advantages of easy tuning of chemical and physical properties, low-cost processing, and mechanical flexibility, and as sensors they offer fast readout on analyte exposure from simple probes and meters. Most OFETs exposed to various nondoping chemical compounds, such as polar solvents including water vapor and nitroaromatic explosive residues, showed decreased output current and mobility. The decreased current levels caused by exposure to the chemical compounds were probably from the local fields around analyte dipoles causing charge trapping at grain boundaries. In the course of the present study, we also found the expected current decrease of poly(3,3‴-didodecyl quaterthiophene) (PQT12) OFETs on exposure to 2,4,6-trinitrotoluene (TNT) explosive. However, for the main experiments of this study, we fabricated blended PQT12 semiconductor with 1 to 20% tetrakis(pentylthio)tetrathiafulvalene (TPT-TTF) as an electron donating/easily oxidized additive. In contrast to pure PQT12 devices, *PQT12:TPT-TTF blend devices exposed to small amounts of TNT analyte showed significant current increase*, which we attribute to complexation between TPT-TTF and TNT. This useful increased current response to TNT exposure of a p-type semiconductor is unusual. For example, we found a 90% PQT12:10% TPT-TTF blend device exposed to 1.9 ng TNT/cm^2 showed eight-fold increased current. *The intentional introduction of trapping subunits, to then be deactivated by an analyte, represents a new electronic sensing mechanism in the field of organic semiconductors.*

- High-Mobility Organic Single-Crystal Microtubes of Soluble Pentacene Semiconductors with Hollow Tetragonal Structures
  Kim, D. H.; Lee, D. Y.; Lee, S. G.; Cho, K. *Chem. Mater.* **2012**, *24*, 2752–2756.
  Abstract:



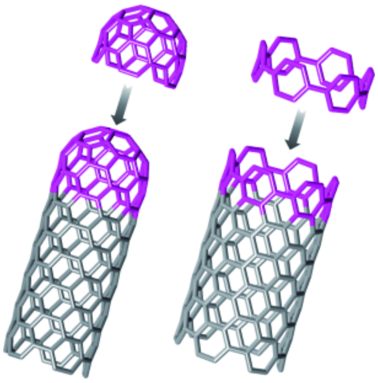
We report a facile but very effective solution phase method for the self-assembly of one-dimensional (1D) single-crystal organic microtubes with hollow tetragonal structures using triisopropylsilylethynyl pentacene (TIPS_PEN). We found that the self-assembled TIPS_PEN microtubes are formed by self-etching of microsolid by residual toluene solvent. The self-etching commences at the ends of the solid rectangular microribbons and then continues toward the interiors along their length axes. The resultant microtubes showed completely well-defined single-crystalline nature. The transistor devices based on individual microtube yielded a high field-effect mobility of 1.73 cm^2/V s and an on/off ratio of $\sim 10^6$, which are among the best values reported up to date for solution-processed micro-TFTs with organic single crystals. We believe that these well-defined microtubular structures of an organic semiconductor will be useful in the fields of p/n heterojunction photovoltaics, optical waveguides, and biological research.

- Europium-Directed Self-Assembly of a Luminescent Supramolecular Gel from a Tripodal Terpyridine-Based Ligand
  Kotova, O.; Daly, R.; dos Santos, C. M. G.; Boese, M.; Kruger, P. E.; Boland, J. J.; Gunnlaugsson, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 7208-7212.
  Abstract:



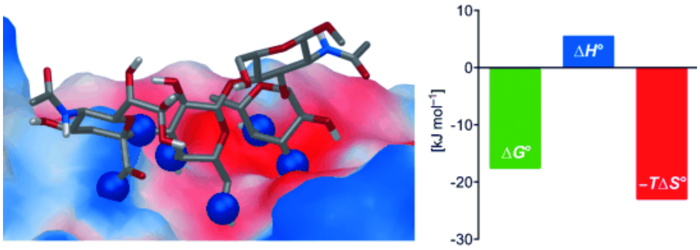
EuIII, the last piece in the puzzle: Europium-induced self-assembly of ligands having a C3-symmetrical benzene-1,3,5-tricarboxamide core results in the formation of luminescent gels. Supramolecular polymers are formed through hydrogen bonding between the ligands. The polymers are then brought together into the gel assembly through the coordination of terpyridine ends by EuIII ions (blue dashed arrow: distance between two ligands in the strand direction).

- para-Connected Cyclophenylenes and Hemispherical Polyarenes: Building Blocks for Single-Walled Carbon Nanotubes?
  Bunz, U. H. F.; Menning, S.; Martín, N. Ang*ew. Chem. Int. Ed.* **2012**, *51*, 7094-7101.
  Abstract:



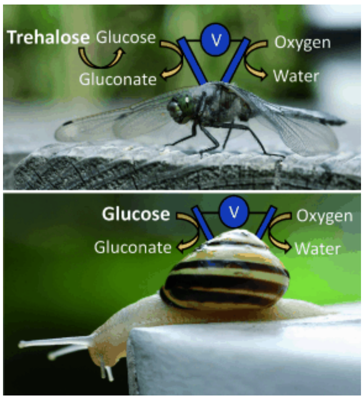
Carbon nanotubes by design? Cyclo-para-phenylenes are monomers for the synthesis of armchair carbon nanotubes (see picture, right), and are also attractive fluorophores that display size-dependent emission properties. Geodesic polyarenes represent a realistic alternative for the rational design of carbon nanotubes through the chemical elongation of the hydrocarbon template (left).

- Sialyl Lewisx: A “Pre-Organized Water Oligomer”?
  Binder, F. P. C.; Lemme, K.; Preston, R. C.; Ernst, B. Ang*ew. Chem. Int. Ed.* **2012**, *51*, 7327-7331.
  Abstract:



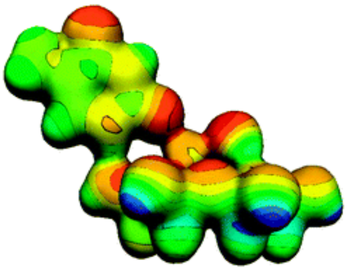
Organized and released: Sialyl Lewisx (sLex) represents a “pre-organized water oligomer”, that is, a surrogate for clustered water molecules attached to a scaffold. The impetus for sLex binding to E-selectin is shown to be the high degree of pre-organization allowing an array of directed hydrogen bonds, and the entropic benefit of the release of water molecules from the large binding interface to bulk water (see picture).

- From In Vitro to In Vivo—Biofuel Cells Are Maturing
  Schröder, U. Angew. *Chem. Int. Ed.* **2012**, *51*, 7370-7372.
  <u>Abstract:</u>



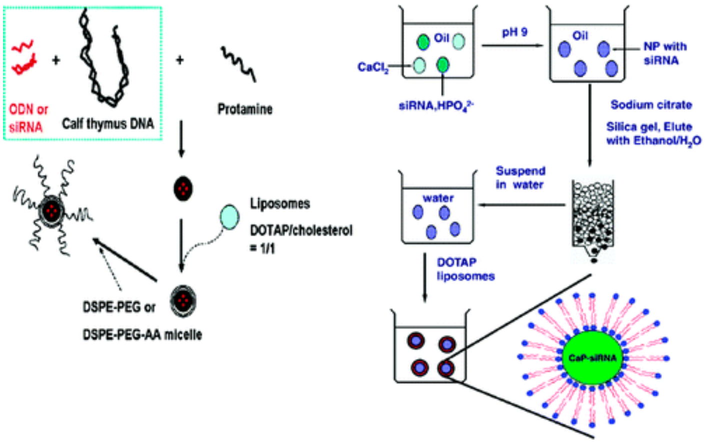
Insects and molluscs as future biological drones for military purposes or environmental monitoring systems (see picture)? Two research groups have demonstrated the successful implantation and operation of biofuel cells in snails, clams, and cockroaches. Owing to their simple circulatory systems, these invertebrates could be used in implantation studies without serious physical damage.

- Mineral–organic interfacial processes: potential roles in the origins of life
  Cleaves II, H. J.; Michalkova Scott, A.; Hill, F. C.; Leszczynski, J.; Sahai, N.; Hazen, R. *Chem. Soc. Rev.* **2012**, *41*, 5502-5525.
  <u>Abstract:</u>



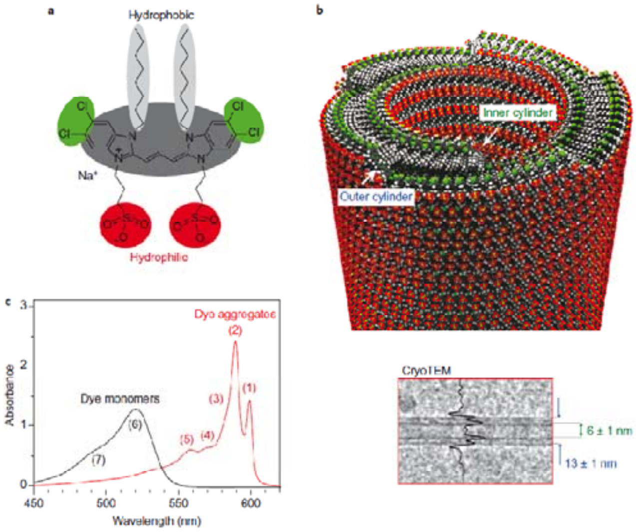
Life is believed to have originated on Earth ~4.4–3.5 Ga ago, *via* processes in which organic compounds supplied by the environment self-organized, in some geochemical environmental niches, into systems capable of replication with hereditary mutation. This process is generally supposed to have occurred in an aqueous environment and, likely, in the presence of minerals. Mineral surfaces present rich opportunities for heterogeneous catalysis and concentration which may have significantly altered and directed the process of prebiotic organic complexification leading to life. We review here general concepts in prebiotic mineral-organic interfacial processes, as well as recent advances in the study of mineral surface-organic interactions of potential relevance to understanding the origin of life.

- Recent Advances in Nonviral Vectors for Gene Delivery
  Guo, X.; Huang, L. *Acc. Chem. Res.* **2012**, *45*, 971–979.
  <u>Abstract:</u>



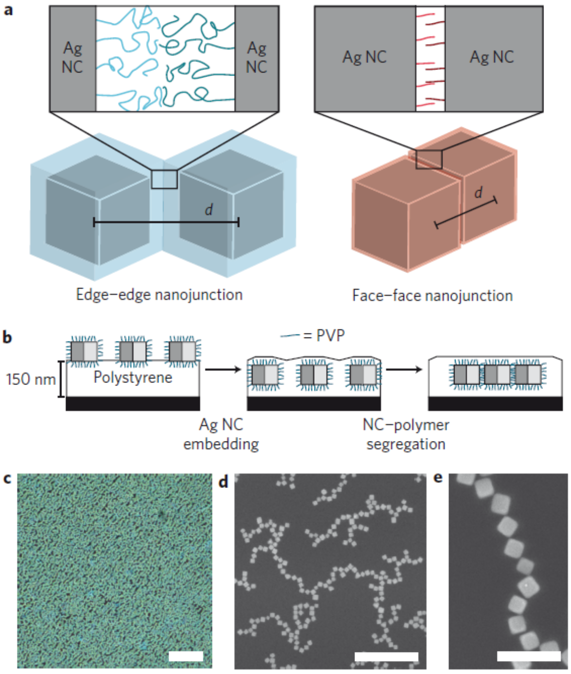
In this Account, we focus on these novel nonviral vectors, which are classified as multifunctional hybrid nucleic acid vectors, novel membrane/core nanoparticles for nucleic acid delivery, and ultrasound-responsive nucleic acid vectors. We highlight systemic delivery studies and consider the future prospects for nucleic acid delivery. A better understanding of the fate of the nanoparticles inside the cell and of the interactions between the parts of hybrid particles should lead to a delivery system suitable for clinical use. We also underscore the value of sustained release of a nucleic acid in this endeavor; making vectors targeted to cells with sustained release *in vivo* should provide an interesting research challenge.

- Utilizing redox-chemistry to elucidate the nature of exciton transitions in supramolecular dye nanotubes
  Eisele, D. M.; Cone, C. W.; Bloemsma, E. A.; Vlaming, S. M.; Van der Kwaak, C. G. F.; Silbey, R. J.; Bawendi, M. G.; Knoester, J.; Rabe, J. P.; Vanden Bout, D. A. *Nature Chemistry* **2012**, *4,* 655–662.
  Abstract:



Supramolecular assemblies that interact with light have recently garnered much interest as well-defined nanoscale materials for electronic excitation energy collection and transport. However, to control such complex systems it is essential to understand how their various parts interact and whether these interactions result in coherently shared excited states (excitons) or in diffusive energy transport between them. Here, we address this by studying a model system consisting of two concentric cylindrical dye aggregates in a light-harvesting nanotube. Through selective chemistry we are able to unambiguously determine the supramolecular origin of the observed excitonic transitions. These results required the development of a new theoretical model of the supramolecular structure of the assembly. Our results demonstrate that the two cylinders of the nanotube have distinct spectral responses and are best described as two separate, weakly coupled excitonic systems. Understanding such interactions is critical to the control of energy transfer on a molecular scale, a goal in various applications ranging from artificial photosynthesis to molecular electronics.

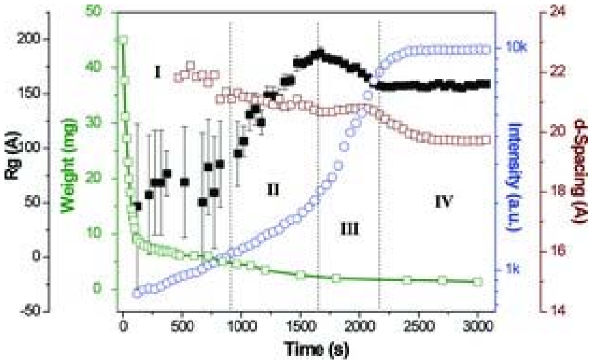
- Self-orienting nanocubes for the assembly of plasmonic nanojunctions
  Gao, B.; Arya, G.; Tao, A. R. *Nature Nanotechnology* **2012,** *7*, 433–437.
  Abstract:



Plasmonic hot spots are formed when metal surfaces with high curvature are separated by nanoscale gaps and an electromagnetic field is localized within the gaps. These hot spots are responsible for phenomena such as subwavelength focusing1, 2, surface-enhanced Raman spectroscopy3 and electromagnetic transparency4, and depend on the geometry of the nanojunctions between the metal surfaces5. Direct-write techniques such as electron-beam lithography can create complex nanostructures with impressive spatial control6 but struggle to fabricate gaps on the order of a few nanometres or manufacture arrays of nanojunctions in a scalable manner. Self-assembly methods, in contrast, can be carried out on a massively parallel scale using metal nanoparticle building blocks of specific shape7, 8. Here, we show that polymer-grafted metal nanocubes can be self-assembled into arrays of one-dimensional strings that have well-defined interparticle orientations and tunable electromagnetic properties. The nanocubes are assembled within a polymer thin film and we observe unique superstructures derived from edge–edge or face–face interactions between the nanocubes. The assembly process is strongly dependent on parameters such as polymer chain length, rigidity or grafting density, and can be predicted by free energy calculations.

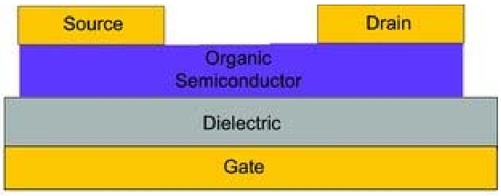
- Efficient Polymer Solar Cells Based on a Low Bandgap Semi-crystalline DPP Polymer-PCBM Blends

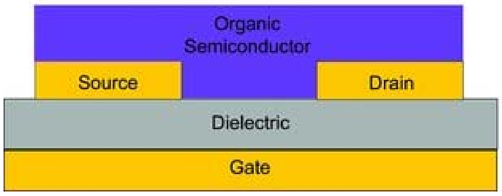
Liu, F.; Gu, Y.; Wang, C.; Zhao, W.; Chen, D.; Briseno, A. L.; Russell, T. P. *Adv. Mater.* **2012**, *24*, 3947–3951.
Abstract:



Solar cell performance and morphology characterization of a diketopyrrolopyrrole-based low bandgap polymer is reported. The polymer adopts an H-type aggregation and solvent mixture processing gives a better morphology. The morphology evolution is characterized by combined GIXD and GISAXS experiments and a four step morphology development mechanism is proposed.

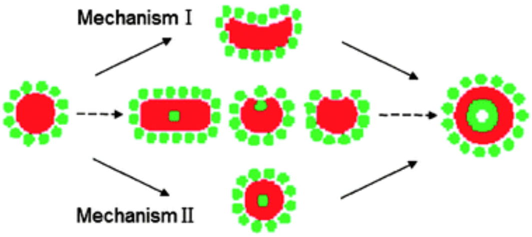
- On the Origin of Contact Resistances of Organic Thin Film Transistors
  Marinkovic, M.; Belaineh, D.; Wagner, V.; Knipp, D. *Adv. Mater.* **2012**, *24*, 4005–4009.
  Abstract:





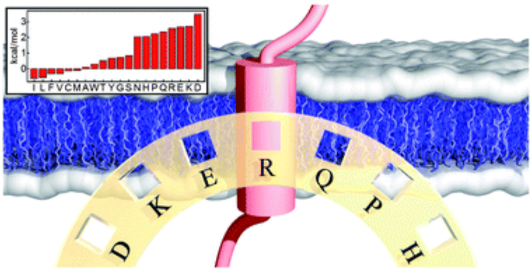
A model is presented that describes the gate-voltage-dependent contact resistance and channel-length-dependent charge carrier mobility of small-molecule-based organic thin-film transistors in top and bottom drain/source contact configuration.

- Controlling the self-assembly pathways of amphiphilic block copolymers into vesicles
  Xiao, M.; Xia, G.; Wang, R.; Xie, D. *Soft Matter* **2012**, *8*, 3865-3874.
  Abstract:



Vesicles and membrane properties play critical roles in reproducing the natural environment of living cells such as nutrient transport and DNA protection. We report how to control the morphology evolutionary stages of the self-assembly of amphiphilic block copolymers composed of hydrophilic–hydrophobic–hydrophilic structure using dissipative particle dynamics method. Two unique intermediate states are obtained by controlling the hydrophobic/hydrophilic block ratio, polymer–solvent interaction, and polymer concentration: (1) bilayer-type membrane such as rod-like, disk-like, or bowl-like micelle (mechanism I), (2) semivesicle originating from the rearranged hydrophilic blocks movement into the center or the trapped hydrophilic blocks during merging (mechanism II). Additionally, during the transition period between these two pathways, vesicles are formed through an in-between pathway. Specifically, instead of the typical mechanism I or mechanism II, hydrophilic blocks gradually diffuse toward the center of some irregular spherical micelles, and then become full vesicles. Most importantly, we show that two factors, the degree of hydrophobicity of the blocks and the probability of the adhesive amphiphile collisions are thought to be of key importance to control the vesicle-formation mechanisms. As a consequence, a crucial balance between the segregation of inner-hydrophobic beads and the attraction of outer-hydrophilic beads drastically affects the self-assembly pathways of amphiphilic block copolymer into vesicles from one mechanism over the other. Furthermore, we demonstrate that when the hydrophilic blocks move toward the center to form a cavity, they can move in randomly and maintain a balanced quantity.

- Assembly and stability of α-helical membrane proteins
  Heyden, M.; Freites, J. A.; Ulmschneider, M. B.; White, S. H.; Tobias, D. J. *Soft Matter* **2012**, *8*, 3742-3752.
  Abstract:



Grease to grease – this is how one might begin to describe the tendency of hydrophobic stretches in protein amino acid sequences to form transmembrane domains. While this simple rule contains a lot of truth, the mechanisms of membrane protein folding, the insertion of hydrophobic protein domains into the lipid bilayer, and the apparent existence of highly polar residues in some proteins in the hydrophobic membrane core are subjects of lively debate – an indication that many details remain unresolved. Here, we present a historical survey of recent insights from experiments and computational studies into the rules and mechanisms of α-helical membrane protein assembly and stability.