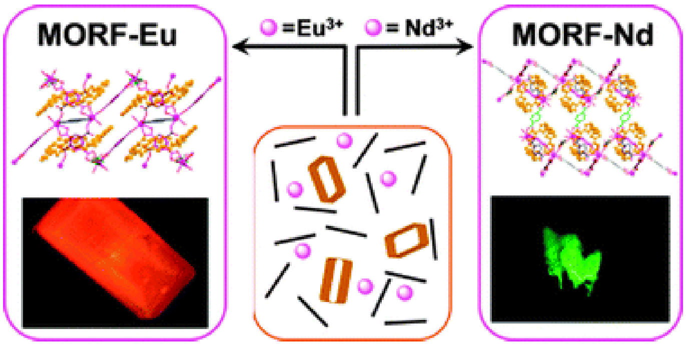
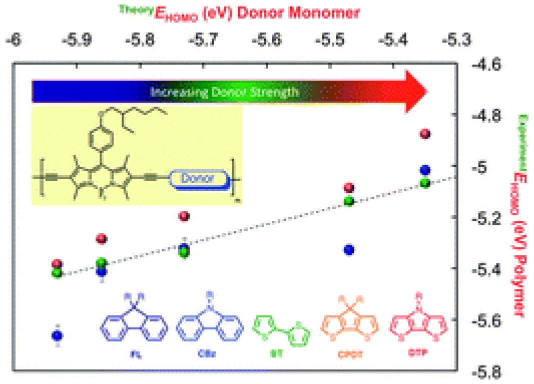
- Rare-earth cation effects on three-dimensional metal–organic rotaxane framework (MORF) self assembly
  Gong, H.-Y.; Rambo, B. M.; Nelson, C. A.; Lynch, V. M.; Zhu, X.; Sessler, J. L. *Chem. Commun.* **2012,** *48,* 10186-10188.
  Abstract:



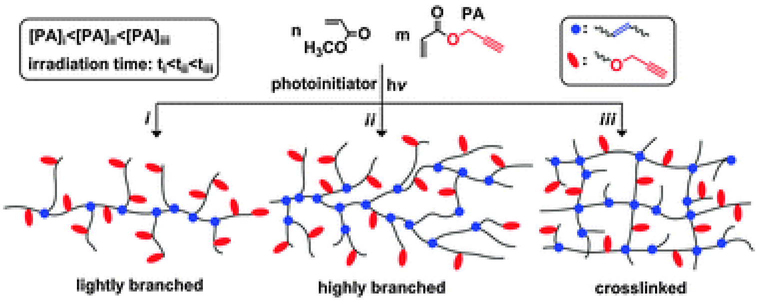
A set of metal–organic rotaxane frameworks (MORFs) are constructed with the use of a tetraimidazolium macrocycle, the terephthalate dianion, and the trivalent lanthanide metal cations Nd(III), Sm(III), Eu(III) or Tb(III) and are reported herein. The specific choice of the metal cation allows for control of the structure and luminescent properties of the resulting molecular frameworks.

- Predictably tuning the frontier molecular orbital energy levels of panchromatic low band gap BODIPY-based conjugated polymers
  Popere, B. C.; Della Pelle, A. M.; Poe, A.; Balaji, G., Thayumanavan, S. *Chem. Sci.* **2012,** *3,* 3093–3102.
  Abstract:



Here we report the synthesis, electrochemical properties, and optical properties of five novel π-conjugated alternating copolymers based on the BODIPY core. These polymers were synthesized *via* the Sonogashira polymerization reaction and contain BODIPY units alternating with comonomers such as 9,9-bis(2-ethylhexyl)-9*H*-fluorene (FL), 9-(2-ethylhexyl)-9*H*-carbazole (CBz), 2,2′-bithiophene (BT), 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene (CPDT) and 4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP). These comonomers were rationally chosen based on their gas phase ionization potential (IP) values estimated by density functional theory (DFT) calculations. Cyclic voltammetry on drop-cast thin films, as well as solutions of these polymers, revealed that the highest occupied molecular orbitals (HOMOs) of the resulting polymers correlated well with the ionization potentials (donor strength) of the comonomers. On the contrary, the lowest unoccupied molecular orbital (LUMO) energy levels of all copolymers were fairly invariant, independent of the comonomer used. This suggests that the BODIPY moiety provides the primary influence on the LUMO levels of the polymer. In addition to the experimentally determined HOMO/LUMO energy levels bearing good correlation with theoretical estimates, all polymers were found to possess broad absorption spectra covering the entire visible range, thus making them truly panchromatic. These polymers provide us with a toolset to tune the frontier molecular orbital energy levels, while retaining the low band gap and broad absorption of these polymers.

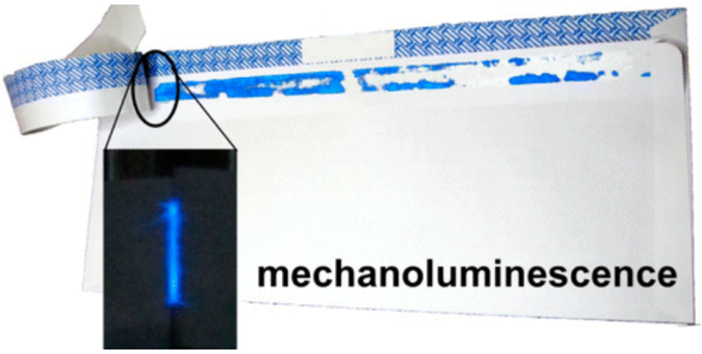
- A simple route to synthesis of branched and cross-linked polymers with clickable moieties by photopolymerization
  Ciftci, M.; U. Kahveci, M.; Yagci, Y.; Allonas, X.; Ley, C.; Tar, H. *Chem. Commun.* **2012**, *48*, 10252-10254.
  Abstract:



Branched and cross-linked polymers with clickable sites were synthesized *via*photoinitiated copolymerization of methyl acrylate (MA) with propargyl acrylate (PA). The method is based on the use of a PA monomer containing two polymerizable groups with different reactivities in photoinitiated free radical copolymerization with MA.

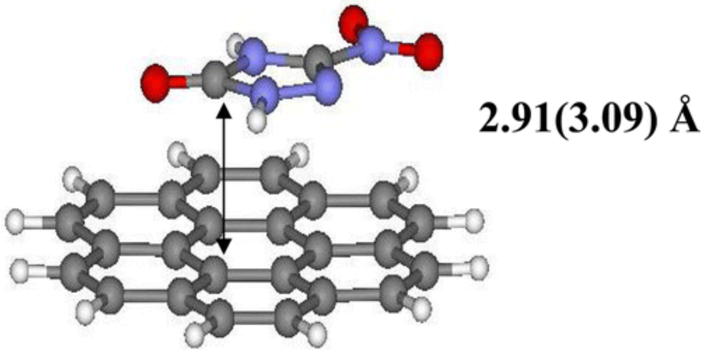
- Interfacial Ion-Transfer Mechanism for the Intense Luminescence Observed When Opening Self-Seal Envelopes

  Alexander, A. J. *Langmuir* **2012**, *28*, 13294-13299.
  Abstract:



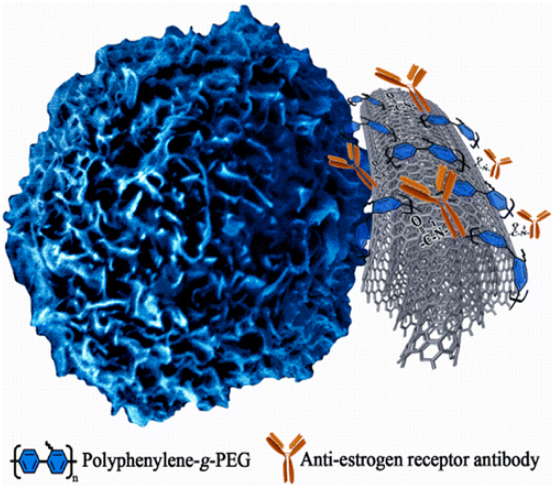
The unusually intense luminescence (commonly called triboluminescence) observed when opening self-seal envelopes has been studied using spectroscopy. Emissions from gas-phase species due to electrical discharge were observed, which in the case of air consists of vibronic transitions of $N_2(C^3\Pi_u–B^3\Pi_g)$ in the ultraviolet (UV) region (280–400 nm). However, the major cause of the intense blue luminescence (around 435 nm) is attributed to optical brightening agents added to the white paper. The results suggest that the emission from the brightening agents may be caused by two mechanisms: (i) fluorescence due to excitation by the UV light from the gas discharge and (ii) nonoptically, by electron transfer. The electrical discharge results from contact electrification; we propose a mechanism for the charge transfer involving a net migration of hydroxide anions out of the paper into the wet latex-adhesive during drying.

- Predictions of Gibbs Free Energies for the Adsorption of Polyaromatic and Nitroaromatic Environmental Contaminants on Carbonaceous Materials: Efficient Computational Approach
  Scott, M.; Gorb, L.; Mobley, E. A.; Hill, F. C.; Leszczynski, J. *Langmuir* **2012**, *28*, 13307-13317.
  Abstract:



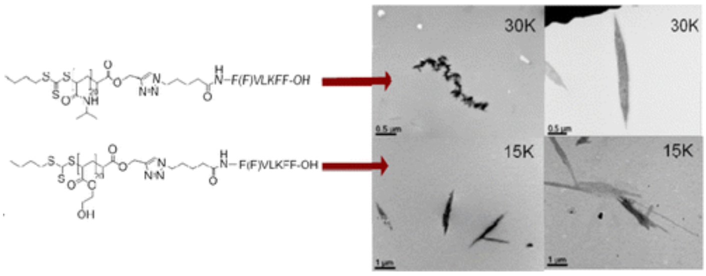
The adsorption of benzene, polycyclic aromatic hydrocarbons (PAHs), and nitroaromatic compounds (NACs) on the carbonaceous surfaces from the gas phase and water solution was investigated. Several different levels of theory were applied, including DFT-, MP2-, and CCSD(T)-based methods, to find an approach that is computationally inexpensive and can provide accurate thermodynamic parameters for studied adsorption phenomena. The methods and techniques used (including cluster and periodic approximations) were evaluated on the basis of comparison with available experimental data. The optimized structures of calculated complexes are obtained, and the interaction energies and Gibbs free energies are predicted. Good agreement was revealed for the theoretical and experimental adsorption energies of benzene and PAHs adsorbed on the carbon surfaces. The adsorption of benzene, PAHs, and NACs on carbon is suggested to be effective from the gas phase for all studied compounds and for PAHs and NACs also from water solution at room temperature.

- Nonionic, Water Self-Dispersible "Hairy-Rod" Poly(p-phenylene)-g-poly(ethylene glycol) Copolymer/Carbon Nanotube Conjugates for Targeted Cell Imaging
  Yuksel, M.; Colak, D. G.; Akin, M.; Cianga, I.; Kukut, M.; Medine, E. I.; Can, M.; Sakarya, S.; Unak, P.; Timur, S.; Yagci, Y. *Biomacromol.* **2012**, *13*, 2680-2691.
  Abstract:



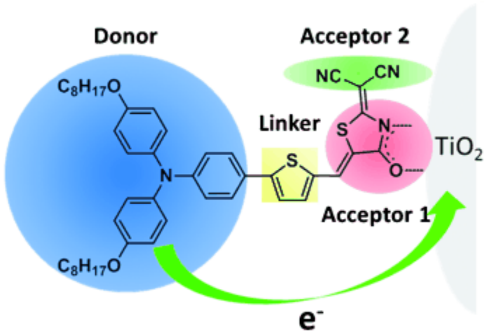
The generation and fabrication of nanoscopic structures are of critical technological importance for future implementations in areas such as nanodevices and nanotechnology, biosensing, bioimaging, cancer targeting, and drug delivery. Applications of carbon nanotubes (CNTs) in biological fields have been impeded by the incapability of their visualization using conventional methods. Therefore, fluorescence labeling of CNTs with various probes under physiological conditions has become a significant issue for their utilization in biological processes. Herein, we demonstrate a facile and additional fluorophore-free approach for cancer cell-imaging and diagnosis by combining multiwalled CNTs with a well-known conjugated polymer, namely, poly(*p*-phenylene) (PP). In this approach, PP decorated with poly(ethylene glycol) (PEG) was noncovalently (π–π stacking) linked to acid-treated CNTs. The obtained water self-dispersible, stable, and biocompatible f-CNT/PP-*g*-PEG conjugates were then bioconjugated to estrogen-specific antibody (anti-ER) via −COOH functionalities present on the side-walls of CNTs. The resulting conjugates were used as an efficient fluorescent probe for targeted imaging of estrogen receptor overexpressed cancer cells, such as MCF-7. In vitro studies and fluorescence microscopy data show that these conjugates can specifically bind to MCF-7 cells with high efficiency. The represented results imply that CNT-based materials could easily be fabricated by the described approach and used as an efficient “fluorescent probe” for targeting and imaging, thereby providing many new possibilities for various applications in biomedical sensing and diagnosis.

- Altering Peptide Fibrillization by Polymer Conjugation
  Dehn, S.; Castelletto, V.; Hamley, I. W.; Perrier, S. *Biomacromol*. **2012**, *13*, 2739-2747.
  Abstract:



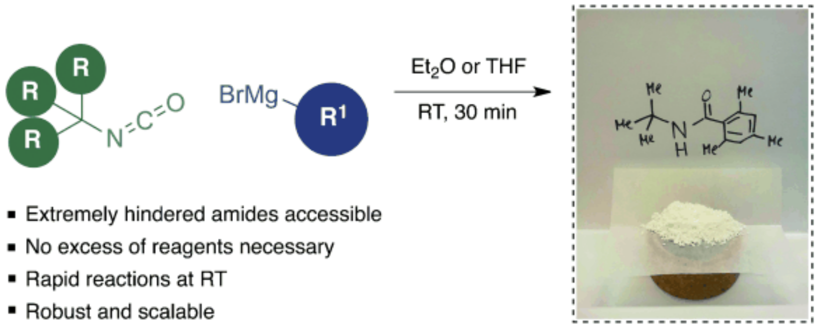
A strategy is presented that exploits the ability of synthetic polymers of different nature to disturb the strong self-assembly capabilities of amyloid based β-sheet forming peptides. Following a convergent approach, the peptides of interest were synthesized via solid-phase peptide synthesis (SPPS) and the polymers via reversible addition–fragmentation chain transfer (RAFT) polymerization, followed by a copper(I) catalyzed azide–alkyne cycloaddition (CuAAC) to generate the desired peptide–polymer conjugates. This study focuses on a modified version of the core sequence of the β-amyloid peptide (Aβ), Aβ(16–20) (KLVFF). The influence of attaching short poly(*N*-isopropylacrylamide) and poly(hydroxyethylacrylate) to the peptide sequences on the self-assembly properties of the hybrid materials were studied via infrared spectroscopy, TEM, circular dichroism and SAXS. The findings indicate that attaching these polymers disturbs the strong self-assembly properties of the biomolecules to a certain degree and permits to influence the aggregation of the peptides based on their β-sheets forming abilities. This study presents an innovative route toward targeted and controlled assembly of amyloid-like fibers to drive the formation of polymeric nanomaterials.

- Stable Dyes Containing Double Acceptors without COOH as Anchors for Highly Efficient Dye-Sensitized Solar Cells
  Mao, J.; He, N.; Ning, Z.; Zhang, Q.; Guo, F.; Chen, L.; Wu, W.; Hua, J.; Tian, H. *Angew. Chem. Int. Ed.* **2012**, 51, 9873-9876.
  <u>Abstract:</u>



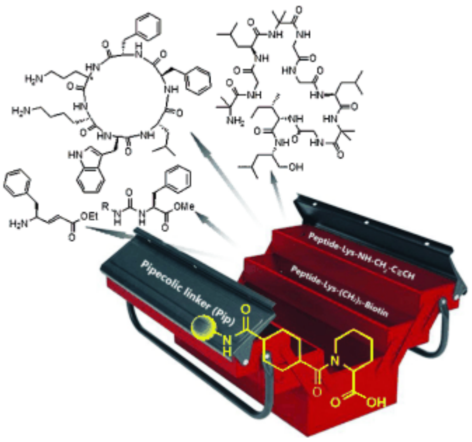
**The electron acceptor** 2-(1,1-dicyanomethylene) rhodanine is a promising alternative to cyanoacrylic acid as an anchoring group for organic dyes. For example, the RD-II-based dye-sensitized solar cell has an overall conversion efficiency of 7.11 % and long-term stability.

- Facile Synthesis of Sterically Hindered and Electron-Deficient Secondary Amides from Isocyanates
  Schäfer, G.; Matthey, C.; Bode, J. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 9173-9175.
  <u>Abstract:</u>



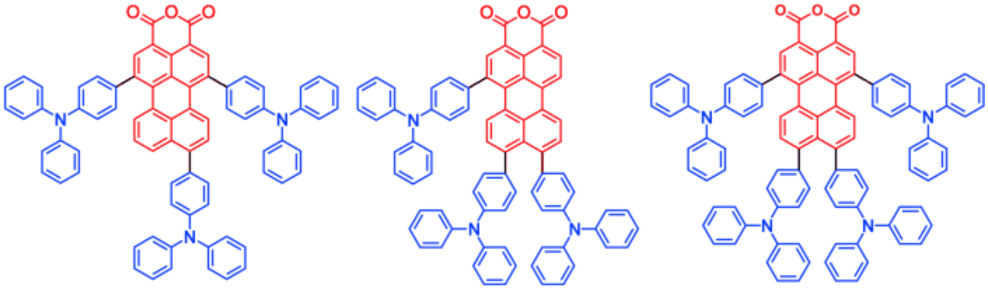
**The big easy:** The direct coupling of Grignard reagents to isocyanates provides a facile and robust solution for the synthesis of sterically hindered and electron-deficient secondary amides. The products are obtained in high yields without the need for excess reagents or chromatographic purification.

- A New Highly Versatile Handle for Chemistry on a Solid Support: The Pipecolic Linker
  Masurier, N.; Zajdel, P.; Verdié, P.; Pawłowski, M.; Amblard, M.; Martinez, J.; Subra, G. *Chem. Eur. J.* **2012**, *18*, 11536–11540.
  <u>Abstract:</u>



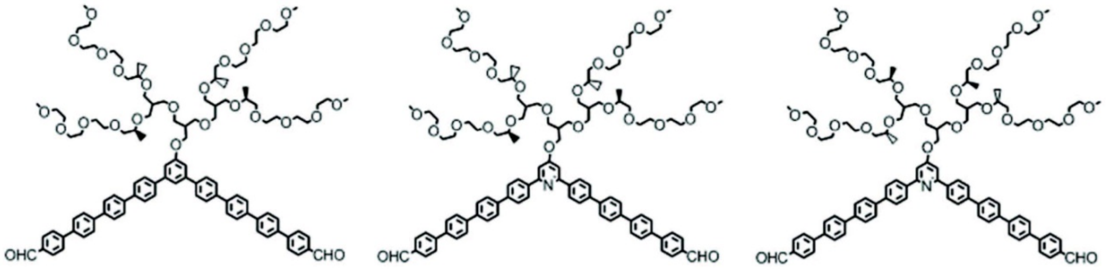
**The versatility of the pipecolic linker** (Pip-linker) is illustrated by the synthesis of modified amino acids, C-terminal-modified pseudopeptides, and cyclic peptides, through side-chain anchoring of a lysine residue (see figure). Introduction of the first residue was easily accomplished and the Pip-linker revealed to be robust enough to support various chemical modifications.

- Synthesis of Perylene Dyes with Multiple Triphenylamine Substituents
  Keerthi, A.; Liu, Y.; Wang, Q.; Valiyaveettil, S. *Chem. Eur. J.* **2012**, *18*, 11669–11676.
  Abstract:



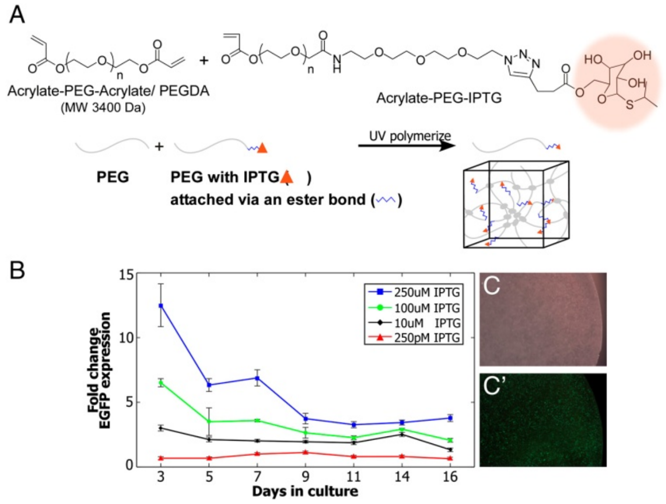
Perylene monoimide (PMI) was brominated to give tetra- and tribrominated molecules, which underwent a Suzuki coupling reaction with 4-(diphenylamino)phenylboronic acid to give PMI derivatives. The photophysical and electrochemical properties of the synthesized compounds were investigated, and theoretical calculations were performed. Single crystals of tetrasubstituted PMI were grown and studied in detail. The structure–property relationships were examined to reveal the effect of the position and number of substituents on the perylene core unit. All molecules showed a broad absorption up to 750 nm. Corresponding anhydrides of PMIs were used for fabrication of dye-sensitized solar cells. The molecule with four triphenylamine units on perylene monoanhydride showed the highest power conversion efficiency.

- Pulsating Tubules from Noncovalent Macrocycles.
  Huang, Z.; Kang, S.-K.; Banno, M.; Yamaguchi, T.; Lee, D.; Seok, C.; Yashima, E.; Lee, M. *Science* **2012**, *337*, 1521-1526.
  Abstract:



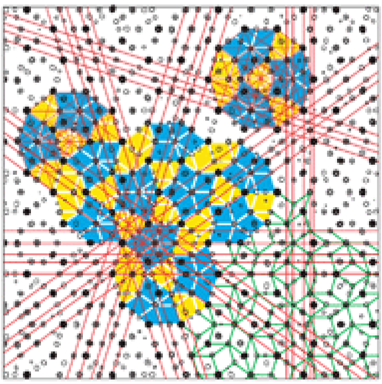
Despite recent advances in synthetic nanometer-scale tubular assembly, conferral of dynamic response characteristics to the tubules remains a challenge. Here, we report on supramolecular nanotubules that undergo a reversible contraction-expansion motion accompanied by an inversion of helical chirality. Bent-shaped aromatic amphiphiles self-assemble into hexameric macrocycles in aqueous solution, forming chiral tubules by spontaneous one-dimensional stacking with a mutual rotation in the same direction. The adjacent aromatic segments within the hexameric macrocycles reversibly slide along one another in response to external triggers, resulting in pulsating motions of the tubules accompanied by a chiral inversion. The aromatic interior of the self-assembled tubules encapsulates hydrophobic guests such as carbon-60 ($C_{60}$). Using a thermal trigger, we could regulate the $C_{60}$-$C_{60}$ interactions through the pulsating motion of the tubules.

- Regulating synthetic gene networks in 3D materials
  Deans, T. L.; Singh, A.; Gibson, M.; Elisseeff, J. H. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 15217-15222.
  Abstract:



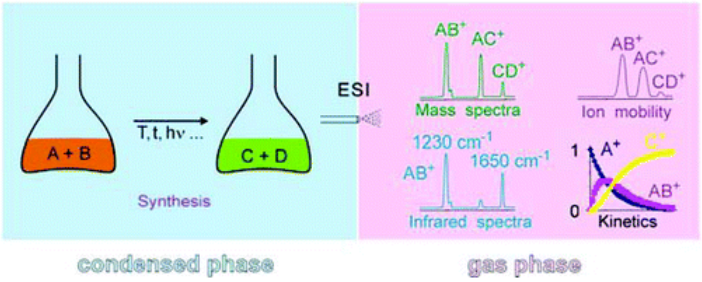
Combining synthetic biology and materials science will enable more advanced studies of cellular regulatory processes, in addition to facilitating therapeutic applications of engineered gene networks. One approach is to couple genetic inducers into biomaterials, thereby generating 3D microenvironments that are capable of controlling intrinsic and extrinsic cellular events. Here, we have engineered biomaterials to present the genetic inducer, IPTG, with different modes of activating genetic circuits in vitro and in vivo. Gene circuits were activated in materials with IPTG embedded within the scaffold walls or chemically linked to the matrix. In addition, systemic applications of IPTG were used to induce genetic circuits in cells encapsulated into materials and implanted in vivo. The flexibility of modifying biomaterials with genetic inducers allows for patterned placement of these inducers that can be used to generate distinct patterns of gene expression. Together, these genetically interactive materials can be used to characterize genetic circuits in environments that more closely mimic cells' natural 3D settings, to better explore complex cell-matrix and cell-cell interactions, and to facilitate therapeutic applications of synthetic biology.

- Why are quasicrystals quasiperiodic?
  Steurer, W. *Chem. Soc. Rev.* **2012**, *41*, 6719-6729.
  Abstract:



In the past two decades significant progress has been made in the search for stable quasicrystals, the determination of their structures and the understanding of their physical properties. Now, quasiperiodic ordering states are not only known for intermetallic compounds, but also for mesoscopic systems such as ABC-star terpolymers, liquid crystals or different kinds of colloids. However, in spite of all these achievements fundamental questions concerning quasicrystal formation, growth and stability are still not fully answered. This *tutorial review* introduces the research in these fields and addresses some of the open questions concerning the origin of quasiperiodicity.

- Applications of Electrospray Ionization Mass Spectrometry in Mechanistic Studies and Catalysis Research
  Schröder, D. *Acc. Chem. Res.* **2012**, *45*, 1521-1532.
  Abstract:

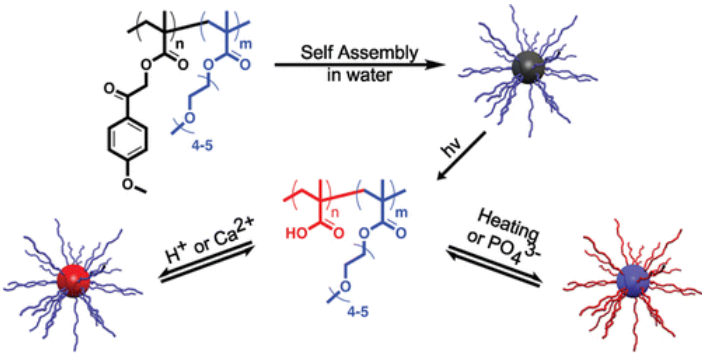


Mechanistic studies form the basis for a better understanding of chemical processes, helping researchers develop more sustainable reactions by increasing the yields of the desired products, reducing waste production, and lowering the consumption of resources and energy overall. Conventional methods for the investigation of reaction mechanisms in solution include kinetic studies, isotope labeling, trapping of reactive intermediates, and advanced spectroscopic techniques. Within the past decade, electrospray ionization mass spectrometry (ESI-MS) has provided an additional tool for mechanistic studies because researchers can directly probe liquid samples by mass spectrometry under gentle conditions.

- Multiresponsive Micellar Systems from Photocleavable Block Copolymers

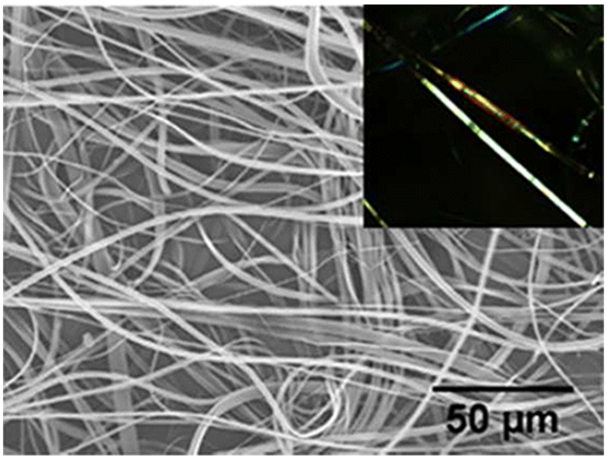
Bertrand, O.; Fustin, C.-A.; Gohy, J.-F. *ACS Macro Lett.* **2012**, *1*, 949–953.

Abstract:



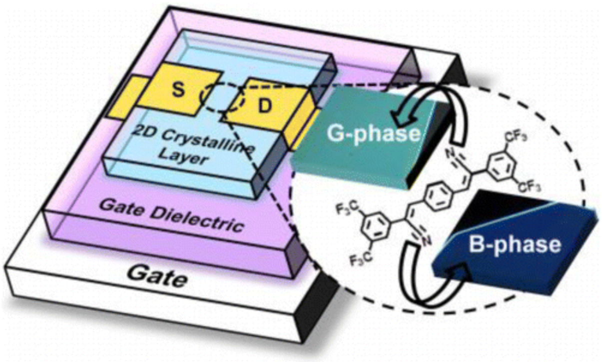
This contribution describes the synthesis and associating behavior in water of a multiresponsive amphiphilic diblock copolymer. This copolymer is composed of an hydrophobic photocleavable poly(*para*-methoxyphenacyl methacrylate) block (PMPMA) and a hydrophilic thermosensitive poly[(oligo ethylene glycol)methacrylate] block (POEGMA). The PMPMA-*b*-POEGMA copolymer forms micelles with a PMPMA core and a POEGMA corona in water. Light irradiation leads to the transformation of PMPMA into poly(methacrylic acid) (PMAA) and to the disruption of the initial micelles. The response of the accordingly obtained PMAA-*b*-POEGMA copolymer to pH, temperature, calcium (Ca$^{2+}$), and phosphate (PO$_4^{3-}$) ions is demonstrated.

- Solventless High Throughput Manufacturing of Poly(butylene terephthalate) Nanofibers
  Shanmuganathan, K.; Fang, Y.; Chou, D. Y.; Sparks, S.; Hibbert, J.; Ellison, C. J. *ACS Macro Lett.* **2012**, *1*, 960–964.
  Abstract:



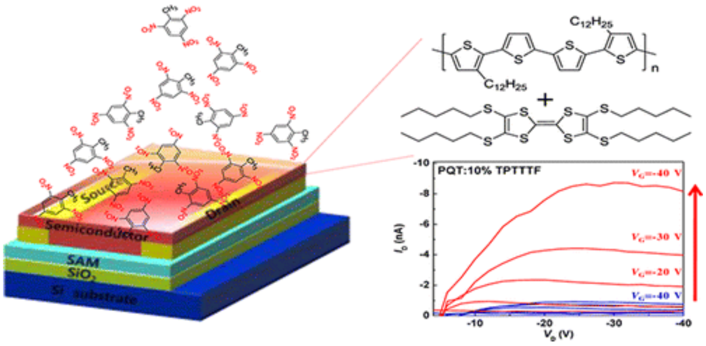
Nanofibers possess high surface area to volume ratios and are particularly attractive for a variety of applications including tissue regeneration, drug delivery, fiber-reinforced composites, filtration, and protective clothing. Though the production of nanofibers from common thermoplastic polymers is relatively well-demonstrated, processing constraints have limited high throughput manufacturing of nanofibers from high performance polymers. This has in turn limited broad technological exploitation of polymer nanofibers in areas such as hot chemical filtration or high-performance lightweight composites for aerospace and defense applications. We report here that nanofibers can be produced in a solventless high throughput process from polymers such as poly(butylene terephthalate) (PBT) using a newly developed technology termed "Forcespinning" that employs centrifugal force to attenuate fibers. Our investigations also show that these nanofibers have a high crystallinity and enhanced molecular orientation which is important for realizing desirable physical and chemical properties of many high-performance polymer fibers.

- High-Performance n-Type Organic Transistor with a Solution-Processed and Exfoliation-Transferred Two-Dimensional Crystalline Layered Film
  Park, S. K.; Kim, J. H.; Yoon, S.-J.; Kwon, O. K.; An, B.-K.; Park, S. Y. *Chem. Mater.* **2012**, *24*, 3263–3268.
  Abstract:



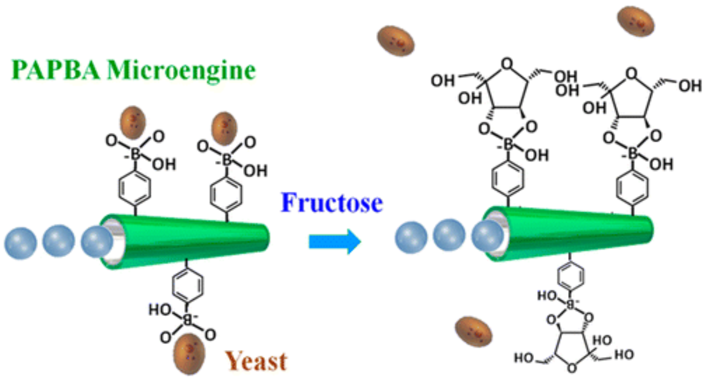
High-performance n-type organic field-effect transistors (OFETs) based on 2-dimensional (2D) crystalline layered films of the novel dicyanodistyrylbenzene (DCS) derivative (2Z,2′Z)-3,3′-(1,4-phenylene)bis(2-(3,5-bis(trifluoromethyl)phenyl)acrylonitrile) (CN-TFPA) were fabricated using a simple solution process. The OFETs showed electron mobilities of up to 0.55 cm2 V–1 s–1, which was attributed to the appropriate electron affinity and dense molecular packing in the well-ordered 2D terrace structure. Because of the easy exfoliation capabilities of the CN-TFPA 2D crystalline layers, 2–10 CN-TFPA molecular monolayers could be successfully transferred onto the substrates, enabling the fabrication of ultrathin OFET devices with an active layer thickness of 30 nm.

- 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.
  Abstract:



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.

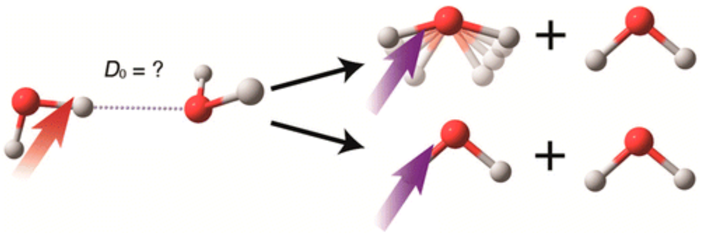
- Self-Propelled Carbohydrate-Sensitive Microtransporters with Built-In Boronic Acid Recognition for Isolating Sugars and Cells
  Kuralay, F.; Sattayasamitsathit, S.; Gao, W.; Uygun, A.; Katzenberg, A.; Wang, J. *J. Am. Chem. Soc.* **2012**, *134*, 15217–15220.
  Abstract:



A new nanomotor-based target isolation strategy, based on a “built-in” recognition capability, is presented. The concept relies on a poly(3-aminophenylboronic acid) (PAPBA)/Ni/Pt microtube engine coupling the selective monosaccharide recognition of the boronic acid-based outer polymeric layer with the catalytic function of the inner platinum layer. The PAPBA-based microrocket is prepared by membrane-templated electropolymerization of 3-aminophenylboronic acid monomer. The resulting boronic acid-based microengine itself provides the target recognition without the need for additional external functionalization. “On-the-fly” binding and transport of yeast cells (containing sugar residues on their wall) and glucose are illustrated. The use of the recognition polymeric layer does not hinder the efficient propulsion of the microengine in aqueous and physiological media. Release of the captured yeast cells is triggered via a competitive sugar binding involving addition of fructose. No such capture and transport are observed in control experiments involving other cells or microengines. Selective isolation of monosaccharides is illustrated using polystyrene particles loaded with different sugars. Such self-propelled nanomachines with a built-in recognition capability hold considerable promise for diverse applications.

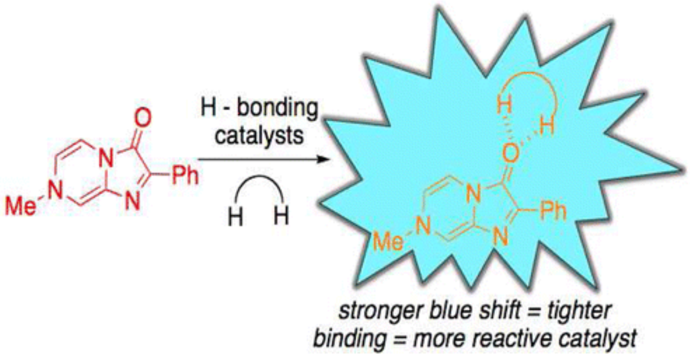
- Experimental and Theoretical Investigations of Energy Transfer and Hydrogen-Bond Breaking in the Water Dimer

Ch’ng, L. C.; Samanta, A. K.; Czakó, G.; Bowman, J. M.; Reisler, H. *J. Am. Chem. Soc.* **2012**, *134*, 15430–15435.
Abstract:



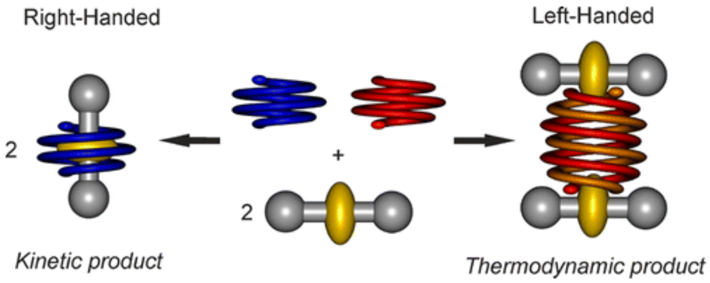
The hydrogen bonding in water is dominated by pairwise dimer interactions, and the predissociation of the water dimer following vibrational excitation is reported here. Velocity map imaging was used for an experimental determination of the dissociation energy (D0) of (D2O)2. The value obtained, 1244 ± 10 cm–1 (14.88 ± 0.12 kJ/mol), is in excellent agreement with the calculated value of 1244 ± 5 cm–1 (14.88 ± 0.06 kJ/mol). This agreement between theory and experiment is as good as the one obtained recently for (H2O)2. In addition, pair-correlated water fragment rovibrational state distributions following vibrational predissociation of (H2O)2 and (D2O)2 were obtained upon excitation of the hydrogen-bonded OH and OD stretch fundamentals, respectively. Quasi-classical trajectory calculations, using an accurate full-dimensional potential energy surface, are in accord with and help to elucidate experiment. Experiment and theory find predominant excitation of the fragment bending mode upon hydrogen bond breaking. A minor channel is also observed in which both fragments are in the ground vibrational state and are highly rotationally excited. The theoretical calculations reveal equal probability of bending excitation in the donor and acceptor subunits, which is a result of interchange of donor and acceptor roles. The rotational distributions associated with the major channel, in which one water fragment has one quantum of bend, and the minor channel with both water fragments in the ground vibrational state are calculated and are in agreement with experiment.

- Rapid Quantification of the Activating Effects of Hydrogen-Bonding Catalysts with a Colorimetric Sensor
  Huynh, P. N. H.; Walvoord, R. R.; Kozlowski, M. C. *J. Am. Chem. Soc.* **2012**, *134*, 15621–15623.
  Abstract:



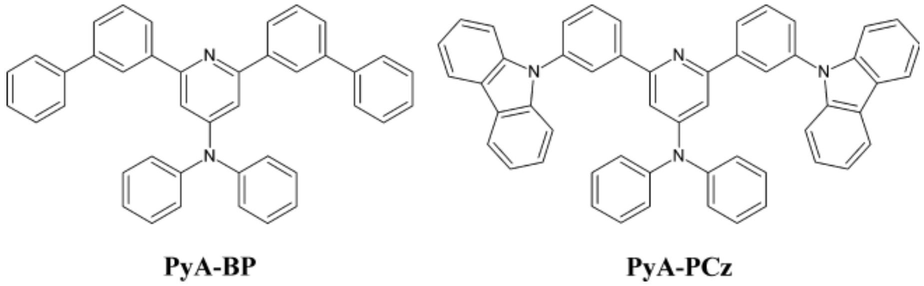
A sensor has been developed to quickly and simply assess the relative reactivity of different hydrogen-bonding catalysts. Specifically, blue-shifts seen upon treatment of H-bonding catalysts with the colorimetric compound 7-methyl-2-phenylimidazo[1,2-a]pyrazin-3(7H)-one correlate well to the $K_{eq}$ of binding to the sensor. The blue-shifts also show a high degree of correlation with relative rates in Diels–Alder reactions of methyl vinyl ketone and cyclopentadiene employing the H-bonding catalysts. The relevance of the sensor blue-shifts to the LUMO-lowering abilities of the H-bonding catalysts is discussed.

- Identification of a Foldaxane Kinetic Byproduct during Guest-Induced Single to Double Helix Conversion
  Gan, Q.; Ferrand, Y.; Chandramouli, N.; Kauffmann, B.; Aube, C.; Dubreuil, D.; Huc, I. *J. Am. Chem. Soc.* **2012**, *134*, 15656–15659.
  Abstract:



An aromatic oligoamide sequence was designed and synthesized to fold in a single helix having a large cavity and to behave as a host for a dumbbell-shaped guest derived from tartaric acid. NMR, molecular modeling, and circular dichroism (CD) evidence demonstrated the rapid formation of this 1:1 host–guest complex and induction of the helix handedness of the host by the guest. This complex was found to be a long-lived kinetic supramolecular byproduct, as it slowly transformed into a 2:2 host–guest complex with two guest molecules bound at the extremities of a double helix formed by the host, as shown by NMR and CD spectroscopy and a solid-state structure. The guest also induced the handedness of the double helical host, but with an opposite bias. The chiroptical properties of the system were thus found to revert with time as the 1:1 complex formed first, followed by the 2:2 complex.

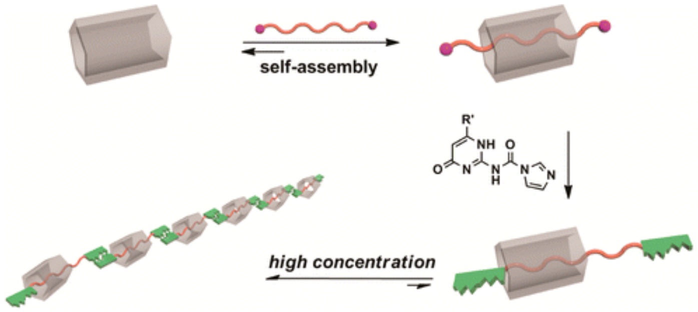
- *N*,*N*-Diphenylpyridin-4-amine as a Bipolar Core Structure of High-Triplet-Energy Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes
  Lee, C. W.; Lee, J. Y. *Chem. Asian J.* **2012**, *7*, 2203–2207.
  Abstract:



**Got the blues**: High-triplet-energy bipolar host materials based on a bipolar *N*,*N*-diphenylpyridin-4-amine (DPPA) core structure were developed for blue phosphorescent organic light-emitting diodes (PHOLEDs). Two DPPA-based host materials (see picture) showed high triplet energy over 2.70 eV and a high quantum efficiency of 15.6 %.

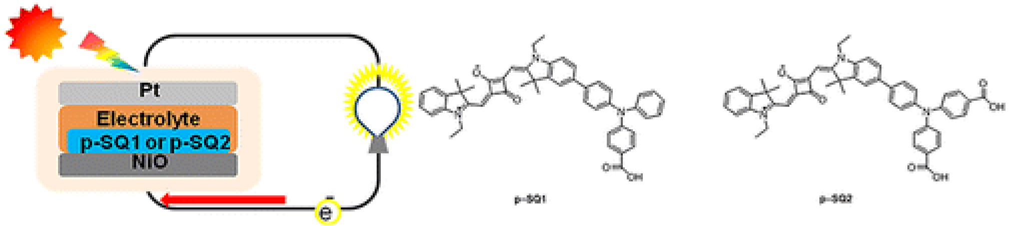
- Novel Pillar[5]arene-Based Dynamic Polyrotaxanes Interlocked by the Quadruple Hydrogen Bonding Ureidopyrimidinone Motif
  Hu, X.-Y.; Wu, X.; Duan, Q.; Xiao, T.; Lin, C.; Wang, L. *Org. Lett.* **2012**, *14*, 4826-4829.

Abstract:



Novel dynamic polyrotaxanes constructed from pillar[5]arenes as wheels and diamines as axles have been successfully synthesized in good yield using quadruple hydrogen bonding ureidopyrimidinone (UPy) motifs, which play a dual role as the end-capping and interlocking units. The present study is the first example of noncovalent bonded dynamic polyrotaxanes constructed by multiple hydrogen bonding interactions.

- Squaraine-Arylamine Sensitizers for Highly Efficient p-Type Dye-Sensitized Solar Cells
  Chang, C.-H.; Chen, Y.-C.; Hsu, C.-Y.; Chou, H.-H.; Lin, J. T. *Org. Lett.* **2012**, *14*, 4726-4729.
  Abstract:

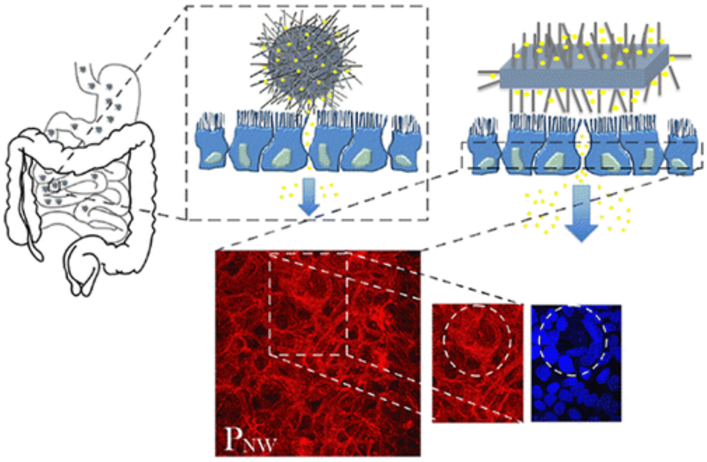


New near-IR (NIR) squaraine dyes (**p-SQ1** and **p-SQ2**) containing one and two anchoring groups were synthesized and used as the sensitizers of p-type DSSCs. The dye (0.113%) with two anchoring groups (**p-SQ2**) shows better performance than the dye (0.053%) with only one anchoring group (**p-SQ1**). Cosensitized p-type DSSCs using two dyes with complementary absorption were tested. They have broadened IPCE spectra and good cell performance.

- Racing with Nature: Artificial Nanomachines That Keep Running on Light, Both Left and Right
  Kopelman, R. *ACS Nano* **2012**, *6*, 7553-7555.
  Abstract:

Nature's molecular motors and nanomachines perform marvelous tasks, especially on the level of single cells. Can artificial ones compete? In this issue, You *et al.* demonstrate a photon-driven molecular machine where switching the color of the light switches the direction of motion of the molecular motor. While having inferior performance characteristics, this novel motor may become the forerunner of a new generation of sophisticated and practical competitors with Nature's ancient, but highly important, nanomachines.

- Shape Effect in the Design of Nanowire-Coated Microparticles as Transepithelial Drug Delivery Devices
  Usković, V.; Lee, K.; Lee, P. P.; Fischer, K. E.; Desai, T. A. *ACS Nano* **2012,** *6*, 7832-7841.
  Abstract:

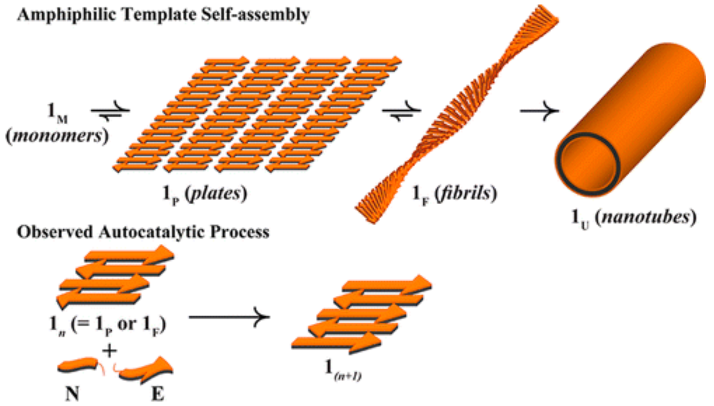


While the oral drug delivery route has traditionally been the most popular among patients, it is estimated that 90% of therapeutic compounds possess oral bioavailability limitations. Thus, the development of novel drug carriers for more effective oral delivery of therapeutics is an important goal. Composite particles made by growing nanoscopic silicon wires from the surface of narrowly dispersed, microsized silica beads were previously shown to be able to (a) adhere well onto the epithelium by interdigitating their nanowires with the apical microvilli and (b) increase the permeability of Caco-2 cell monolayers with respect to small organic molecules in direct proportion to their concentration. A comparison between the effects of spherical and planar particle morphologies on the permeability of the epithelial cell layer *in vitro* and *in vivo* presented the subject of this study. Owing to their larger surface area, the planar particles exhibited a higher drug-loading efficiency than their spherical counterparts, while simultaneously increasing the transepithelial permeation of a moderately sized model drug, insulin. The insulin elution profile for planar nanowire-coated particles displayed a continual increase in the cumulative amount of the released drug, approaching a constant release rate for a 1–4 h period of the elution time. An immunohistochemical study confirmed the ability of planar silica particles coated with nanowires to loosen the tight junction of the epithelial cells to a greater extent than the spherical particles did, thus, enabling a more facile transport of the drug across the epithelium. Transepithelial permeability tests conducted for model drugs ranging in size from 0.4 to 150 kDa yielded three categories of molecules depending on their permeation propensities. Insulin belonged to the category of molecules deliverable across the epithelium only with the assistance of nanowire-coated particles. Other groups of drugs, smaller and bigger, respectively, either did not need the carrier to permeate the epithelium or were not able to cross it even with the support from the nanowire-coated particles. Bioavailability of insulin orally administered to rabbits was also found to be increased when delivered in conjunction with the nanowire-coated planar particles.

- Transient Fibril Structures Facilitating Nonenzymatic Self-Replication

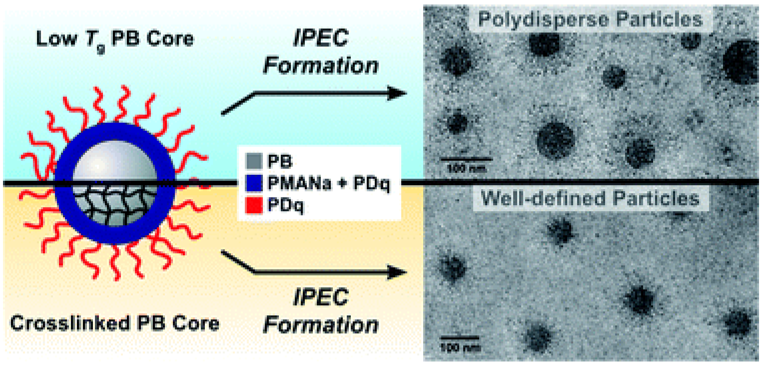
Rubinov, B.; Wagner, N.; Matmor, M.; Regev, O.; Ashkenasy, N.; Ashkenasy, G. *ACS Nano* **2012,** *6*, 7893-7901.

Abstract:



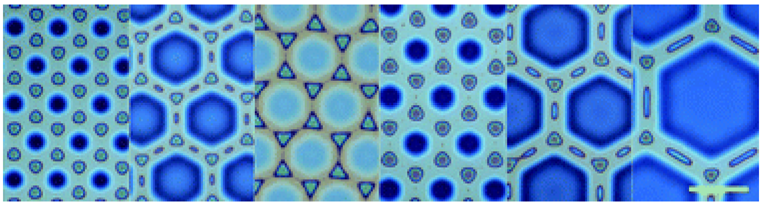
An emerging new direction of research focuses on developing "self-synthesizing materials", those supramolecular structures that can promote their own formation by accelerating the synthesis of building blocks and/or an entire assembly. It was postulated recently that practical design of such systems can benefit from the ability to control the assembly of amphiphilic molecules into nanostructures. We describe here the self-assembly pathway of short amphiphilic peptides into various forms of soluble β-sheet structures—β-plates, fibrils, and hollow nanotubes—and their consequent activity as autocatalysts for the synthesis of monomeric peptides from simpler building blocks. A detailed kinetic analysis of both the self-assembly and self-replication processes allows us to suggest a full model and simulate the replication process, revealing that only specific structures, primarily fibrils that are stable within the solution for a time shorter than a few hours, can be active as catalysts. Interestingly, we have found that such a process also induces fibril reproduction, in a mechanism very similar to the propagation of prion proteins by transmission of misfolded states.

- Stimuli-responsive micellar interpolyelectrolyte complexes – control of micelle dynamics via core crosslinking
  Betthausen, E.; Drechsler, M.; Förtsch, M.; Pergushov, D. V.; Schacher, F. H.; Müller, A. H. E. *Soft Matter* **2012**, *8*, 10167-10177.
  Abstract:



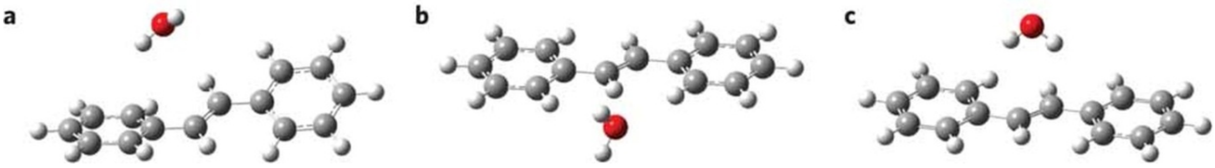
Multi-layered micellar interpolyelectrolyte complexes (IPECs) were built up by the complexation of two oppositely charged homo- or block copolymer systems. First, an ampholytic polybutadiene-*block*-poly(sodium methacrylate)-*block*-poly{2-[(methacryloyloxy)-ethyl]trimethylammonium methylsulfate} (PB-*b*-PMANa-*b*-PDMAEMAq) ABC triblock terpolymer formed stimuli-responsive micelles in a pH 10 aqueous solution with a soft PB core, a PMANa/PDMAEMAq intramicellar IPEC (*im*-IPEC) shell, and a positively charged PDMAEMAq corona. With the addition of either negatively charged homopolymers (poly(sodium 4-styrenesulfonate) (PSSNa)) or bis-hydrophilic block copolymers comprising a neutral segment (poly(sodium acrylate)-*block*-poly(*N*-isopropylacrylamide) (PANa-*b*-PNIPAAm)), a second IPEC shell was formed. The structure of the resulting complex particles at different ratios of oppositely charged segments was investigated using cryogenic transmission electron microscopy (cryo-TEM) and dynamic light scattering (DLS). We show that the initial terpolymer micelles with the *im*-IPEC shell exhibit significant dynamic behavior upon further complexation, resulting in changes in core size distribution and aggregation number. We attribute this to the soft core-forming PB block. Upon crosslinking of the PB core such dynamic processes are suppressed, thus more uniform IPEC particles are formed. We further demonstrate that the PNIPAAm corona formed after complexation with PANa-*b*-PNIPAAm diblock copolymers renders these multicompartment particles thermo-responsive.

- Ordered arrays of polymer droplets with triangular, circular, and rod-like shapes
  Moungthai, S.; Pham, T. C. H.; Rajaendran, A. A.; Stein, G. E. *Soft Matter* **2012**, *8*, 10026-10031.
  Abstract:



We demonstrate that topographically patterned oxide surfaces can direct the dewetting of an overlying polystyrene film and produce triangular, circular, or rod-like droplets. Thin films of polystyrene on oxide surfaces are unstable and will rupture by spinodal dewetting. For our studies, spinodal dewetting is suppressed because the dimensions of oxide patterns are smaller than the dominant instability wavelength. Dewetting is initiated at specific points on the surface by modulating the film curvature, and this drives the formation of unstable polymer rims that break apart into discrete droplets. The symmetry of oxide patterns controls the direction of polymer flow during dewetting, and these dynamics determine the locations and shapes of polymer droplets. Patterns with two-fold symmetry generate drops shaped like rods or bullets, and patterns with three-fold symmetry will produce triangles, distorted circles, or perfect circles.

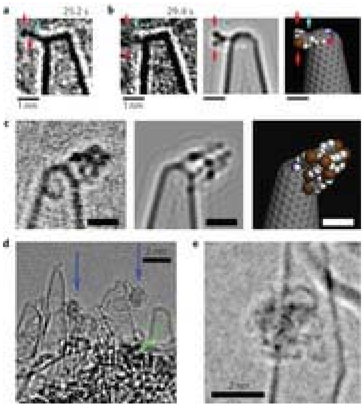
- Unification of trap-limited electron transport in semiconducting polymers
  Nicolai, H. T.; Kuik, M.; Wetzelaer, G. A. H.; de Boer, B.; Campbell, C.; Risko, C.; Brédas, J. L.; Blom, P. W. M. *Nature Mater.* **2012**, *11*, 882–887.
  Abstract:



Electron transport in semiconducting polymers is usually inferior to hole transport, which is ascribed to charge trapping on isolated defect sites situated within the energy bandgap. However, a general understanding of the origin of these omnipresent charge traps, as well as their energetic position, distribution and concentration, is lacking. Here we investigate electron transport in a wide range of

semiconducting polymers by current–voltage measurements of single-carrier devices. We observe for this materials class that electron transport is limited by traps that exhibit a Gaussian energy distribution in the bandgap. Remarkably, the electron-trap distribution is identical for all polymers considered: the number of traps amounts to $3 \times 10^{23}$ traps per $m^3$ centred at an energy of ~3.6 eV below the vacuum level, with a typical distribution width of ~0.1 eV. This indicates that the electron traps have a common origin that, we suggest, is most likely related to hydrated oxygen complexes. A consequence of this finding is that the trap-limited electron current can be predicted for any polymer.

- Heterogeneous nucleation of organic crystals mediated by single-molecule templates
  Harano, K.; Homma, T.; Niimi, Y.; Koshino, M.; Suenaga, K.; Leibler, L.; Nakamura, E. *Nature Mater.* **2012**, *11,* 877–881.
  Abstract:



Fundamental understanding of how crystals of organic molecules nucleate on a surface remains limited because of the difficulty of probing rare events at the molecular scale. Here we show that single-molecule templates on the surface of carbon nanohorns can nucleate the crystallization of two organic compounds from a supersaturated solution by mediating the formation of disordered and mobile molecular nanoclusters on the templates. Single-molecule real-time transmission electron microscopy indicates that each nanocluster consists of a maximum of approximately 15 molecules, that there are fewer nanoclusters than crystals in solution, and that in the absence of templates physisorption, but not crystal formation, occurs. Our findings suggest that template-induced heterogeneous nucleation mechanistically resembles two-step homogeneous nucleation.