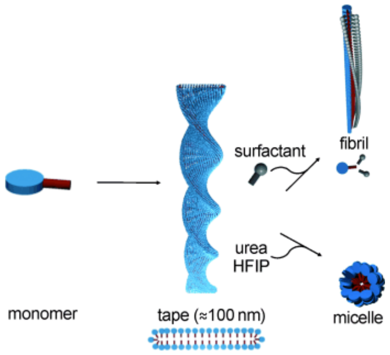
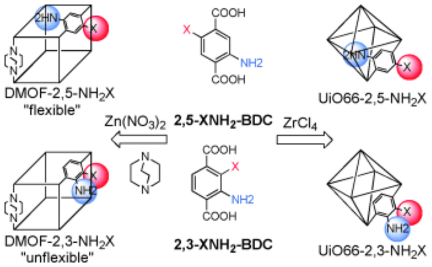
- Programmed Morphological Transitions of Multisegment Assemblies by Molecular Chaperone Analogues
  Boekhoven, J.; Brizard, A. M.; Rijn, P.; Stuart, M. C. A.; Eelkema, R.; Esch, J. H. *Angew. Chem, Int. Ed.* **2011**, *50,* 12285–12289.
  Abstract:



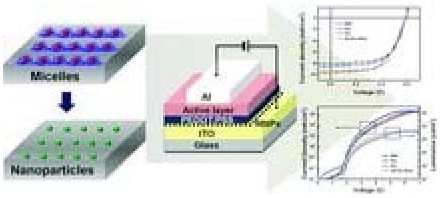
A multisegment amphiphile, made of a gelator and a surfactant, self-assembles into architectures with properties inherited from both segments. By addition of a surfactant, the surfactant segment of the amphiphile is selectively switched off, leading to the formation of fibrils. The addition of urea or hexafluoroisopropyl alcohol (HFIP) switches off the gelator segment, giving micelles.

- Metal–Organic Framework Regioisomers Based on Bifunctional Ligands
  Kim, M.; Boissonnault, A.; Dau, V.; Cohen, S. M. *Angew. Chem. Int. Ed.* **2011**, *50,* 12193–12196.
  Abstract:



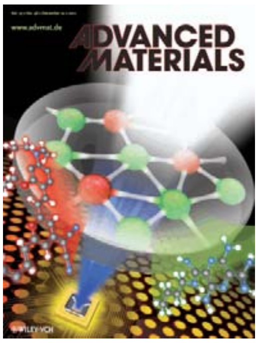
Regioisomeric MOFs: A series of bifunctional metal–organic framework (MOF) regioisomers has been produced from amino-halo benzene dicarboxylate (NH2X-BDC) ligands. ZrIV- and ZnII-based MOFs were synthesized and for the flexbile ZnII-based MOFs, gas sorption properties were dependent on the ligand substitution pattern.

- High-Performance Organic Optoelectronic Devices Enhanced by Surface Plasmon Resonance
  Heo, M.; Cho, H.; Jung, J. W.; Jeong, J. R.; Park, S.; Kim J. Y. *Adv. Mater.* **2011,** *23,* 5689–5693.
  Abstract:



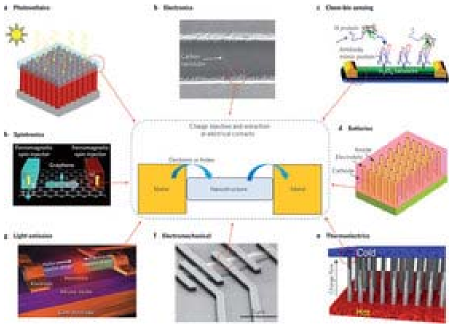
The surface plasmon effect on polymer solar cells and polymer light-emitting diodes is demonstrated by using metal nanoparticles prepared from block copolymer templates. Light absorption of the polymer thin layer is increased with the incorporation of metallic nanostructures, resulting in a significant surface plasmon effect in the optoelectronic devices.

- Practical Roadmap and Limits to Nanostructured Photovoltaics
  Lunt, R. R.; Osedach, T. P.; Brown, P. R.; Rowehl, J. A.; Bulović, V. *Adv. Mater.* **2011**, *23*, 5712–5727.
  Abstract:



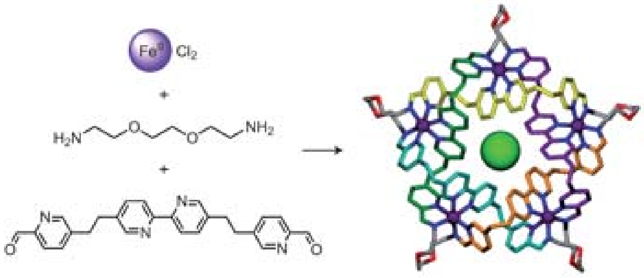
The significant research interest in the engineering of photovoltaic (PV) structures at the nanoscale is directed toward enabling reductions in PV module fabrication and installation costs as well as improving cell power conversion efficiency (PCE). With the emergence of a multitude of nanostructured photovoltaic (nano-PV) device architectures, the question has arisen of where both the practical and the fundamental limits of performance reside in these new systems. Here, the former is addressed a posteriori. The specific challenges associated with improving the electrical power conversion efficiency of various nano-PV technologies are discussed and several approaches to reduce their thermal losses beyond the single bandgap limit are reviewed. Critical considerations related to the module lifetime and cost that are unique to nano-PV architectures are also addressed. The analysis suggests that a practical single-junction laboratory power conversion efficiency limit of 17% and a two-cell tandem power conversion efficiency limit of 24% are possible for nano-PVs, which, when combined with operating lifetimes of 10 to 15 years, could position them as a transformational technology for solar energy markets.

- Electrical contacts to one- and two-dimensional nanomaterials
  Léonard, F.; Talin, A. A. *Nature Nanotech.* **2011**, *6*, 773-783.
  Abstract:



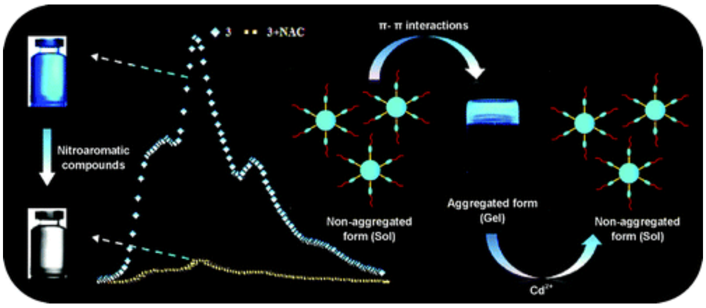
Existing models of electrical contacts are often inapplicable at the nanoscale because there are significant differences between nanostructures and bulk materials arising from unique geometries and electrostatics. In this Review, we discuss the physics and materials science of electrical contacts to carbon nanotubes, semiconductor nanowires and graphene, and outline the main research and development challenges in the field. We also include a case study of gold contacts to germanium nanowires to illustrate these concepts.

- A synthetic molecular pentafoil knot
  Ayme, J. F.; Beves, J. E.; Leigh, D. A.; McBurney, R. T.; Rissanen, K.; Schultz, D. *Nature Chem*. **2012**, *4*, 15–20.
  Abstract:



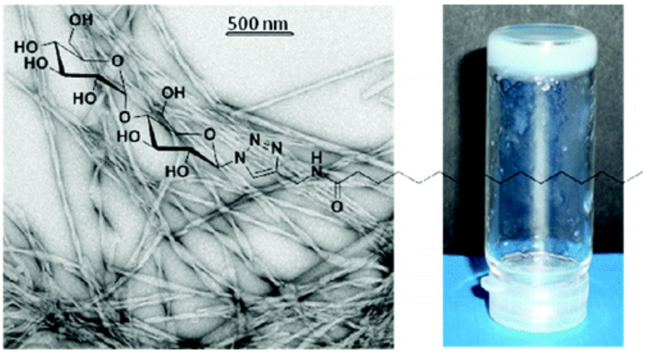
Knots are being discovered with increasing frequency in both biological and synthetic macromolecules and have been fundamental topological targets for chemical synthesis for the past two decades. Here, we report on the synthesis of the most complex non-DNA molecular knot prepared to date: the self-assembly of five bis-aldehyde and five bis-amine building blocks about five metal cations and one chloride anion to form a 160-atom-loop molecular pentafoil knot (five crossing points). The structure and topology of the knot is established by NMR spectroscopy, mass spectrometry and X-ray crystallography, revealing a symmetrical closed-loop double helicate with the chloride anion held at the centre of the pentafoil knot by ten CH···Cl$^-$ hydrogen bonds. The one-pot self-assembly reaction features an exceptional number of different design elements—some well precedented and others less well known within the context of directing the formation of (supra)molecular species. We anticipate that the strategies and tactics used here can be applied to the rational synthesis of other higher-order interlocked molecular architectures.

- Triazole-Modified Triphenylene Derivative: Self-Assembly and Sensing Applications
  Bhalla, V.; Singh, H.; Kumar, M.; Prasad, S. K. *Langmuir* **2011**, *27*, 15275-15281.
  Abstract:



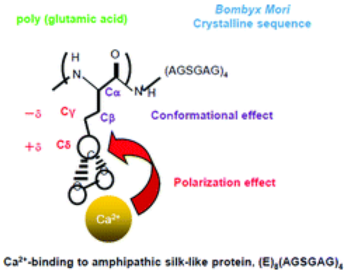
Triphenylene-based discotic liquid crystal **3** bearing 1,2,3-triazole groups has been synthesized using “click” chemistry. Discotic mesogen **3** has good thermal stability, and incorporation of triazole groups results in stabilization of columnar mesophases down to room temperature and formation of organogels in cyclohexane and mixed solvents such as hexane and dichloromethane (4:1 v/v). Characterization of the organogel of **3** in cyclohexane revealed a porous network. However, presence of Cd^{2+} ions in solution obstructed the self-assembly of this derivative due to preferred interactions between Cd^{2+} ions and triphenylene units over π–π interactions among triphenylene groups. Further, strong emission of derivative **3** in its nonaggregated form makes it a promising fluorescence sensory material for nitroaromatic compounds.

- Synthesis and Characterization of Maltose-Based Amphiphiles as Supramolecular Hydrogelators
  Clemente, M. J.; Fitremann, J.; Mauzac, M.; Serrano, J. L.; Oriol, L. *Langmuir* **2011**, *27*, 15236-15247.
  Abstract:



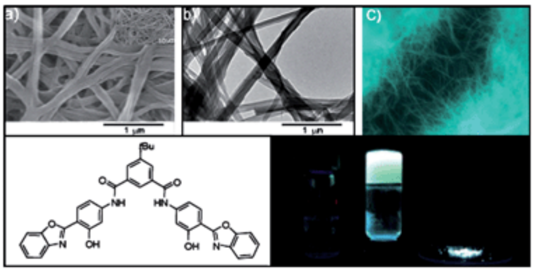
Low molecular mass amphiphilic glycolipids have been prepared by linking a maltose polar head and a hydrophobic linear chain either by amidation or copper(I)-catalyzed azide–alkyne [3 + 2] cycloaddition. The liquid crystalline properties of these amphiphilic materials have been characterized. The influence of the chemical structure of these glycolipids on the gelation properties in water has also been studied. Glycolipids obtained by the click coupling of the two components give rise to stable hydrogels at room temperature. The fibrillar structure of supramolecular hydrogels obtained by the self-assembly of these gelators have been characterized by electron microscopy. Fibers showed some torsion, which could be related with a chiral supramolecular arrangement of amphiphiles, as confirmed by circular dichroism (CD). The sol–gel transition temperature was also determined by differential scanning calorimetry (DSC) and NMR.

- Characterization of a Ca binding-amphipathic silk-like protein and peptide with the sequence $(Glu)_8(Ala\text{-}Gly\text{-}Ser\text{-}Gly\text{-}Ala\text{-}Gly)_4$ with potential for bone repair
  Nagano, A.; Sato, H.; Tanioka, Y.; Nakazawa, Y.; Knight, D.; Asakura, T. *Soft Matter* **2012**, *8*, 741-748.
  Abstract:



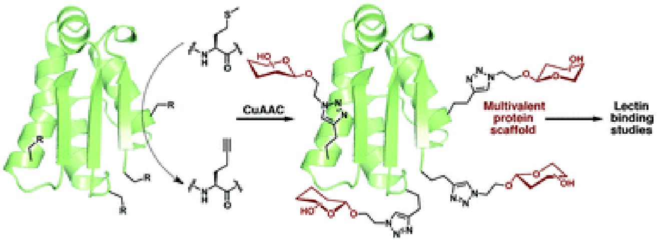
Bombyx mori silk fibroin with the main sequence $(Ala\text{-}Gly\text{-}Ser\text{-}Gly\text{-}Ala\text{-}Gly)_n$ is a promising scaffold for bone regeneration not only on account of its excellent mechanical property as a structural matrix, but also for its slow biodegradability with adequate control of hydroxyapatite (HAP) deposition. Seeking to develop a material that might stimulate bone regeneration, we prepared a recombinant calcium binding-amphipathic silk-like protein $[(Glu)_8(Ala\text{-}Gly\text{-}Ser\text{-}Gly\text{-}Ala\text{-}Gly)_4]_4$ by expression in *E. coli*. We also prepared the homologous peptide $(Glu)_8(Ala\text{-}Gly\text{-}Ser\text{-}Gly\text{-}Ala\text{-}Gly)_4$ by solid phase synthesis. The poly-L-glutamic acid was introduced into both protein and peptide because this sequence is involved in HAP-nucleating domains of bone sialoprotein. The recombinant protein was shown to bind relatively large quantities of Ca^{2+} ions in solution by a spectrophotometric assay and in the solid state by X-ray photoelectron spectroscopy. Changes in the electronic structure and local conformation of the peptide resulting from Ca^{2+} binding were studied using ^{13}C solution NMR, especially ^{13}C chemical shifts. We obtained evidence that Ca^{2+} bound to the poly-L-glutamic acid domains but not to the predominantly hydrophobic $(Ala\text{-}Gly\text{-}Ser\text{-}Gly\text{-}Ala\text{-}Gly)_4$ domains. A remarkable conformational change induced by adsorption of the synthetic peptide on the HAP surface was also demonstrated using ^{13}C solid state NMR.

- A nonpolymeric highly emissive ESIPT organogelator with neither dendritic structures nor long alkyl/alkoxy chains
  Qian, Y.; Li, S.; Wang, Q.; Sheng, X.; Wu, S.; Wang, S.; Li, J.; Yang, G. *Soft Matter* **2012**, *8*, 757-764.
  <u>Abstract:</u>



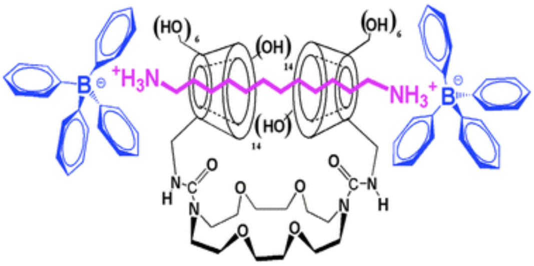
A highly fluorescent excited state intramolecular proton transfer (ESIPT) small molecular organic gelator based on 2-(2′-hydroxy)phenylbenzoxazole, N,N′-bis(4-(benzo[d]oxazol-2-yl)-3-hydroxyphenyl)-5-*tert*-butylisophthalamide, is developed in the present study. The ESIPT organogelator does not have a dendritic structure or long alkyl chains, but has a specific bent molecular structure. The intermolecular H-bonding (N–H ···O =C) between the *J*-aggregated dimers is the main driving force in the formation of the subsequent long-range one-dimensional assemblies in gel. The ESIPT gelator shows characteristics of aggregation-induced enhanced emission (AIEE). With its AIEE characteristics, ESIPT properties, simple and scalable fabrication of elongated nanobelts, as well as easy synthetic procedures, the versatile multifunctional fluorescent gelator has good prospects for future application in photoelectrical nanodevices.

- Site-selective modification of proteins for the synthesis of structurally defined multivalent scaffolds
  Artner, L. M.; Merkel, L.; Bohlke, N.; Beceren-Braun, F.; Weise, C.; Dernedde, J.; Budisa N.; Hackenberger, C. P. R. *Chem. Commun.* **2012**, *48*, 522-524.
  <u>Abstract :</u>



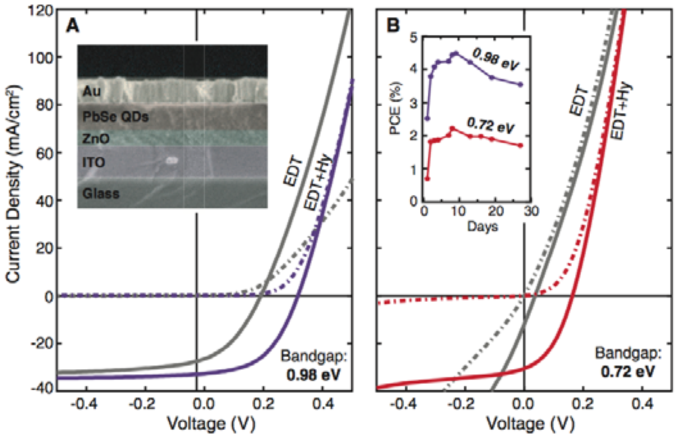
A combination of classical site-directed mutagenesis, genetic code engineering and bioorthogonal reactions delivered a chemically modified barstar protein with one or four carbohydrates installed at specific residues. These protein conjugates were employed in multivalent binding studies, which support the use of proteins as structurally defined scaffolds for the presentation of multivalent ligands.

- Expeditious synthesis of bis-β-cyclodextrinyl-diazacrown-[2]cryptorotaxanes
  Dumarcay-Charbonnier, F.; Marsura, A. *Chem. Commun.* **2012**, *48*, 732-734.
  Abstract :



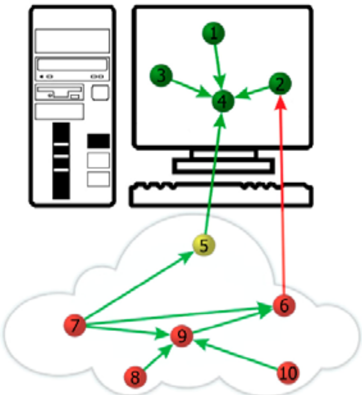
An efficient synthesis of original bis-β-cyclodextrin-[2]cryptorotaxanes in moderate to high yields is described. A synthetic approach based on the template-directed self-assembly threading process in aqueous medium gives a structure stabilized exclusively through non-covalent interactions. This procedure reveals a simple and efficient way to prepare highly organized supramolecular receptors from carefully designed subunits.

- Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell.
  Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H.-Y.; Gao, J.; Nozik, A. J.; Beard, M. C. *Science* **2011**, *334*, 1530-1533.
  Abstract :



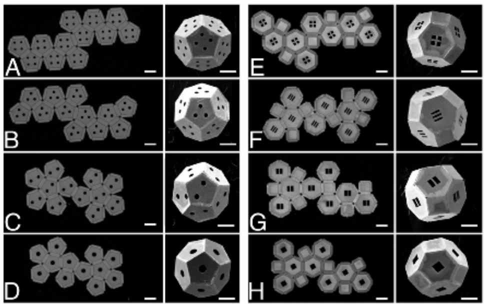
Multiple exciton generation (MEG) is a process that can occur in semiconductor nanocrystals, or quantum dots (QDs), whereby absorption of a photon bearing at least twice the bandgap energy produces two or more electron-hole pairs. Here, we report on photocurrent enhancement arising from MEG in lead selenide (PbSe) QD-based solar cells, as manifested by an external quantum efficiency (the spectrally resolved ratio of collected charge carriers to incident photons) that peaked at 114 ± 1% in the best device measured. The associated internal quantum efficiency (corrected for reflection and absorption losses) was 130%. We compare our results with transient absorption measurements of MEG in isolated PbSe QDs and find reasonable agreement. Our findings demonstrate that MEG charge carriers can be collected in suitably designed QD solar cells, providing ample incentive to better understand MEG within isolated and coupled QDs as a research path to enhancing the efficiency of solar light harvesting technologies.

- Evolution of a modular software network.
  Fortuna, M. A.; Bonachela, J. A.; Levin, S. A. *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 19985-19989.
  Abstract :



“Evolution behaves like a tinkerer” (François Jacob, *Science*, 1977). Software systems provide a singular opportunity to understand biological processes using concepts from network theory. The Debian GNU/Linux operating system allows us to explore the evolution of a complex network in a unique way. The modular design detected during its growth is based on the reuse of existing code in order to minimize costs during programming. The increase of modularity experienced by the system over time has not counterbalanced the increase in incompatibilities between software packages within modules. This negative effect is far from being a failure of design. A random process of package installation shows that the higher the modularity, the larger the fraction of packages working properly in a local computer. The decrease in the relative number of conflicts between packages from different modules avoids a failure in the functionality of one package spreading throughout the entire system. Some potential analogies with the evolutionary and ecological processes determining the structure of ecological networks of interacting species are discussed.

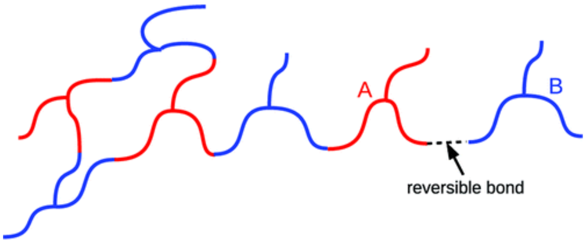
- Algorithmic design of self-folding polyhedra.
  Pandey, S.; Ewing, M.; Kunas, A.; Nguyen, N.; Gracias, D. H.; Menon, G. *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 19885-19890.
  Abstract :



Self-assembly has emerged as a paradigm for highly parallel fabrication of complex three-dimensional structures. However, there are few principles that guide a priori design, yield, and defect

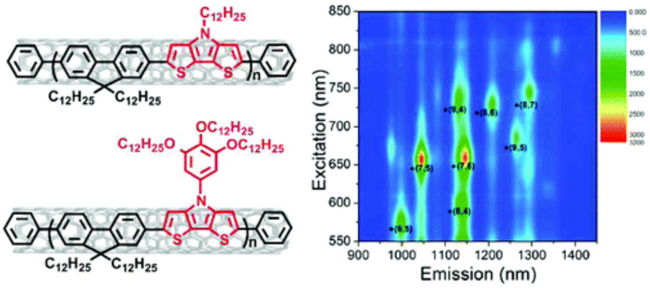
tolerance of self-assembling structures. We examine with experiment and theory the geometric principles that underlie self-folding of submillimeter-scale higher polyhedra from two-dimensional nets. In particular, we computationally search for nets within a large set of possibilities and then test these nets experimentally. Our main findings are that (*i*) compactness is a simple and effective design principle for maximizing the yield of self-folding polyhedra; and (*ii*) shortest paths from 2D nets to 3D polyhedra in the configuration space are important for rationalizing experimentally observed folding pathways. Our work provides a model problem amenable to experimental and theoretical analysis of design principles and pathways in self-assembly.

- Macro- and Microphase Separation in Multifunctional Supramolecular Polymer Networks
  Mester, Z.; Mohan, A.; Fredrickson, G. H. *Macromolecules* **2011,** *44*, 9411–9423.
  Abstract:



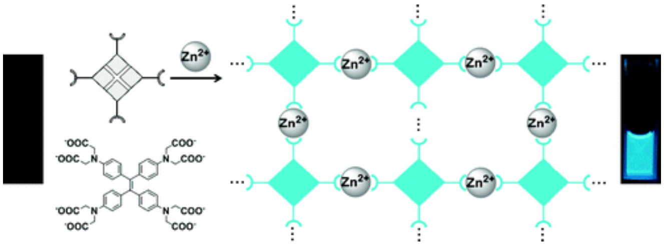
We present a field-based model for the phase separation and gelation of a binary melt of multifunctional monomeric units that can reversibly bond to form copolymer networks. The mean-field phase separation behavior of several model networks with heterogeneous bonding is calculated via the random phase approximation (RPA). By this technique, the spinodal phase boundary (stability limit of the homogeneous disordered phase) is obtained by a combination of analytical and numerical methods. It is demonstrated that higher functionality and more favorable bonding energy suppresses macroscopic phase separation due to greater connectivity between unlike species. Gelation occurs with sufficiently high connectivity of tri- or higher functional monomeric units and microphase separation of the copolymer network can occur either preceding or after the gel point. Eutectic-like behavior of the spinodal is seen in highly connected networks due to excess loosely connected material in systems having nonstoichiometric ratios of the two components.

- Supramolecular Functionalization of Single-Walled Carbon Nanotubes (SWNTs) with Dithieno[3,2-b:2′,3′-d]pyrrole (DTP) Containing Conjugated Polymers
  Imin, P.; Imit, M.; Adronov, A. *Macromolecules* **2011,** *44*, 9138–9145.
  Abstract:



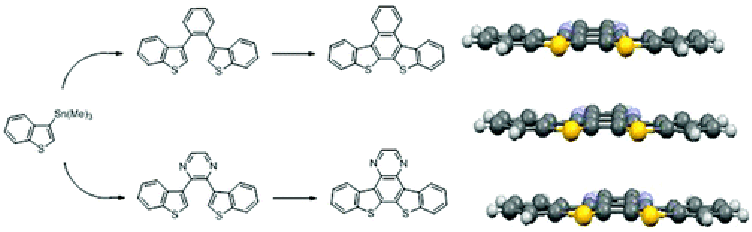
Fluorene and dithieno[3,2-b:2′,3′-d]pyrrole (DTP) containing conjugated polymers, {2,7-[9,9-didodecylfluorene]-alt-2,6-[N-dodecyldithieno(3,2-b:2′,3′-d)pyrrole]} (PF-DTP1) and {2,7-[9,9-didodecylfluorene]-alt-2,6-[N-3,4,5(n-dodecyloxy)phenyldithieno(3,2-b:2′,3′-d)pyrrole]} (PF-DTP2), have been successfully synthesized using Suzuki polycondensation. These polymers possess excellent thermal stability with decomposition temperatures over 365 °C under Ar. The introduction of soluble side chains on the DTP units and incorporation with soluble dialkyl-substituted fluorene resulted in highly soluble polymers with novel optoelectronic properties. The supramolecular complex formation of these DTP containing polymers with single-walled carbon nanotubes (SWNTs) has been studied, and it was found that these polymers can form strong supramolecular polymer–nanotube assemblies and produce stable complexes in solution. UV–vis–NIR absorption, photoluminescence excitation (PLE), and Raman spectroscopy were used for the characterization and identification of the nanotube species that are present in THF solution. The strong nanotube emission was observed from individual SWNTs even after removal of excess free polymer by filtration and washing. On the basis of these two polymers, it was found that the interactions with the SWNT surface are more strongly dictated by the polymer backbone than the side chain, though further studies may be warranted.

- Aqueous Fluorescence Turn-on Sensor for Zn^{2+} with a Tetraphenylethylene Compound
  Sun, F.; Zhang, G.; Zhang, D.; Xue, L.; Jiang, H. *Org. Lett.* **2011**, *13*, 6378–6381.
  Abstract:



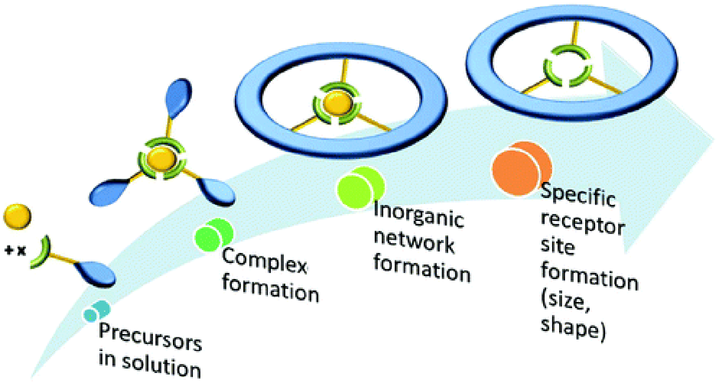
A new sensitive and selective fluorescence turn-on sensor for Zn2+ (1) was developed by taking advantage of the aggregation-induced emission of the tetraphenylethylene framework. In addition, the corresponding ester precursor of 1 was successfully used for intracellular Zn2+ imaging.

- Synthesis, Crystal Structures, and Electronic Properties of Nonlinear Fused Thienoacene Semiconductors
  Black, H. T.; Liu, S.; Ashby, V. S. *Org. Lett.* **2011**, *13*, 6492–6495.
  Abstract :



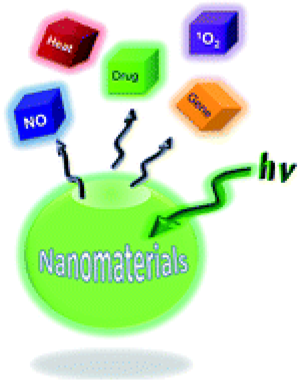
Two fused thienoacene compounds with two-dimensional ring connectivity were synthesized, and their semiconducting properties were characterized. Both compounds have a crystal structure comprised of herringbone arrays of tight π–π stacks. Strong π–π interactions lead to self-assembly into well-defined crystalline thin films from the vapor phase for both compounds. Field effect transistors were fabricated, affording identical hole mobilities of 3.0×10^{-3} $cm^2/(V\ s)$ and $I_{on/off} > 10^5$.

- pH-Responsive Bridged Silsesquioxane
  Fertier, L.; Theron, C.; Carcel, C.; Trens, P.; Chi Man, M. W. *Chem. Mater.* **2011**, *23*, 2100-2106
  Abstract:



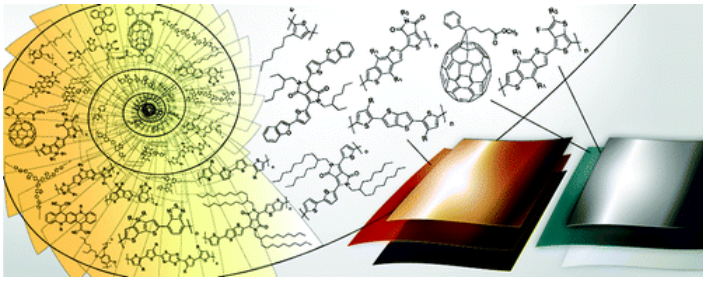
A pH-responsive bridged silsesquioxane was obtained via the sol-gel process from a bis-silylated triazine derivative bearing a triple DAD (donor-acceptor-donor) moiety which was strongly hydrogen-bonded to the three ADA (acceptor-donor-acceptor) sites of cyanuric acid. The latter template molecule was easily removed from the resulting hybrid material upon acidic treatment, which yielded the template-free bridged silsesquioxane with preserved morphology and unaltered particle size as demonstrated by SEM. As expected, the surface area of the acid-treated hybrid was significantly higher than that of the untreated material, as demonstrated by nitrogen adsorption measurements. The absence of cyanuric acid in this material was confirmed by solid state NMR and by IR. It was shown that a mild acidic medium (pH=5.5) is sufficient to release the cyanuric acid template, thus providing a novel route to new hybrid materials with potential applications as efficient carriers for pH-responsive delivery systems.

- Photoactivated nanomaterials for biomedical release applications
  Sortino, S. *J. Mater. Chem.* **2012**, *22*, 301-318
  Abstract:



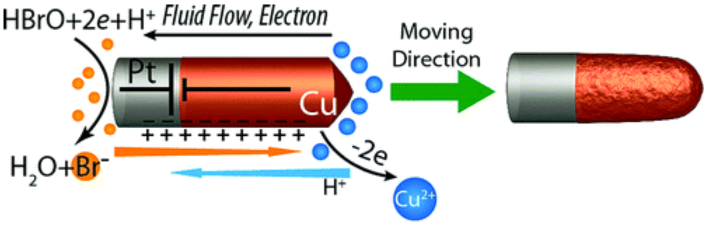
The achievement of nanomaterials able to release therapeutic agents in a controlled fashion is a major challenge in the burgeoning field of nanomedicine. Light represents the most elegant and non-invasive trigger to deliver bio-active compounds on demand since it allows the accurate control of three key factors determining the therapeutic outcome including site, timing and dosage. Recent breakthroughs in nanotechnology offer the opportunity to characterize, manipulate and organize matter at the nanometre scale, controlling the size and shape of the resulting nanomaterials and greatly improving the biocompatibility and the cellular uptake efficiency. This feature article illustrates some recent advances in the fabrication of light-triggered nanomaterials for biomedical delivery, describing representative examples from our laboratory and others, underlying the logical design and highlighting the potential applications in some major areas such as drug and gene release, photodynamic and photothermal therapy.

- Molecular Design and Ordering Effects in π-Functional Materials for Transistor and Solar Cell Applications
  Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2011**, *133*, 20009-20029.
  Abstract:



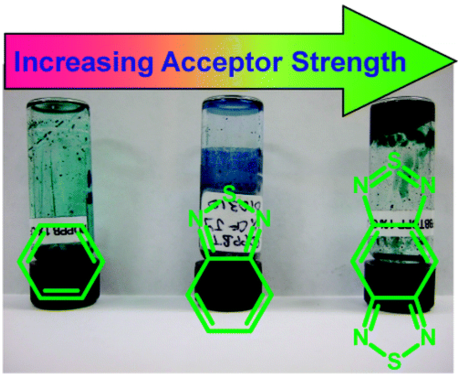
Organic electronics are broadly anticipated to impact the development of flexible thin-film device technologies. Among these, solution-processable π-conjugated polymers and small molecules are proving particularly promising in field-effect transistors and bulk heterojunction solar cells. This Perspective analyzes some of the most exciting strategies recently suggested in the design and structural organization of π-functional materials for transistor and solar cell applications. Emphasis is placed on the interplay between molecular structure, self-assembling properties, nanoscale and mesoscale ordering, and device efficiency parameters. A critical look at the various approaches used to optimize both materials and device performance is provided to assist in the identification of new directions and further advances.

- Autonomous Nanomotor Based on Copper–Platinum Segmented Nanobattery
  Liu, R.; Sen, A. *J. Am. Chem. Soc.* **2011**, *133*, 20064-20067.
  Abstract:



We describe an efficient, bubble-free nanoscale motor consisting of a copper–platinum (Cu–Pt) segmented rod that operates as a nanobattery in dilute aqueous Br_2 or I_2 solutions. The motion of the rod is powered by self-electrophoresis caused by redox reactions occurring on the two different metal segments. Asymmetric ratchet-shaped pure copper nanorods were also found to rotate and tumble in aqueous Br_2 solution because of the ion gradient arising from asymmetric dissolution of copper.

- High Performance Weak Donor–Acceptor Polymers in Thin Film Transistors: Effect of the Acceptor on Electronic Properties, Ambipolar Conductivity, Mobility, and Thermal Stability
  Yuen, J. D.; Fan, J.; Seifter, J.; Lim, B.; Hufschmid, R.; Heeger, A. J.; Wudl, F. *J. Am. Chem. Soc.* **2011**, *133*, 20799–20807.
  Abstract:

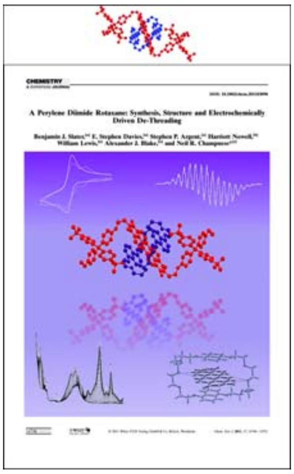


We have studied the electronic, physical, and transistor properties of a family of donor–acceptor polymers consisting of diketopyrrolopyrrole (DPP) coupled with different accepting companion units in order to determine the effects of donor–acceptor interaction. Using the electronically neutral benzene (B), the weakly accepting benzothiadiazole (BT), and the strongly accepting benzobisthiadiazole (BBT), the accepting strength of the companion unit was systematically modulated. All polymers exhibited excellent transistor performance, with mobilities above 0.1 cm^{2}V^{-1}s^{-1}, even exceeding 1 cm^{2}V^{-1}s^{-1} for one of the BBT-containing polymers. We find that the BBT is the strongest acceptor, enabling the BBT-containing polymers to be strongly ambipolar. The BBT moiety also strengthens interchain interactions, which provides higher thermal stability and performance for transistors with BBT-containing polymers as the active layer.

- Great expectations: can artificial molecular machines deliver on their promise?
  Coskun, A.; Banaszak, M.; Astumian, R. D.; Stoddart, J. F.; Grzybowski, B. A. *Chem. Soc. Rev.* **2012**, *41*, 19-30.
  Abstract:

The development and fabrication of mechanical devices powered by artificial molecular machines is one of the contemporary goals of nanoscience. Before this goal can be realized, however, we must learn how to control the coupling/uncoupling to the environment of individual switchable molecules, and also how to integrate these bistable molecules into organized, hierarchical assemblies that can perform significant work on their immediate environment at nano-, micro- and macroscopic levels. In this *tutorial review*, we seek to draw an all-important distinction between artificial molecular switches which are now ten a penny—or a dime a dozen—in the chemical literature and artificial molecular machines which are few and far between despite the ubiquitous presence of their naturally occurring counterparts in living systems. At the single molecule level, a prevailing perspective as to how machine-like characteristics may be achieved focuses on harnessing, rather than competing with, the ineluctable effects of thermal noise. At the macroscopic level, one of the major challenges inherent to the construction of machine-like assemblies lies in our ability to control the spatial ordering of switchable molecules—*e.g.*, into linear chains and then into muscle-like bundles—and to influence the cross-talk between their switching kinetics. In this regard, situations where all the bistable molecules switch synchronously appear desirable for maximizing mechanical power generated. On the other hand, when the bistable molecules switch "out of phase," the assemblies could develop intricate spatial or spatiotemporal patterns. Assembling and controlling synergistically artificial molecular machines housed in highly interactive and robust architectural domains heralds a game-changer for chemical synthesis and a defining moment for nanofabrication.

- A Perylene Diimide Rotaxane: Synthesis, Structure and Electrochemically Driven De-Threading
  Slater, B. J.; Davies, E. S.; Argent, S. P.; Nowell, H.; Lewis, W.; Blake, A. J.; Champness, N. R. *Chem. Eur. J.* **2011**, *17*, 14746–14751.
  <u>Abstract:</u>



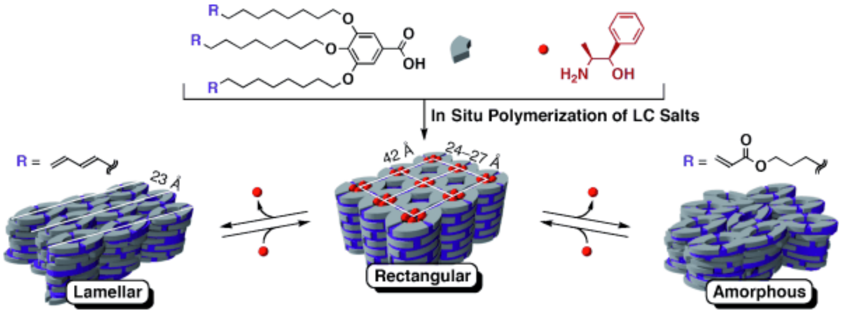
CHEMISTRY

A Perylene Diimide Rotaxane: Synthesis, Structure and Electrochemically Driven De-Threading

Benjamin J. Slater, E. Stephen Davies, Stephen P. Argent, Harriott Nowell, William Lewis, Alexander J. Blake, and Neil R. Champness

The first example of a [2]-rotaxane in which a perylene diimide acts as a recognition site has been synthesised and characterised. The interlocked nature of the compound has been verified by both NMR studies and an X-ray structure determination. Electrochemical investigations confirm that the nature of the redox processes associated with the perylene diimide are modified by the complexation process and that it is possible to mono-reduce the [2]-rotaxane to give a radical anion based rotaxane. Further reduction of the compound leads to de-threading of the macrocycle from the reduced PTCDI recognition site. Our synthetic strategies confirm the potential of PTCDI-based rotaxanes as viable targets for the preparation of complex interlocked species.

- Guest-Responsive Covalent Frameworks by the Cross-Linking of Liquid-Crystalline Salts: Tuning of Lattice Flexibility by the Design of Polymerizable Units
  Ishida, Y.; Sakata, H.; Achalkumar, A. S.; Yamada, K.; Matsuoka, Y.; Iwahashi, N.; Amano, S.; Saigo, K. *Chem. Eur. J.* **2011**, *17*, 14752–14762.
  <u>Abstract:</u>



Cross-linked polymers prepared by the in-situ polymerization of liquid-crystalline salts were found to work as solid-state hosts with a flexible framework. As a component of such hosts, four kinds of polymerizable amphiphilic carboxylic acids bearing alkyl chains with acryloyloxy (A), dienyl (D), and/or nonreactive (N) chain ends (monomeric carboxylic acids; $\mathbf{M}_{\mathrm{AAA}}$, $\mathbf{M}_{\mathrm{ANA}}$, $\mathbf{M}_{\mathrm{DDD}}$, and $\mathbf{M}_{\mathrm{DND}}$) were used. The carboxylic acids were mixed with an equimolar amount of a template unit, (1*R*,2*S*)-norephedrine (guest amine; $\mathbf{G}_{\mathrm{RS}}$), to form the corresponding salts. Every salt exhibited a rectangular columnar LC phase at room temperature, which was successfully polymerized by ^{60}Co γ-ray-induced polymerization without serious structural disordering to afford the salt of cross-linked carboxylic acid (polymeric carboxylic acid; $\mathbf{P}_{\mathrm{AAA}}$, $\mathbf{P}_{\mathrm{ANA}}$, $\mathbf{P}_{\mathrm{DDD}}$, and $\mathbf{P}_{\mathrm{DND}}$) with $\mathbf{G}_{\mathrm{RS}}$. Owing to the noncovalency of the interactions between the polymer framework **P** and the template $\mathbf{G}_{\mathrm{RS}}$, the cross-linked polymers could reversibly release and capture a meaningful amount of $\mathbf{G}_{\mathrm{RS}}$. In response to the desorption and adsorption of $\mathbf{G}_{\mathrm{RS}}$, the cross-linked polymers dramatically switched their nanoscale structural order. A systematic comparison of the polymers revealed that the choice of polymerizable groups has a significant influence on the properties of the resultant polymer frameworks as solid-state hosts. Among these polymers, $\mathbf{P}_{\mathrm{DDD}}$ was found to be an excellent solid-state host, in terms of guest-releasing/capturing ability, guest-recognition ability, durability to repetitive usage, and unique structural switching mode.