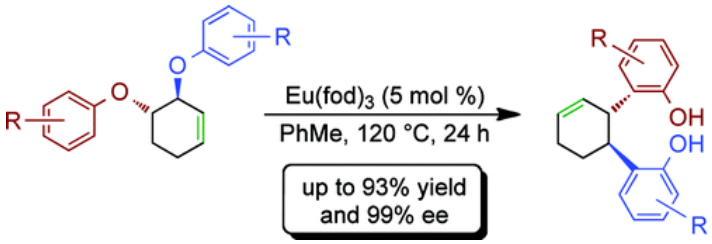
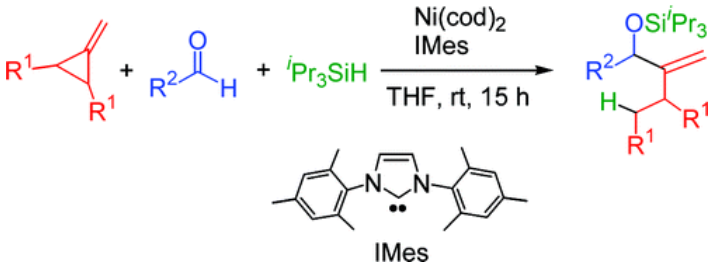
- Stereocontrolled Synthesis of Contiguous C(sp3)-C(aryl) Bonds by Lanthanide(III)-Catalyzed Domino Aryl-Claisen [3,3]-Sigmatropic Rearrangements
  Ramadhar, T. R.; Kawakami, J.; Lough, A. J.; Batey, R. A. *Org. Lett.* **2010**, *12*, 4446-4449.
  Abstract:



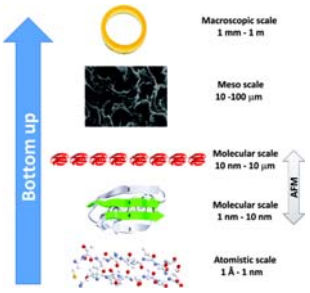
A domino [3,3]-sigmatropic aryl-Claisen rearrangement of cyclic and acyclic bisaryloxy-substituted alkenes can be performed in high yield byusing Ln(fod)3 catalysis to obtain bisphenolic products incorporating two contiguous aryl-C(sp3) bonds. Stereospecific rearrangement was observed for cyclic substrates. The precursor diaryl ethers were typically synthesized from the corresponding diols by double arylation procedures using either copper catalyzed coupling of aryltrifluoroborate salts or by SNAr reaction.

- Nickel-Catalyzed Ring-Opening Three-Component Coupling of Methylenecyclopropane with Aldehydes and Silanes
  Ogata, K.; Atsuumi, Y.; Fukuzawa, S. *Org. Lett.* **2010**, *12*, 4536-4539.
  Abstract:



A nickel-catalyzed three-component coupling between methylenecyclopropane, aldehydes, and silanes afforded silylated allylic alcohols that possess an alkyl substituent at the 2-position via cleavage of the proximal C-C bond of methylenecyclopropane.

- Protein Mechanics: From Single Molecules to Functional Biomaterials
  Li, H.; Cao, Y. *Acc. Chem. Res.* **2010**, *43*, 1331–1341.
  Abstract:



Elastomeric proteins act as the essential functional units in a wide variety of biomechanical machinery and serve as the basic building blocks for biological materials that exhibit superb mechanical properties. These proteins provide the desired elasticity, mechanical strength, resilience, and toughness within these materials. Understanding the mechanical properties of elastomeric

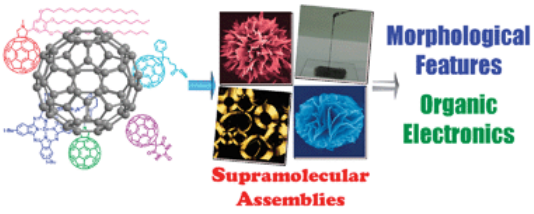
protein-based biomaterials is a multiscale problem spanning from the atomistic/molecular level to the macroscopic level. Uncovering the design principles of individual elastomeric building blocks is critical both for the scientific understanding of multiscale mechanics of biomaterials and for the rational engineering of novel biomaterials with desirable mechanical properties.

The development of single-molecule force spectroscopy techniques has provided methods for characterizing mechanical properties of elastomeric proteins one molecule at a time. Single-molecule atomic force microscopy (AFM) is uniquely suited to this purpose. Molecular dynamic simulations, protein engineering techniques, and single-molecule AFM study have collectively revealed tremendous insights into the molecular design of single elastomeric proteins, which can guide the design and engineering of elastomeric proteins with tailored mechanical properties. Researchers are focusing experimental efforts toward engineering artificial elastomeric proteins with mechanical properties that mimic or even surpass those of natural elastomeric proteins.

In this Account, we summarize our recent experimental efforts to engineer novel artificial elastomeric proteins and develop general and rational methodologies to tune the nanomechanical properties of elastomeric proteins at the single-molecule level. We focus on general design principles used for enhancing the mechanical stability of proteins. These principles include the development of metal-chelation-based general methodology, strategies to control the unfolding hierarchy of multidomain elastomeric proteins, and the design of novel elastomeric proteins that exhibit stimuli-responsive mechanical properties.

Moving forward, we are now exploring the use of these artificial elastomeric proteins as building blocks of protein-based biomaterials. Ultimately, we would like to rationally tailor mechanical properties of elastomeric protein-based materials by programming the molecular sequence, and thus nanomechanical properties, of elastomeric proteins at the single-molecule level. This step would help bridge the gap between single protein mechanics and material biomechanics, revealing how the mechanical properties of individual elastomeric proteins are translated into the properties of macroscopic materials.

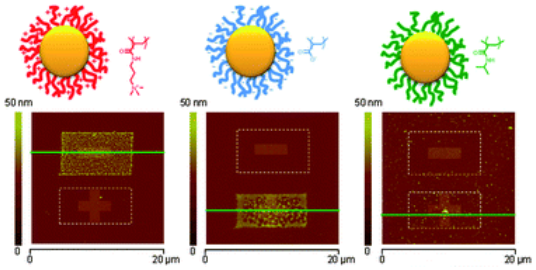
- Recent progress in morphology control of supramolecular fullerene assemblies and its applications
  Babu, S. S.; Möhwald, H.; Nakanishi, T. *Chem. Soc. Rev.* **2010**, *39*, 4021-4035.
  Abstract:



Self-organisation is an elegant tool for the creation of assemblies controlled in all dimensions with tunable properties in natural as well as artificial supramolecular systems. Especially, the supramolecular organisation of fullerene (C_{60}) using π-stacking interaction to form various functional assemblies is of particular importance as it can provide excellent optoelectronic properties. Interestingly, the insufficient solubility of C_{60} has been overcome through the noncovalent interaction with other hosts and covalent functionalisation with organic moieties. This has resulted in supramolecular assemblies at the nano/micro/macro scales under different preparation conditions. The developments in the area of fullerene self-assembly during the last few decades have significantly contributed to the sensible design and fabrication of organic electronic devices. A

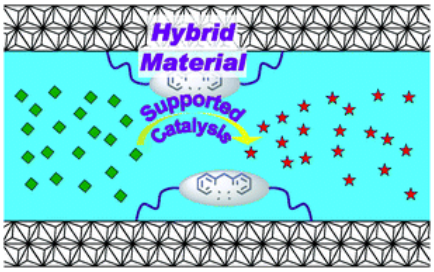
summary of the very recent reports regarding the organisation of pristine C_{60}, its coassembly with other hosts, unique polymorphs of fullerene derivatives, functional liquid crystalline assemblies, donor/acceptor heterojunctions and its applications will be presented in this *tutorial review*. Future research directions in which the supramolecular fullerene assembly may achieve more precision and improve the efficiency of the photovoltaic devices are also discussed.

- Control of the catalytic properties and directed assembly on surfaces of MADIX/RAFT polymer-coated gold nanoparticles by tuning polymeric shell charge
  Beija, M.; Palleau, E.; Sistach, S.; Zhao, X.; Ressier, L.; Mingotaud, C.; Destarac, M.; Marty, J.-D. *J. Mater. Chem.* **2010**, *20*, 9433-9442.
  Abstract :



This paper reports the use of MADIX/RAFT polymers to modulate the surface net charge of gold nanoparticles (AuNPs) with the aim of controlling their catalytic properties and their directed assembly on surfaces using AFM nanoxerography. A cationic polymer, poly[(3-acrylamidopropyl) trimethyl ammonium chloride], a pH-responsive polymer that is anionic under basic conditions, poly(acrylic acid), and a thermoresponsive neutral polymer, poly(*N*-isopropyl acrylamide) were synthesised and employed to coat preformed AuNPs. Depending on the polymer nature, different optical and surface charge properties were conferred to the nanohybrids. Their net surface charge was found to be a crucial parameter to modulate their catalytic properties and directed assembly on surfaces.

- Hybrid materials: versatile matrices for supporting homogeneous catalysts
  Zamboulis, A.; Moitra, N.; Moreau, J.; Cattoën, X.; Wong Chi Man, M. *J. Mater. Chem.* **2010**, *20*, 9322-9338.
  Abstract:

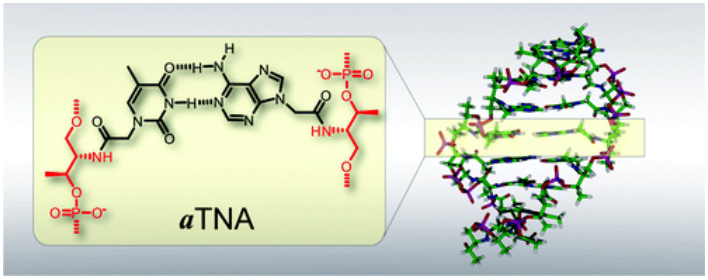


Hybrid materials are increasingly used for supporting homogeneous catalysts. This review describes the various methodologies used to synthesize such hybrid materials or to graft catalysts on inorganic or hybrid supports. Applications of these materials for reactions mediated by supported organometallic or organic catalysts are presented.

- Unexpectedly Stable Artificial Duplex from Flexible Acyclic Threoninol

Asanuma, H.; Toda, T.; Murayama, K.; Liang, X.; Kashida, H. *J. Am. Chem. Soc.* **2010**, *132*, 14702–14703.

Abstract:

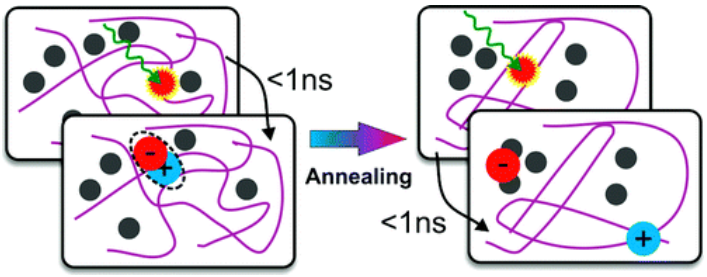


A new foldamer, acyclic threoninol nucleic acid (aTNA), has been synthesized by tethering each of the genetic nucleobases A, G, C, and T to d-threoninol molecules, which were then incorporated as building blocks into a scaffold bearing phosphodiester linkages. We found that with its fully complementary strand in an antiparallel fashion, the aTNA oligomer forms an exceptionally stable duplex that is far more stable than corresponding DNA or RNA duplexes, even though single-stranded aTNA is rather flexible and thus does not take a preorganized structure.

- Effect of Morphology on Ultrafast Free Carrier Generation in Polythiophene:Fullerene Organic Solar Cells

  Howard, I. A.; Mauer, R.; Meister, M.; Laquai, F. *J. Am. Chem. Soc.* **2010**, *132*, 14866–14876.

  Abstract:

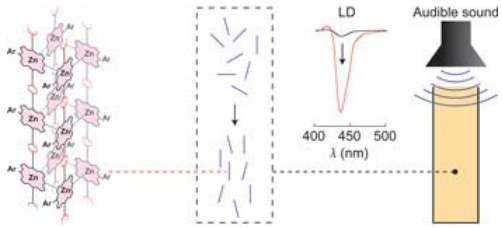


Despite significant study, the precise mechanisms that dictate the efficiency of organic photovoltaic cells, such as charge separation and recombination, are still debated. Here, we directly observe efficient ultrafast free charge generation in the absence of field in annealed poly(3-hexylthiophene):methanofullerene (P3HT:PCBM). However, we find this process is much less efficient in unannealed and amorphous regiorandom blends, explaining the superior short-circuit current and fill-factor of annealed RR-P3HT:PCBM solar cells. We use transient optical spectroscopy in the visible and near-infrared spectral region covering, but not limited to, the previously unobserved and highly relevant time scale spanning 1 to 100 ns, to directly observe both geminate and nongeminate charge recombination. We find that exciton quenching leads directly (time scale less than 100 fs) to two populations: bound charges and free charges. The former do not lead to photocurrent in a photovoltaic cell; they recombine geminately within 2 ns and are a loss channel. However, the latter can be efficiently extracted in photovoltaic cells. Therefore, we find that the probability of ultrafast free charge formation after exciton quenching directly limits solar cell efficiency. This probability is low in disordered P3HT:PCBM blends but approaches unity in annealed blends.

- Spectroscopic visualization of sound-induced liquid vibrations using a supramolecular nanofibre

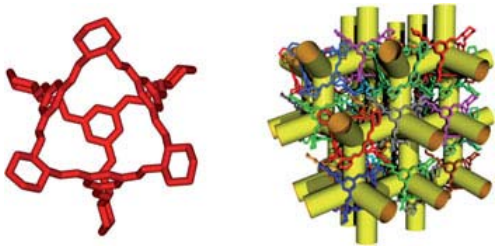
Tsuda, A.; Nagamine, Y.; Watanabe, R.; Agatani, Y.; Ishii, N.; Aida, T. *Nature Chem.* **2010**, *2*, 977–983.

Abstract:



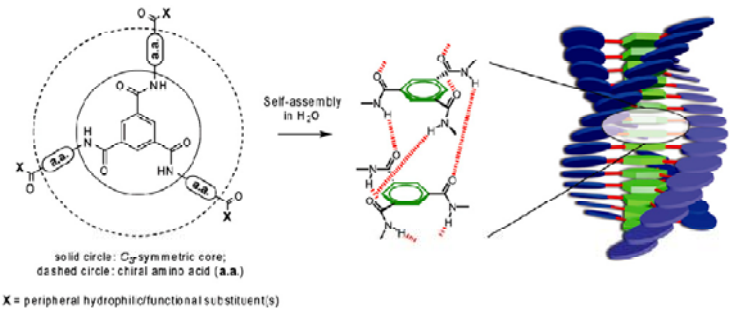
The question of whether sound vibration of a medium can bring about any kind of molecular or macromolecular events is a long-standing scientific controversy. Although it is known that ultrasonic vibrations with frequencies of more than 1 MHz are able to align certain macromolecules in solution, no effect has yet been reported with audible sound, the frequency of which is much lower (20–20,000 Hz). Here, we report on the design of a supramolecular nanofibre that in solution becomes preferentially aligned parallel to the propagation direction of audible sound. This phenomenon can be used to spectroscopically visualize sound-induced vibrations in liquids and may find application in a wide range of vibration sensing technologies.

- Porous organic molecules
  Holst, J. R.; Trewin, A.; Cooper, A. I. *Nature Chem.* **2010**, *2*, 915–920.
  Abstract:



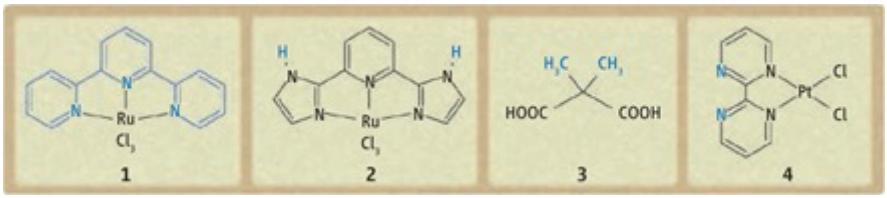
Most synthetic materials that show molecular-scale porosity consist of one-, two- or three-dimensional networks. Porous metal-organic frameworks in particular have attracted a lot of recent attention. By contrast, discrete molecules tend to pack efficiently in the solid state, leaving as little empty space as possible, which leads to non-porous materials. This Perspective discusses recent developments with discrete organic molecules that are porous in the solid state. Such molecules, which may be either crystalline or amorphous, can be categorized as either intrinsically porous (containing permanent covalent cavities) or extrinsically porous (inefficiently packed). We focus on the possible advantages of organic molecules over inorganic or hybrid systems in terms of molecular solubility, choice of components and functionalities, and structural mobility and responsiveness in non-covalent extended solids. We also highlight the potential for 'undiscovered' porous systems among the large number of cage-like organic molecules that are already known.

- Controlling the growth and shape of chiral supramolecular polymers in water
  Besenius, P.; Portale, G.; Bomans, P. H. H.; Janssen, H. M.; Palmans, A. R. A.; Meijer, E. W. *Proc. Nat. Acad. Sci.* **2010**, *107*, 17888-17893.
  Abstract:



A challenging target in the noncovalent synthesis of nanostructured functional materials is the formation of uniform features that exhibit well-defined properties, e.g., precise control over the aggregate shape, size, and stability. In particular, for aqueous-based one-dimensional supramolecular polymers, this is a daunting task. Here we disclose a strategy based on self-assembling discotic amphiphiles that leads to the control over stack length and shape of ordered, chiral columnar aggregates. By balancing out attractive noncovalent forces within the hydrophobic core of the polymerizing building blocks with electrostatic repulsive interactions on the hydrophilic rim we managed to switch from elongated, rod-like assemblies to small and discrete objects. Intriguingly this rod-to-sphere transition is expressed in a loss of cooperativity in the temperature-dependent self-assembly mechanism. The aggregates were characterized using circular dichroism, UV and 1H-NMR spectroscopy, small angle X-ray scattering, and cryotransmission electron microscopy. In analogy to many systems found in biology, mechanistic details of the self-assembly pathways emphasize the importance of cooperativity as a key feature that dictates the physical properties of the produced supramolecular polymers.

- Creating Ligands with Multiple Personalities
  Crabtree, R. H. *Science* **2010**, 330, 455 – 456.
  Abstract:

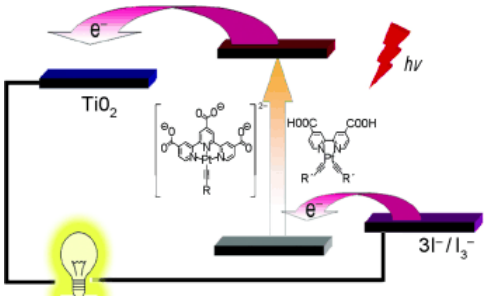


Ligands, once mere spectators in reactions catalyzed by transition metal complexes, are now being designed with additional functions that can augment the reactivity of the metal center. Classical ligands, such as the terpyridine in compound **1** (see the figure), often simply help to fill the coordination sphere of the metal and remain unchanged throughout a cycle of reactions. Even ligands that exert inductive effects—donating or withdrawing electrons to or from the metal's orbitals—can be tuned only by synthesizing a modified ligand. Multifunctional ligands that respond to effects such as changes in pH are now being developed, as illustrated by recent work by Hashiguchi *et al.* (*1*). They describe a ruthenium (Ru) complex **2** in which the ligand has a pair of labile protons (depicted in blue in the figure). The ligand is neutral but can lose one or two protons in strongly basic solution. This gain of one or two negative charges activates the Ru atom for carbon-hydrogen (C–H) bond reactions. In effect, three very different ligands can be generated from a single core structure simply by changing pH.

- Functionalized Alkynylplatinum(II) Polypyridyl Complexes for Use as Sensitizers in Dye-Sensitized Solar Cells

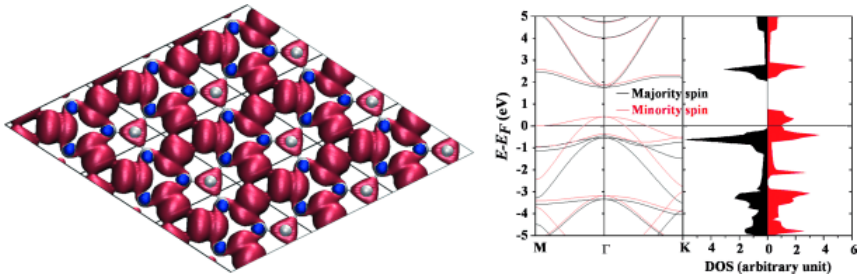
Kwok, E. C.-H.; Chan, M.-Y.; Wong, K. M.-C.; Lam, W. H.; Yam, V. W.-W. *Chem.-Eur. J.* **2010**, *16*, 12244-12254.

Abstract:



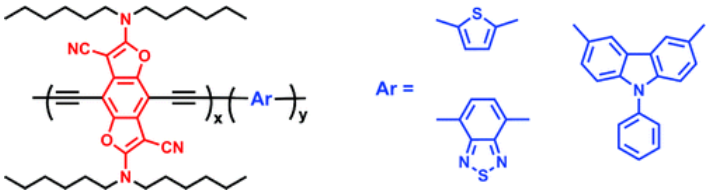
A series of platinum(II) alkynyl-based sensitizers has been synthesized and found to show light-to-electricity conversion properties. These dyes were developed as sensitizers for the application in nanocrystalline TiO_2 dye-sensitized solar cells (DSSCs). Their photophysical and electrochemical properties were studied. The excited-state property was probed using nanosecond transient absorption spectroscopy, which showed the formation of a charge-separated state that arises from the intramolecular photoinduced charge transfer from the platinum(II) alkynylbithienylbenzothiadiazole moiety (donor) to the polypyridyl ligand (acceptor). A lifetime of 3.4 μs was observed for the charge-separated state. A dye-sensitized solar cell based on one of the complexes showed a short-circuit photocurrent of 7.12 mA cm^{-2}, an open circuit voltage of 780 mV, and a fill factor of 0.65, thus giving an overall power conversion efficiency of 3.6%.

- A Radical Polymer as a Two-Dimensional Organic Half Metal
  Lee, E. C.; Choi, Y. C.; Kim, W. Y.; Singh, N. J.; Lee, S.; Shim, J. H.; Kim, K. S. *Chem.-Eur. J.* **2010**, *16*, 12141-1146.
  Abstract:



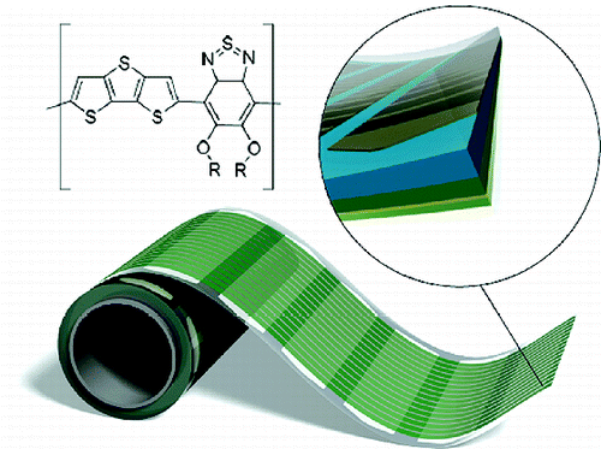
Given that half-metals are promising futuristic materials for spintronics, organic materials showing half-metal character are highly desirable for spintronic devices, not only owing to their weak spin-orbit and hyperfine interactions, but also their light and flexible properties. We predict that a two-dimensional organic 2,4,6-tri-(1,3,5-triazinyl)methyl radical polymer has half-metallic properties as well as a spontaneous magnetic ordering at ambient temperature. The quantum transmission is studied based on the non-equilibrium Green function theory coupled with density functional theory. The half-metallic property in the triazine-based polymer depends mainly on the nature of the p-band in contrast to of conventional half metals in which the nature of the d-band is more important.

- Benzodifuran-Based π-Conjugated Copolymers for Bulk Heterojunction Solar Cells
  Li, H.; Jiang, P.; Yi, C.; Li, C.; Liu, S.-X.; Tan, S.; Zhao, B.; Braun, J.; Meier, W.; Wandlowski, T.; Decurtins, S. *Macromolecules* **2010**, *43*, 8058–8062.
  Abstract:



Novel π-conjugated copolymers based on a soluble electroactive benzo[1,2-*b*:4,5-*b*′]difuran (BDF) chromophore have been synthesized by the introduction of thiophene/benzo[*c*][1,2,5]thiadiazole/9-phenylcarbazole comonomer units. These copolymers cover broad absorption ranges from 250 to 700 nm with narrow optical band gaps of 1.71−2.01 eV. Moreover, their band gaps as well as their molecular electronic energy levels are readily tuned by copolymerizing the BDF core with different π-conjugated electron-donating or withdrawing units in different ratios. Bulk heterojunction solar cell devices are fabricated using the copolymers as the electron donor and PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) as the electron acceptor. Preliminary research has revealed power conversion efficiencies of 0.17−0.59% under AM 1.5 illumination (100 mW/cm^2).

- Bundgaard, E.; Hagemann, O.; Manceau, M.; Jørgensen, M.; Krebs, F. C. *Macromolecules* **2010**, *43*, 8115–8120.
  Abstract:

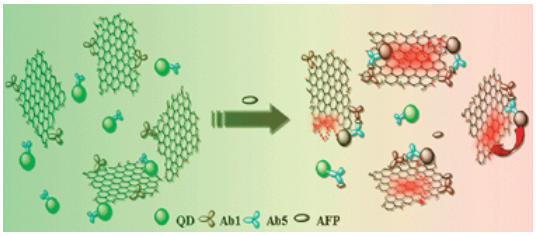


We present the synthesis of a low band gap copolymer based on dithienothiophene and dialkoxybenzothiadiazole (poly(dithienothiophene-co-dialkoxybenzothiadiazole), PDTTDABT). The optical properties of the polymer showed a band gap of 1.6 eV and a sky-blue color in solid films. The polymer was explored in roll-to-roll coating experiments and was optimized with respect to the manufacturing process and mixing ratio with [60]PCBM through a series of experiments with variation of the composition in steps of 1% w/w of respectively PDTTDABT and [60]PCBM and a relatively broad optimimum was found around a 1:2 mixing ratio. Roll-to-roll coated polymer solar cell devices were prepared under ambient conditions employing solution processing in all steps including the metallic back electrode that was printed as a grid giving semitransparent solar cell devices. Solar cell modules comprising 16 serially connected cells were prepared with a total module active area of 96 cm^2. The devices were tested for operational stability under simulated sunlight (AM1.5G) and natural sunlight, and the photochemical stability of the polymer was examined using a combination of UV−vis and IR spectroscopy.

- Distance-independent quenching of quantum dots by nanoscale-graphene in self-assembled sandwich immunoassay

Liu, M.; Zhao, H.; Quan, X.; Chen, S.; Fan, X. *Chem. Commun.* **2010**, *46*, 7909–7911.

Abstract:

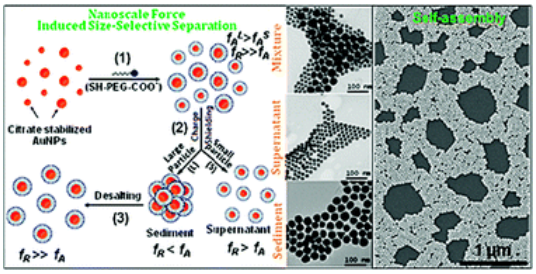


A promising one-step homogeneous fluoroimmunoassay based on nanoscale-graphene sheets as powerful fluorescence acceptors and CdTe quantum dots as vigorous donors was designed to detect trace biomarker protein with distance-independent quenching efficiency, which significantly broke the distance limit (100Å) in traditional fluorescent biosensors.

- Nanoscale force induced size-selective separation and self-assembly of metal nanoparticles: sharp colloidal stability thresholds and hcp ordering

  Zheng, Y.; Lalander, C. H.; Bach, U. *Chem. Commun.* **2010**, *46*, 7963–7965.

  Abstract:

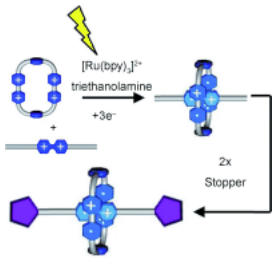


A simple and versatile nanoscale force induced precipitation approach for the separation of gold nanoparticles (AuNPs) was developed. The AuNPs show sharp size-dependent colloidal stability thresholds as a function of salt concentration. Upon separation, the AuNPs were electrostatically self-assembled onto silicon substrates by fine-tuning interparticle and particlesubstrate forces, forming 2D AuNP networks with a high degree of hexagonal closest pack (hcp) superstructures.

- Mechanical Bond Formation by Radical Templation

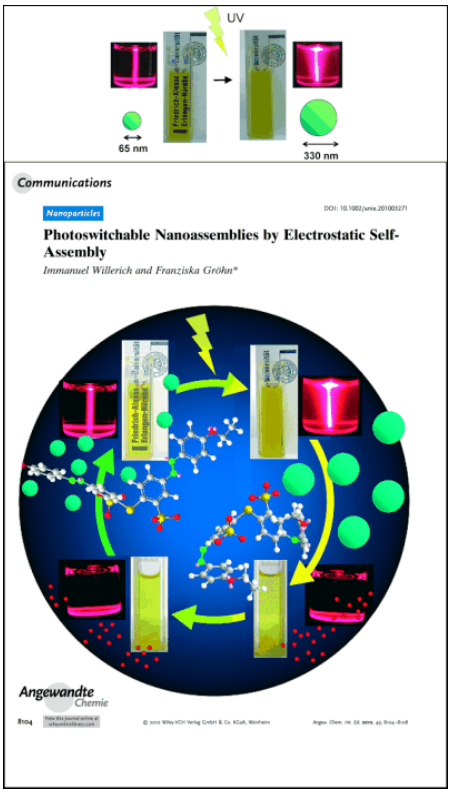
  Li, H.; Fahrenbach, A. C.; Dey, S. K.; Basu, S.; Trabolsi, A.; Zhu, Z.; Botros, Y. Y.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 8260–8265.

  Abstract :



A radical interaction has been employed as the recognition motif in the template-directed synthesis of a [2]rotaxane composed of cyclobis(paraquat-p-phenylene) and a viologen derivative. The ruthenium tris(bipyridine)/triethanolamine system is used as the electron-transfer photocatalyst to generate the necessary radical cation components that result in the formation of an inclusion complex. A stoppering reaction follows to form the mechanical bond.

- Photoswitchable Nanoassemblies by Electrostatic Self-Assembly
  Willerich, I.; Gröhn, F. *Angew. Chem. Int. Ed.* **2010**, *49*, 8104–8108.
  Abstract :



Light controls size: A novel type of self-organized supramolecular nanoparticles can change their size upon irradiation with UV light (see picture). The doubly responsive system combines a light-triggered size with a pH-induced switching between nanoscale aggregates and molecular building blocks. The nano-objects form by a combination of ionic and π–π interactions between macro-ions and dye ions.