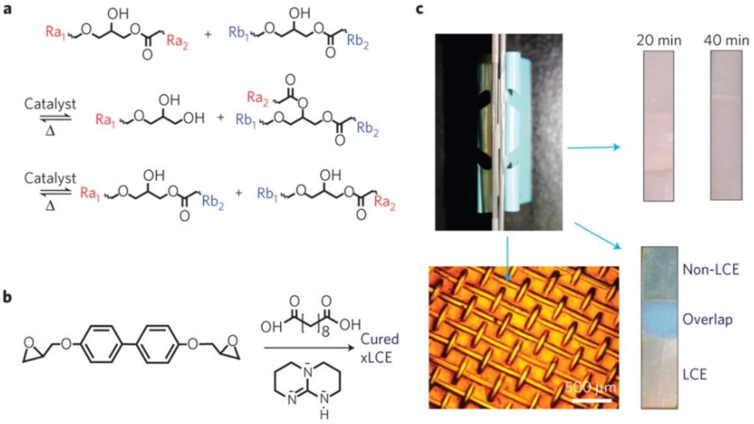
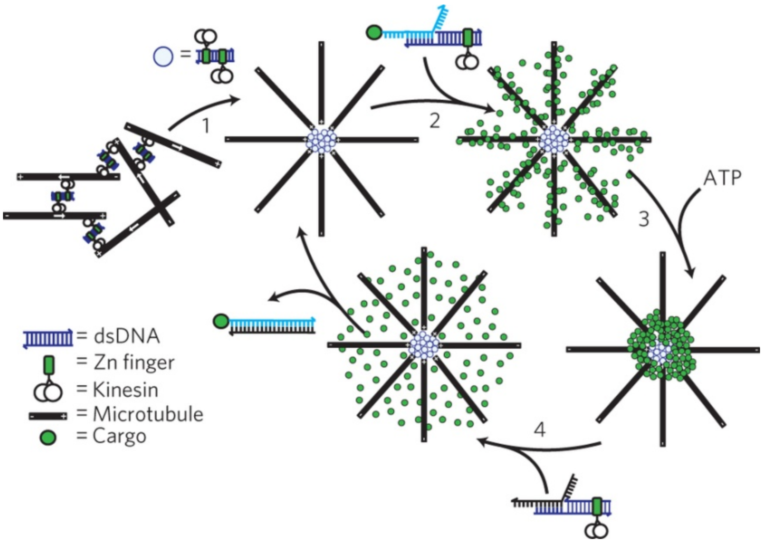
- Mouldable liquid-crystalline elastomer actuators with exchangeable covalent bonds
  Pei, Z.; Yang, Y.; Chen, Q.; Terentjev, E. M.; Wei, Y.; Ji, Y. *Nature Mater.* **2014**, *13,* 36-41.
  Abstract:



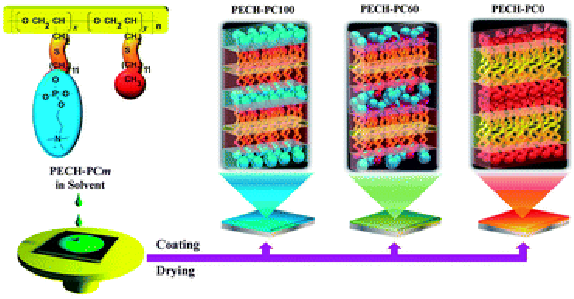
Liquid-crystal elastomers (LCEs) are a class of actively moving polymers with remarkable practical potential for converting external stimuli into mechanical actuation. However, real-world applications of LCEs are lacking because macroscopic orientation of liquid-crystal order, which is required for reversible actuations, is hard to achieve in practice. Here we show that the processing bottleneck of LCEs can be overcome by introducing exchangeable links in place of permanent network crosslinks, a concept previously demonstrated for vitrimers. Liquid-crystal elastomers with exchangeable links (xLCEs) are mouldable, allow for easy processing and alignment, and can be subsequently altered through remoulding with different stress patterns, thus opening the way to practical xLCE actuators and artificial muscles. Surprisingly, instead of external-stress relaxation through the creep of non-liquid-crystal transient networks with exchangeable links, xLCEs develop strong liquid-crystal alignment as an alternative mechanism of mechanical relaxation.

- Transport and self-organization across different length scales powered by motor proteins and programmed by DNA
  Wollman, A. J.; Sanchez-Cano, C.; Carstairs, H. M.; Cross, R. A.; Turberfield, A. J. *Nature Nanotechnol.* **2014**, *9,* 44-7.
  Abstract:



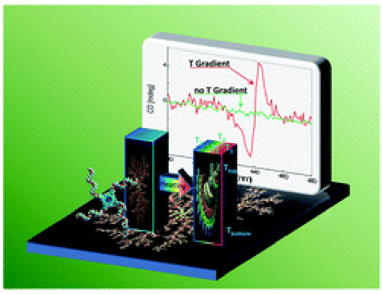
In eukaryotic cells, cargo is transported on self-organized networks of microtubule trackways by kinesin and dynein motor proteins. Synthetic microtubule networks have previously been assembled in vitro, and microtubules have been used as shuttles to carry cargoes on lithographically defined tracks consisting of surface-bound kinesin motors. Here, we show that molecular signals can be used to program both the architecture and the operation of a self-organized transport system that is based on kinesin and microtubules and spans three orders of magnitude in length scale. A single motor protein, dimeric kinesin-1, is conjugated to various DNA nanostructures to accomplish different tasks. Instructions encoded into the DNA sequences are used to direct the assembly of a polar array of microtubules and can be used to control the loading, active concentration and unloading of cargo on this track network, or to trigger the disassembly of the network.

- Self-assembly of novel lipid-mimicking brush polymers in nanoscale thin films
  Jung, J.; Kim, H.; Ree, M. *Soft Matter* **2014**, *10,* 701-708.
  Abstract:



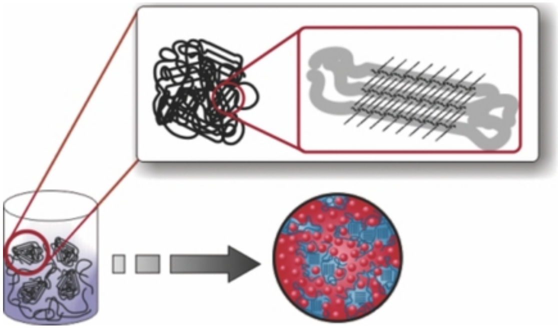
A series of well-defined poly(oxy(11-phosphorylcholineundecylthiomethyl)ethylene-ran-oxy(n-dodecylthiomethyl)ethylene) (PECH-PC*m*: m = 0–100 mol% phosphorylcholine (PC)) polymers were used to prepare nanoscale thin films that were characterized by synchrotron X-ray reflectivity (XR) analysis. The quantitative XR analysis provided structural insights into the PECH-PC*m* thin films. The PECH-PC0 polymer film formed a well-ordered in-plane oriented molecular multibilayer structure, whose individual layers consisted of two sublayers. One sublayer was composed of the fully extended backbones and inner part of the bristles, exhibiting a relatively low electron density, whereas the other sublayer was composed of a bilayer of the outer parts of the bristles without interdigitation. The PECH-PC100 polymer film also formed a well-ordered in-plane oriented molecular multibilayer structure, the individual layers of which were composed of four sublayers rather than two. The bristles in the layer were interdigitated in part via the zwitterionic interactions of the PC end groups. Surprisingly, regardless of the copolymer composition, the PECH-PCm random copolymer molecules in the thin films self-assembled to form a multilayered structure that resembled the structure formed by the PECH-PC100 polymer. These properties have not been observed in other conventional random brush copolymer films. The remarkable multibilayer structures originated from the zwitterionic PC end groups and their favorable interactions and interdigitated structures, which overcame any negative contributions caused by the heterogeneity of the bristles. The unique self-assembly properties of the PECH-PC*m* polymers always provide a PC-rich surface. The PECH-PC*m* random copolymers successfully mimicked the molecular bilayer structures formed by natural lipids.

- Supramolecular chirality induced by a weak thermal force
  Mineo, P.; Villari, V.; Scamporrino, E.; Micali, N. *Soft Matter* **2014**, *10,* 44-47.
  Abstract:



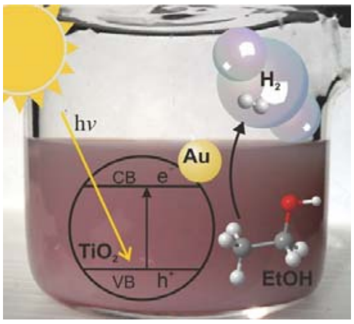
We show that the unexpected chirality of aggregated structures based on an uncharged achiral porphyrin system originates from small temperature gradients that act as an asymmetrical physical perturbation; the consequent thermal force gives rise to the thermophoretic motion of the aggregates. We establish that the induced optical activity can be controlled, and even vanished, by minimizing the thermal force.

- A Mechanistic Understanding of Processing Additive-Induced Efficiency Enhancement in Bulk Heterojunction Organic Solar Cells
  Schmidt, K.; Tassone, C. J.; Niskala, J. R.; Yiu, A. T.; Lee, O. P.; Weiss, T. M.; Wang, C.; Fréchet, J. M. J.; Beaujuge, P. M.; Toney, M. F. *Adv. Mater*. **2014**, *26*, 300-305.
  Abstract:



The addition of processing additives is a widely used approach to increase power conversion efficiencies for many organic solar cells. We present how additives change the polymer conformation in the casting solution leading to a more intermixed phase-segregated network structure of the active layer which in turn results in a 5-fold enhancement in efficiency.

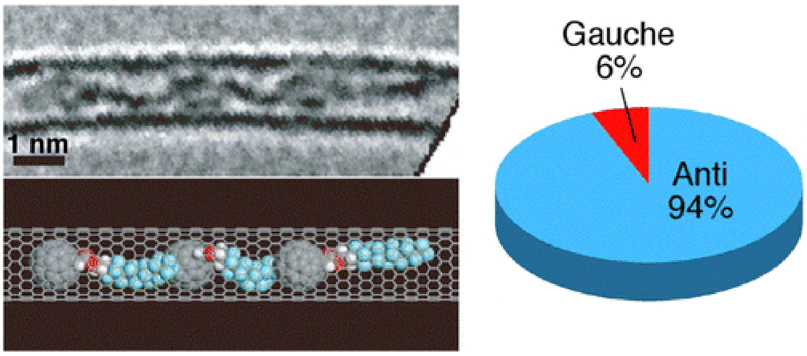
- Production of H_2 by Ethanol Photoreforming on Au/TiO_2
  Puga, A. V.; Forneli, A.; García, H.; Corma, A. *Adv. Funct. Mater*. **2014**, *24*, 241-248.
  Abstract:



Simulated solar light irradiation of ethanolic Au/TiO_2 photocatalyst suspensions yields gaseous effluents of which ca. 99% is H_2, produced by reduction. Minor products are hydrocarbons, CO, and

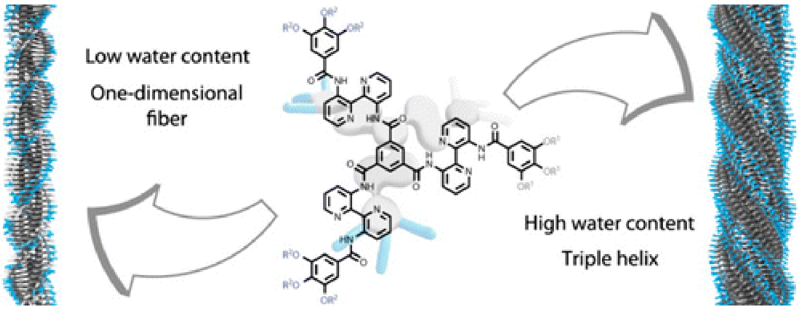
CO_2, whereas acetaldehyde, produced by oxidation, accumulates in the liquid phases. Production rates can be enhanced by using UV-richer light sources, up to 30 mmol gcat^{-1} h^{-1}.

- Conformational Analysis of Single Perfluoroalkyl Chains by Single-Molecule Real-Time Transmission Electron Microscopic Imaging
  Harano, K.; Takenaga, S.; Okada, S.; Niimi, Y.; Yoshikai, N.; Isobe, H.; Suenaga, K.; Kataura, H.; Koshino, M.; Nakamura, E. *J. Am. Chem. Soc.* **2014**, *136*, 466-473.
  Abstract:



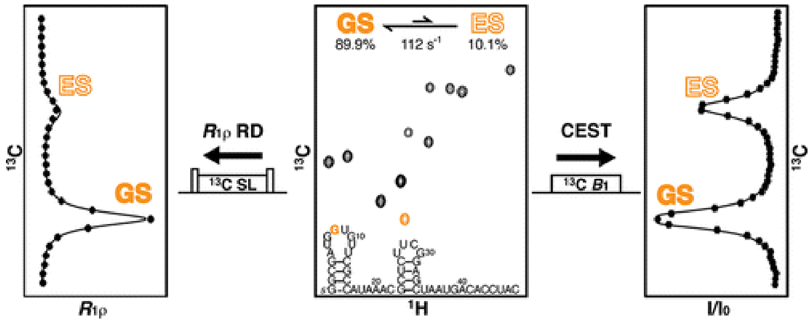
Whereas a statistical average of molecular ensembles has been the conventional source of information on molecular structures, atomic resolution movies of single organic molecules obtained by single-molecule real-time transmission electron microscopy have recently emerged as a new tool to study the time evolution of the structures of individual molecules. The present work describes a proof-of-principle study of the determination of the conformation of each C–C bond in single perfluoroalkyl fullerene molecules encapsulated in a single-walled carbon nanotube (CNT) as well as those attached to the outer surface of a carbon nanohorn (CNH). Analysis of 82 individual molecules in CNTs under a 120 kV electron beam indicated that 6% of the CF_2–CF_2 bonds and about 20% of the CH_2–CH_2bonds in the corresponding hydrocarbon analogue are in the gauche conformation. This comparison qualitatively matches the known conformational data based on time- and molecular-average as determined for ensembles. The transmission electron microscopy images also showed that the molecules entered the CNTs predominantly in one orientation. The molecules attached on a CNH surface moved more freely and exhibited more diverse conformation than those in a CNT, suggesting the potential applicability of this method for the determination of the dynamic shape of flexible molecules and of detailed conformations. We observed little sign of any decomposition of the specimen molecules, at least up to 10^7 e·nm^{-2} (electrons/nm^2) at 120 kV acceleration voltage. Decomposition of CNHs under irradiation with a 300 kV electron beam was suppressed by cooling to 77 K, suggesting that the decomposition is a chemical process. Several lines of evidence suggest that the graphitic substrate and the attached molecules are very cold.

- Triple Helix Formation in Amphiphilic Discotics: Demystifying Solvent Effects in Supramolecular Self-Assembly
  Gillissen, M. A. J.; Koenigs, M. M. E.; Spiering, J. J. H.; Vekemans, J. A. J; M.; Palmans, A. R. A.; Voets, I. K.; Meijer, E. W. *J. Am. Chem. Soc.* **2014**, *136*, 336-343.
  Abstract:



A set of chiral, amphiphilic, self-assembling discotic molecules based on the 3,3′-bis(acylamino)-2,2′-bipyridine-substituted benzene-1,3,5-tricarboxamide motif (BiPy-BTA) was prepared. Amphiphilicity was induced into the discotic molecules by an asymmetrical distribution of alkyl and oligo(ethylene oxide) groups in the periphery of the molecules. Small-angle X-ray scattering, cryogenic transmission electron microscopy, and circular dichroism spectroscopy measurements were performed on the discotic amphiphiles in mixtures of water and alcohol at temperatures between 0 °C an 90 °C. The combined results show that these amphiphilic discotic molecules self-assemble into supramolecular fibers consisting of either one or three discotic molecules in the fiber cross-section and that the presence of water induces the bundling of the supramolecular fibers. The rich phase behavior observed for these molecules proves to be intimately connected to the mixing thermodynamics of the water–alcohol mixtures.

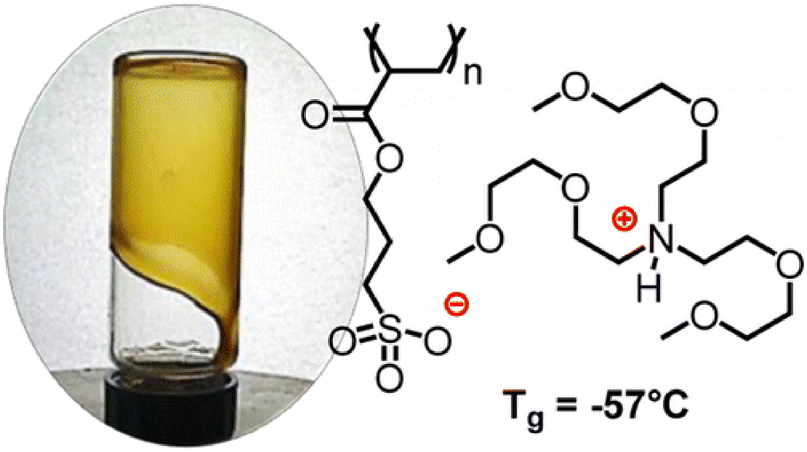
- Characterizing Slow Chemical Exchange in Nucleic Acids by Carbon CEST and Low Spin-Lock Field R1ρ NMR Spectroscopy
  Zhao, B.; Hansen, A. L.; Zhang, Q. *J. Am. Chem. Soc.* **2014**, *136*, 20–23.
  Abstract:



Quantitative characterization of dynamic exchange between various conformational states provides essential insights into the molecular basis of many regulatory RNA functions. Here, we present an application of nucleic-acid-optimized carbon chemical exchange saturation transfer (CEST) and low spin-lock field R1ρ relaxation dispersion (RD) NMR experiments in characterizing slow chemical exchange in nucleic acids that is otherwise difficult if not impossible to be quantified by the ZZ-exchange NMR experiment. We demonstrated the application on a 47-nucleotide fluoride riboswitch in the ligand-free state, for which CEST and R1ρ RD profiles of base and sugar carbons revealed slow exchange dynamics involving a sparsely populated (p 10%) and shortly lived (τ 10 ms) NMR “invisible” state. The utility of CEST and low spin-lock field R1ρ RD experiments in studying slow exchange was further validated in characterizing an exchange as slow as 60 s^{-1}.

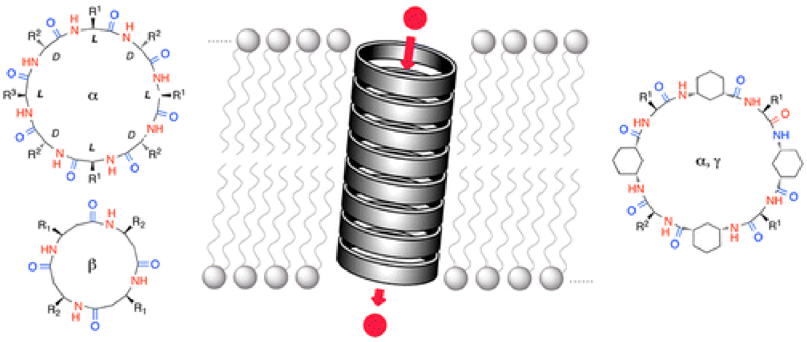
- Polyelectrolyte as Solvent and Reaction Medium
  Prescher, S.; Polzer, F.; Yang, Y.; Siebenbürger, M.; Ballauff, M.; Yuan, *J. Am. Chem. Soc.*, **2014**, *136*, 12–15.

Abstract:



A poly(ionic liquid) with a rather low glass transition temperature of −57°C was synthesized via free radical polymerization of an acrylate-type ionic liquid monomer. It exhibits fluidic behavior in a wide temperature range from room temperature to the threshold of the thermal decomposition. We demonstrate that it could act as a unique type of macromolecular solvent to dissolve various compounds and polymers and separate substances. In addition, this polyelectrolyte could serve successfully as reaction medium for catalysis and colloid particle synthesis. The synergy in the solvation and stabilization properties is a striking character of this polymer to downsize the in situ generated particles.

- Ion Channel Models Based on Self-Assembling Cyclic Peptide Nanotubes
  Montenegro, J.; Ghadiri, M. R.; Granja, J. R. *Acc. Chem. Res.* **2013**, *46*, 2955–2965.
  Abstract:

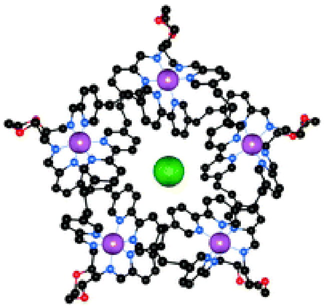


The lipid bilayer membranes are Nature's dynamic structural motifs that individualize cells and keep ions, proteins, biopolymers and metabolites confined in the appropriate location. The compartmentalization and isolation of these molecules from the external media facilitate the sophisticated functions and connections between the different biological processes accomplished by living organisms. However, cells require assistance from minimal energy shortcuts for the transport of molecules across membranes so that they can interact with the exterior and regulate their internal environments.

Ion channels and pores stand out from all other possible transport mechanisms due to their high selectivity and efficiency in discriminating and transporting ions or molecules across membrane barriers. Nevertheless, the complexity of these smart "membrane holes" has driven researchers to develop simpler artificial structures with comparable performance to the natural systems. As a broad range of supramolecular interactions have emerged as efficient tools for the rational design

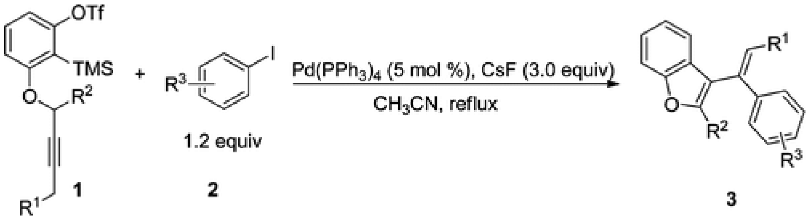
and preparation of stable 3D superstructures, these results have stimulated the creativity of chemists to design synthetic mimics of natural active macromolecules and even to develop artificial structures with functions and properties.
In this Account, we highlight results from our laboratories on the construction of artificial ion channel models that exploit the self-assembly of conformationally flat cyclic peptides (CPs) into supramolecular nanotubes. Because of the straightforward synthesis of the cyclic peptide monomers and the complete control over the internal diameter and external surface properties of the resulting hollow tubular suprastructure, CPs are the optimal candidates for the fabrication of ion channels. The ion channel activity and selective transport of small molecules by these structures are examples of the great potential that cyclic peptide nanotubes show for the construction of functional artificial transmembrane transporters. Our experience to date suggests that the next steps for achieving conceptual devices with better performance and selectivity will derive from the topological control over cyclic peptide assembly and the functionalization of the lumen.

- Anion receptor chemistry: highlights from 2011 and 2012
  Gale, P.A.; Busschaert, N.; Haynes, C. J. E.; Karagiannidisa, L. E.; Kirbya, I. L. *Chem. Soc. Rev.* **2014**, *43*, 205-241.
  Abstract:



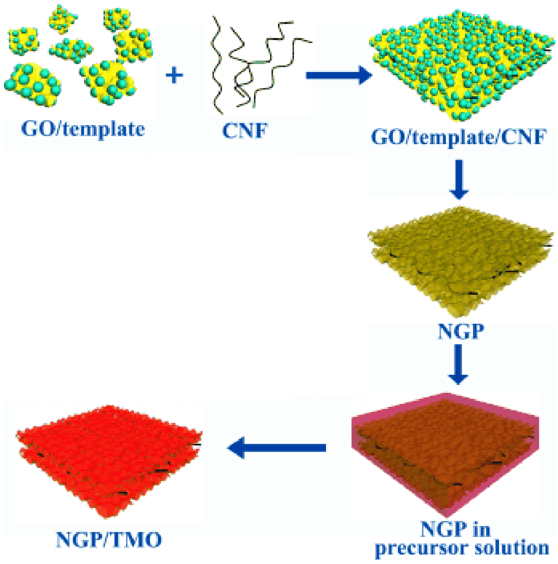
This review covers advances in anion complexation in the years 2011 and 2012. The review covers both organic and inorganic systems and also highlights the applications to which anion receptors can be applied such as self-assembly and molecular architecture, sensing, catalysis and anion transport.

- Benzofuran Derivatives from Alkynyl-Substituted Benzynes and Aryl Halides.
  Yuan, W.; Ma, S., *Org. Lett.* **2013,** *16*, 193-195.
  Abstract:



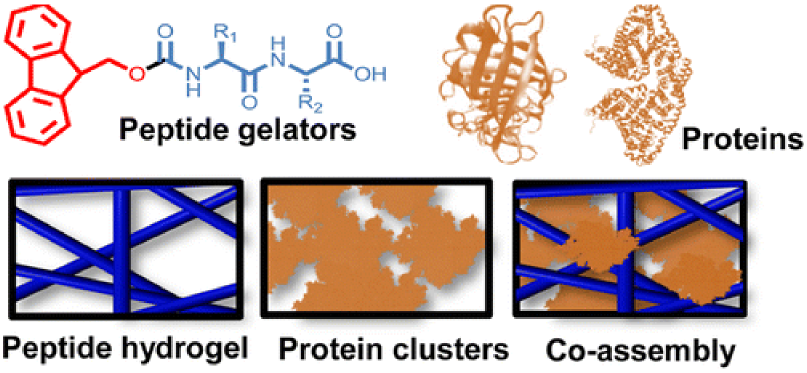
A palladium(0)-catalyzed cascade reaction for the efficient synthesis of 2,3-disubstituted benzofuran derivatives 3 containing a 3-trisubstituted alkene functional group in moderate yields from alkynyl-substituted benzynes 1 and aryl halides 2 has been developed. This method provides an efficient and alternative approach to benzofurans which are very useful heterocyclic compounds with biological and pharmacological potentials. A plausible mechanism involving intramolecular ene reaction, intermolecular insertion, and β-H elimination is proposed.

- Self-Assembling Synthesis of Free-standing Nanoporous Graphene–Transition-Metal Oxide Flexible Electrodes for High-Performance Lithium-Ion Batteries and Supercapacitors
  Huang, X.; Sun, B.; Chen, S.; Wang, G. *Chem. Asian J.* **2014,** *9*, 206-211.
  Abstract:



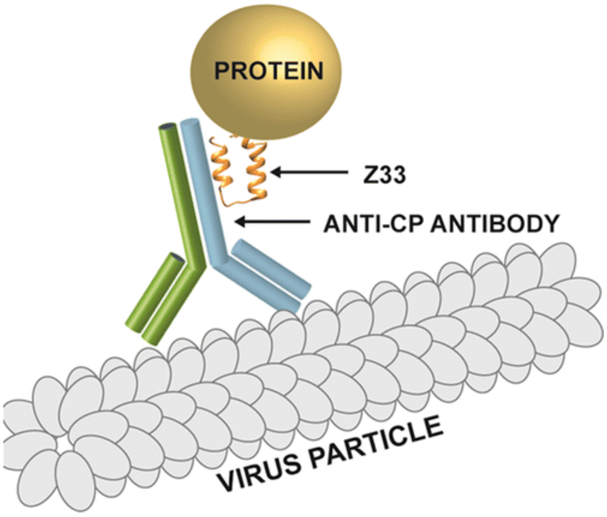
The synthesis of nanoporous graphene by a convenient carbon nanofiber assisted self-assembly approach is reported. Porous structures with large pore volumes, high surface areas, and well-controlled pore sizes were achieved by employing spherical silica as hard templates with different diameters. Through a general wet-immersion method, transition-metal oxide (Fe_3O_4, Co_3O_4, NiO) nanocrystals can be easily loaded into nanoporous graphene papers to form three-dimensional flexible nanoarchitectures. When directly applied as electrodes in lithium-ion batteries and supercapacitors, the materials exhibited superior electrochemical performances, including an ultra-high specific capacity, an extended long cycle life, and a high rate capability. In particular, nanoporous Fe_3O_4–graphene composites can deliver a reversible specific capacity of 1427.5 mAh g^{-1} at a high current density of 1000 mA g^{-1} as anode materials in lithium-ion batteries. Furthermore, nanoporous Co_3O_4–graphene composites achieved a high supercapacitance of 424.2 F g^{-1}. This work demonstrated that the as-developed freestanding nanoporous graphene papers could have significant potential for energy storage and conversion applications.

- Cooperative Self-Assembly of Peptide Gelators and Proteins
  Javid, N.; Roy, S.; Zelzer, M.; Yang, Z.; Sefcik, J.; Ulijn, R. V. *Biomacromolecules*, **2013**, *14*, 4368–4376.
  Abstract:



Molecular self-assembly provides a versatile route for the production of nanoscale materials for medical and technological applications. Herein, we demonstrate that the cooperative self-assembly of amphiphilic small molecules and proteins can have drastic effects on supramolecular nanostructuring of resulting materials. We report that mesoscale, fractal-like clusters of proteins form at concentrations that are orders of magnitude lower compared to those usually associated with molecular crowding at room temperature. These protein clusters have pronounced effects on the molecular self-assembly of aromatic peptide amphiphiles (fluorenylmethoxycarbonyl-dipeptides), resulting in a reversal of chiral organization and enhanced order through templating and binding. Moreover, the morphological and mechanical properties of the resultant nanostructured gels can be controlled by the cooperative self-assembly of peptides and protein fractal clusters, having implications for biomedical applications where proteins and peptides are both present. In addition, fundamental insights into cooperative interplay of molecular interactions and confinement by clusters of chiral macromolecules is relevant to gaining understanding of the molecular mechanisms of relevance to the origin of life and development of synthetic mimics of living systems.

- General Strategy for Ordered Noncovalent Protein Assembly on Well-Defined Nanoscaffolds
  Pille, J.; Cardinale, D.; Carette, N.; Di Primo, C.; Besong-Ndika, J.; Walter, J.; Lecoq, H.; van Eldijk, M. B.; Smits, F. C. M.; Schoffelen, S.; van Hest, J. C. M.; Mäkinen, K.; Michon, T. *Biomacromolecules* **2013**, *14*, 4351–4359.
  Abstract:

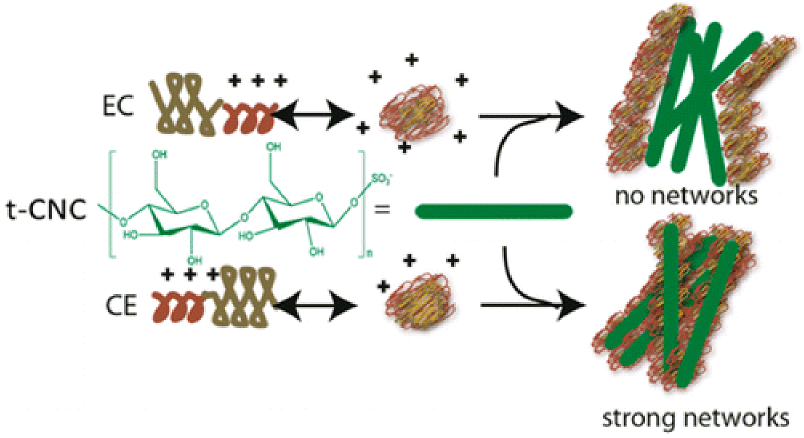


Here we develop a novel approach allowing the noncovalent assembly of proteins on well-defined nanoscaffolds such as virus particles. The antibody-binding peptide Z33 was genetically fused to the monomeric yellow fluorescent protein and 4-coumarate:CoA-ligase 2. This Z33 “tag” allowed their patterning on the surface of zucchini yellow mosaic virus by means of specific antibodies directed against the coat protein of the virus. The approach was validated by affinity assays and correlative microscopy. The coverage efficiency was ~87%. Fluorescence and enzymatic activity were fully retained after assembly. The principle of using the combination of a scaffold-specific antibody and Z33-fusion proteins can be extended to a wide variety of proteins/enzymes and antigenic scaffolds to support coupling for creating functional “biochips” with optical or catalytic properties.

- Bionanocomposites: Differential Effects of Cellulose Nanocrystals on Protein Diblock Copolymers

Haghpanah, J. S.; Tu, R.; Da Silva, S.; Yan, D.; Mueller, S.; Weder, C.; Foster, E. J.; Sacui, I.; Gilman, J. W.; Montclare, J. K. *Biomacromolecules* **2013**, *14*, 4360–4367.

Abstract:

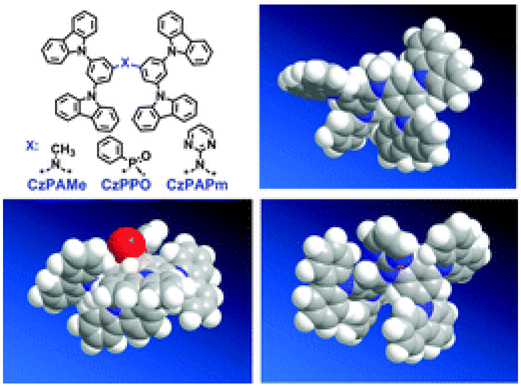


We investigate the effects of mixing a colloidal suspension of tunicate-derived cellulose nanocrystals (t-CNCs) with aqueous colloidal suspensions of two protein diblock copolymers, EC and CE, which bear two different self-assembling domains (SADs) derived from elastin (E) and the coiled-coil region of cartilage oligomeric matrix protein (C). The resulting aqueous mixtures reveal improved mechanical integrity for the CE+t-CNC mixture, which exhibits an elastic gel network. This is in contrast to EC+t-CNC, which does not form a gel, indicating that block orientation influences the ability to interact with t-CNCs. Surface analysis and interfacial characterization indicate that the differential mechanical properties of the two samples are due to the prevalent display of the E domain by CE, which interacts more with t-CNCs leading to a stronger network with t-CNCs. On the other hand, EC, which is predominantly C-rich on its surface, does not interact as much with t-CNCs. This suggests that the surface characteristics of the protein polymers, due to folding and self-assembly, are important factors for the interactions with t-CNCs, and a significant influence on the overall mechanical properties. These results have interesting implications for the understanding of cellulose hydrophobic interactions, natural biomaterials and the development of artificially assembled bionanocomposites.

- Solution-processed bipolar small molecular host materials for single-layer blue phosphorescent organic light-emitting diodes

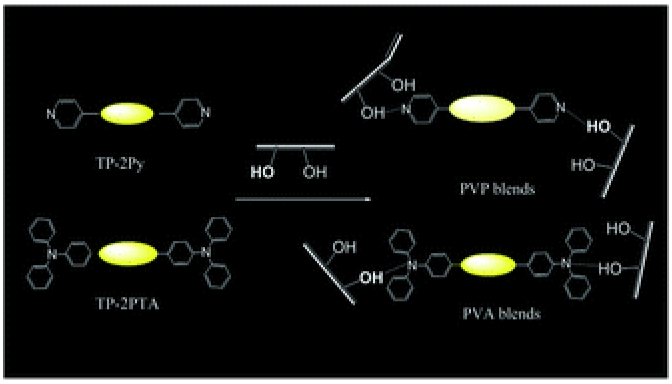
  Lee, Y.-T.; Chang, Y.-T.; Lee, M.-T.; Chiang, P.-H.; Chen, C.-T.; Chen, C.-T. *J. Mater. Chem. C,* **2014***, 2, 382*–391.

  Abstract:



Three new solution processable small molecular host materials based on the bis-[3,5-di(9*H*-carbazol-9-yl)phenyl] structural moiety have been developed for blue phosphorescent (FIrpic dopant) organic light-emitting diodes. All three host materials have been characterized as having high glass transition temperatures (T_gs), 155–175 °C, indicative of good morphological stability of their amorphous thin films prepared from the solution process. Whereas *N*,*N*-bis-[3,5-di(9*H*-carbazol-9-yl)phenyl]methylamine (**CzPAMe**) has the highest solid state triplet energy gap (E_T) of 2.73 eV, tetrakis-[3,3′,5,5′-(9*H*-carbazol-9-yl)]triphenylphosphine oxide (**CzPPO**) and *N*,*N*-bis-[3,5-di(9*H*-carbazol-9-yl)phenyl]pyrimidin-2-amine (**CzPAPm**) are two host materials which are potentially bipolar for charge transport due to the electron deficient units of phenylphosphine oxide and pyrimidine, respectively. Due to the insufficient E_T (2.56 eV) of **CzPAPm**, **CzPPO** or **CzPAMe** devices are significantly better than **CzPAPm** devices with or without a 1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) co-host. Particularly, having no OXD-7 co-host and no vacuum thermal-deposited extra electron transporting layer, single-layer devices of **CzPPO** surpass **CzPAMe** devices and reach current efficiencies as high as 9.32 cd A^{-1} (or power efficiency of 4.97 lm W^{-1}), one of the highest efficiencies among small molecular devices with the same fabrication process and same device configuration.

- Aggregation-enhanced emission in fluorophores containing pyridine and triphenylamine terminals: restricted molecular rotation and hydrogen-bond interaction
  Deng, S.-L.; Chen, T.-L.; Chiena, W.-L.; Hong, J.-L. *J. Mater. Chem. C,* **2014***, 2,* 651–659.
  Abstract:

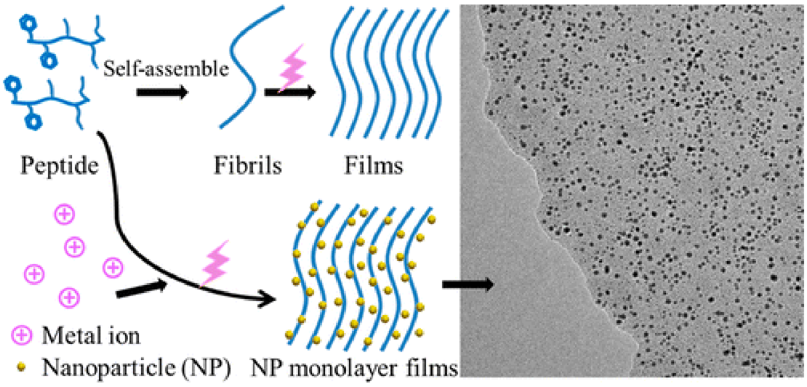


Restriction on molecular rotation of fluorophores reduces non-radiative decay channels and promotes strong fluorescence due to aggregation-enhanced emission (AEE) behavior. To evaluate the important role of restricted molecular rotation on AEE behavior, tetraphenylthiophene (TP) derivatives with two pyridine (Py) or two triphenylamine (TPA) terminals were synthesized and characterized to be AEE-active fluorophores. Because of the efficient hindered molecular rotation of the larger TPA terminals, TP-2TPA emitted with higher emission efficiency than TP-2Py with smaller Py terminals. In addition, Py and TPA terminals can serve as hydrogen-bond (H-bond) accepting groups to bind with H-bond donating hydroxyl groups in poly(vinyl phenol) (PVPh) and poly(vinyl alcohol) (PVA) to further reinforce rotational restriction on the TP-2Py and TP-2PTA fluorophores. TP-2Py and TP-2PTA were therefore blended with PVPh and PVA and the emissive properties of the resultant blends were characterized and compared with the unblended TP-2Py and TP-2PTA to emphasize the role of H-bond on restricted molecular rotation.

- One-Step Fabrication of Self-Assembled Peptide Thin Films with Highly Dispersed Noble Metal Nanoparticles

Yan, J.; Pan, Y.; Cheetham, A. G.; Lin, Y.-A.; Wang, W.; Cui, H.; Liu, C.-J. *Langmuir* **2013**, *52*, 16051–16057.

Abstract:

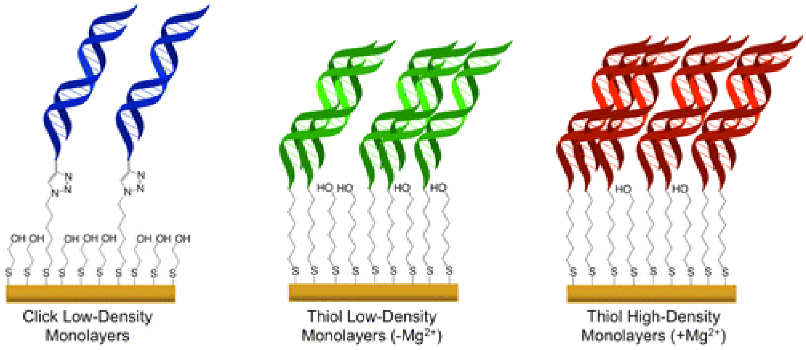


Fabrication of organic thin films with highly dispersed inorganic nanoparticles is a very challenging topic. In this work, a new approach that combines electron-induced molecular self-assembly with simultaneous nanoparticle formation by room temperature electron reduction was developed to prepare peptide thin films with highly dispersed noble metal nanoparticles. Argon glow discharge was employed as the resource of electrons. The peptide motif KLVFF (Aβ_{16-20}) self-assembled into two-dimensional membranes under the influence of hydrated electrons, while the metal ions in solution can be simultaneously reduced by electrons to form nanoparticles. Our TEM imaging reveals that metal nanoparticles were well-distributed in the resulting peptide thin films. Our results also suggest that the size of metal nanoparticles can be tuned by varying the initial concentration of the metal ion. This simple approach can be viewed as a promising strategy to create hybrid thin films that integrate functional inorganics into biomolecule scaffolds.

- DNA-Modified Electrodes Fabricated Using Copper-Free Click Chemistry for Enhanced Protein Detection

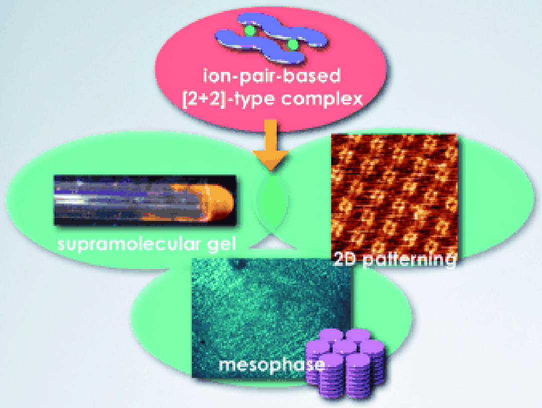
  Furst, A. L.; Hill, M. G.; Barton, J. K. *Langmuir* **2013**, *52*, 16141–16149.

  Abstract:



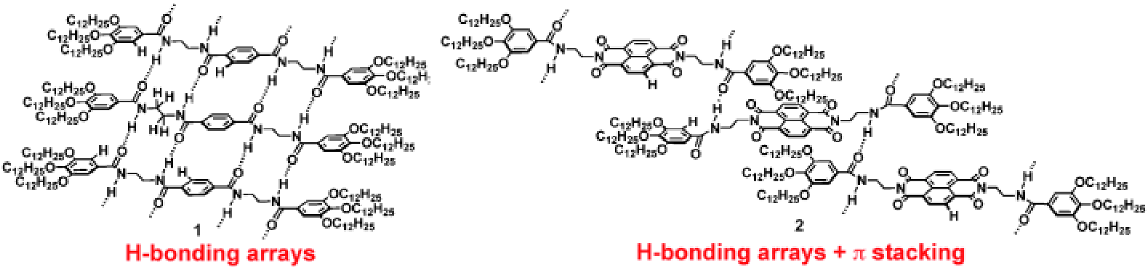
A method of DNA monolayer formation has been developed using copper-free click chemistry that yields enhanced surface homogeneity and enables variation in the amount of DNA assembled; extremely low-density DNA monolayers, with as little as 5% of the monolayer being DNA, have been formed. These DNA-modified electrodes (DMEs) were characterized visually, with AFM, and electrochemically, and were found to facilitate DNA-mediated reduction of a distally bound redox probe. These low-density monolayers were found to be more homogeneous than traditional thiol-modified DNA monolayers, with greater helix accessibility through an increased surface area-to-volume ratio. Protein binding efficiency of the transcriptional activator TATA-binding protein (TBP) was also investigated on these surfaces and compared to that on DNA monolayers formed with standard thiol-modified DNA. Our low-density monolayers were found to be extremely sensitive to TBP binding, with a signal decrease in excess of 75% for 150 nM protein. This protein was detectable at 4 nM, on the order of its dissociation constant, with our low-density monolayers. The improved DNA helix accessibility and sensitivity of our low-density DNA monolayers to TBP binding reflects the general utility of this method of DNA monolayer formation for DNA-based electrochemical sensor development.

- Ion-Pair-Based Assemblies Comprising Pyrrole–Pyrazole Hybrids.
  Maeda, H.; Chigusa, K.; Sakurai, T.; Ohta, K.; Uemura, S.; Seki, S. *Chem. Eur. J.* **2013**, *19*, 9224–9233.
  Abstract:



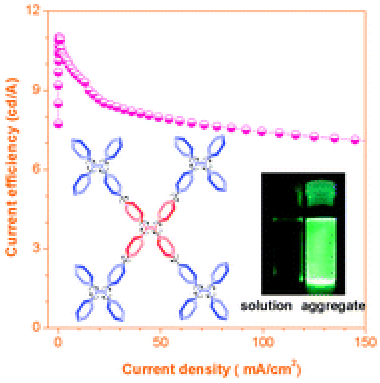
Modified 3,5-dipyrrolylpyrazole (DPP) derivatives in their protonated form produce planar [2+2]-type complexes with trifluoroacetate (TFA) ions. These complexes serve as constituent components of ion-pair-based assemblies. An essential strategy for the construction of dimension-controlled organized structures based on these [2+2]-type complexes is the introduction of aryl rings bearing long alkyl chains, which enables the formation of 2D patterns at interfaces, supramolecular gels, and mesophases.

- Thermodynamics of the Helical, Supramolecular Polymerization of Linear Self-Asembling Molecules: Influence of Hydrogen Bonds and π Stacking
  Aparicio, F.; Sánchez, L. *Chem. Eur. J.* **2013**, *19*, 10482–10486.
  Abstract:



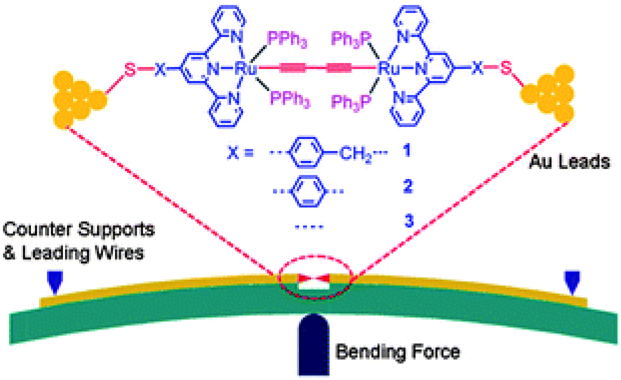
The cooperative supramolecular polymerization of **1** and **2** show very similar thermodynamic parameters ($\Delta H^{0}_{\mathrm{ele}}$, ΔS^{0}, and $\Delta H^{0}_{\mathrm{nucl}}$), but very different organization of the self-assembling units to constitute helical structures. The results presented allow the quantification of the influence of the type and number of non-covalent interactions in supramolecular polymerization.

- Aggregation-enhanced emission and efficient electroluminescence of tetraphenylethene-cored luminogens
  Chang, Z.; Jiang, Y.; He, B.; Chen, J.; Yang, Z.; Lu, P.; Kwok, H. S.; Zhao, Z.; Qiu, H.; Tang, B. Z. *Chem. Commun.* **2013**, *49,* 594-596.
  Abstract:



A new design of luminescent materials by decorating a tetraphenylethene core with four aromatic chromophores is proposed. The generated luminogens exhibit aggregation-enhanced emission and excellent solid-state fluorescent efficiency (93-99%). Efficient non-doped OLEDs based on them afford remarkable efficiencies up to 11 cd A^{-1}.

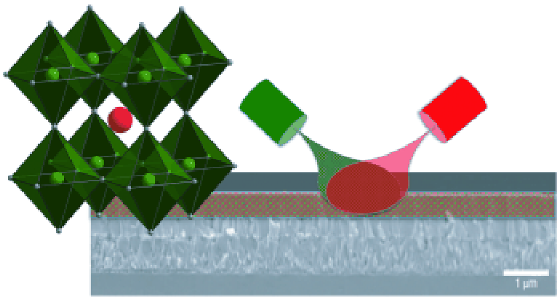
- Electrical conductance study on 1,3-butadiyne-linked dinuclear ruthenium(Ⅱ) complexes within single molecule break junctions
  Wen, H.-M.; Yang, Y.; Zhou, X.-S.; Liu, J.-Y.; Zhang, D.-B.; Chen, Z.-B.; Wang, J.-Y.; Chen, Z.-N.; Tian, Z.-Q. *Chem. Sci.* **2013**, *4*, 2471-2477.
  Abstract:



Single-molecule conductance of three sulphur-functionalized organometallic wires with two ruthenium(II) centres spaced by 1,3-butadiyne was firstly investigated using an electrochemically assisted-mechanically controllable break junction (EC-MCBJ) approach. It is demonstrated that single-molecular conductance of these diruthenium(II) incorporated systems is significantly higher than oligo(phenylene-ethynylene) (OPE) having comparable lengths and exhibits weaker length dependence. The conductance improvement in these diruthenium(II) molecules is ascribable to the better energy match of the Fermi level of gold electrodes with the HOMO that is mainly resident on the Ru–C≡C–C≡C–Ru backbone. Furthermore, modulation of molecular conductance is achieved by changing the length and π-conjugated system of the chelating 2,2′:6′,2″-terpyridyl ligand.

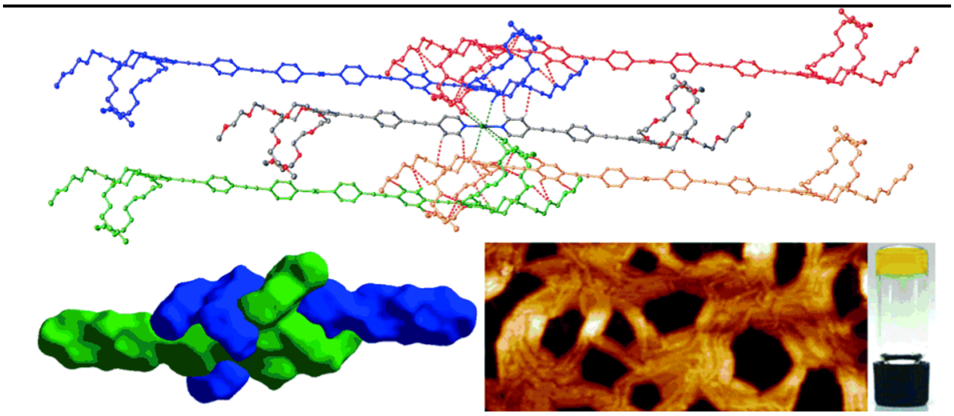
- New Light on an Old Story: Perovskites Go Solar

Lotsch, B. V. *Angew. Chem. Int. Ed.* **2014**, *53*, 635–637.
Abstract:



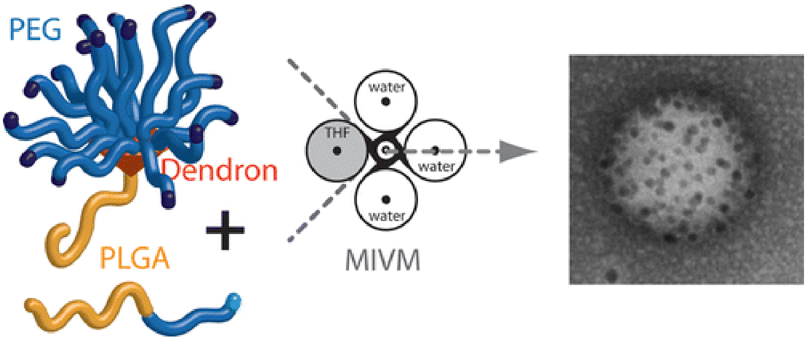
All in one: Perovskites are currently undergoing a renaissance as "allrounder" materials for solar cells. For a special type of methylammonium lead halide perovskites, a unique combination of properties, including high charge-carrier mobilities, exciton lifetimes, and panchromatic absorption, was observed, which renders this class of hybrid perovskites one of the most promising absorber and ambipolar charge-transport materials for all-solid-state solar cells.

- Self-Assembly and (Hydro)gelation Triggered by Cooperative π–π and Unconventional C—H⋯X Hydrogen Bonding Interactions
  Rest, C.; Mayoral, M. J.; Fucke, K.; Schellheimer, J.; Stepanenko, V.; Fernández, G. *Angew. Chem. Int. Ed.* **2014**, *53*, 700–705.
  Abstract:



Weak C—H⋯X hydrogen bonds are important stabilizing forces in crystal engineering and anion recognition in solution. In contrast, their quantitative influence on the stabilization of supramolecular polymers or gels has thus far remained unexplored. Herein, we report an oligophenyleneethynylene (OPE)-based amphiphilic Pt^{II} complex that forms supramolecular polymeric structures in aqueous and polar media driven by π–π and different weak C-H⋯X (X=Cl, O) interactions involving chlorine atoms attached to the Pt^{II} centers as well as oxygen atoms and polarized methylene groups belonging to the peripheral glycol chains. A collection of experimental techniques (UV/Vis, 1D and 2D NMR, DLS, AFM, SEM, and X-Ray diffraction) demonstrate that the interplay between different weak noncovalent interactions leads to the cooperative formation of self-assembled structures of high aspect ratio and gels in which the molecular arrangement is maintained in the crystalline state.

- Kinetically Arrested Assemblies of Architecturally Distinct Block Copolymers
  Santos, J. L.; Herrera-Alonso, M. *Macromolecules* **2014**, *47*, 137–145.
  Abstract:

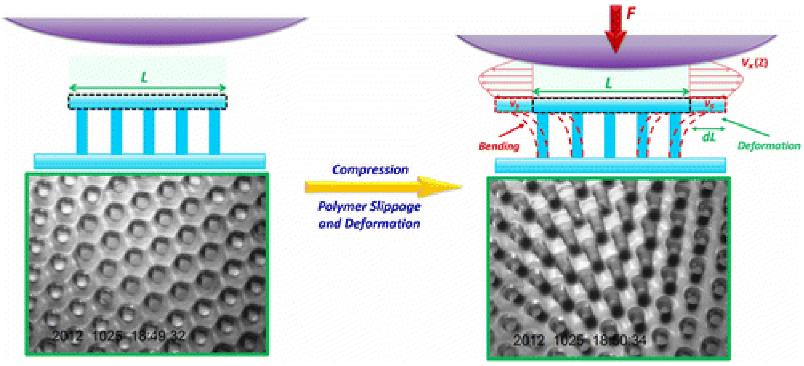


The rapid coassembly of linear and linear–dendritic amphiphiles from homogeneous solution and high supersaturation produces kinetically arrested nanoparticles, the morphologies of which are distinct from equilibrium structures. The binary system of poly(d,l-lactide-co-glycolide)-block-poly(ethylene glycol) with a linear or dendritic architecture of the hydrophilic component, forms spherical hybrid nanoparticles regardless of dendron generation or poly(ethylene glycol) length. Controlled variation in nanoparticle size was achieved through a balance of amphiphile architecture, blend composition, and final solvent content. These results demonstrate how kinetic features of the assembly process influence the formation of hybrid copolymer nanoparticles.

- Bioinspired Functionally Graded Adhesive Materials: Synergetic Interplay of Top Viscous–Elastic Layers with Base Micropillars

  Shahsavan, H.; Zhao, B. *Macromolecules* **2014**, *47*, 353–364.

  Abstract:



Inspired by the amazing adhesion abilities of the toe pads of geckos and tree frogs, we report an experimental study on the integration of a dissipative material (resembling the dissipative and wet nature of the tree frog toe pads) to an elastic fibrillar interface (resembling the dry and fibrillar nature of the gecko foot pads). Accordingly, a new type of functionally graded adhesive is introduced, which is composed of an array of elastic micropillars at the base, a thin elastic intermediate layer and a viscoelastic top layer. A systematic investigation of this bioinspired graded adhesive structure was performed in comparison with three control adhesive materials: a viscoelastic film, a viscoelastic film coated on a soft elastomer, and elastic film-terminated micropillars. The results showed that this graded structure bestows remarkable adhesive properties in terms of pull-off force, work of adhesion, and structural integrity (i.e., inhibited cohesive failure). Moreover, an extraordinary compliance was observed, which is attributed to the polymer slippage at the top layer. Overall, we attribute the improved adhesive properties to the synergetic interplay of top viscous–elastic layers with the base biomimetic micropillars.