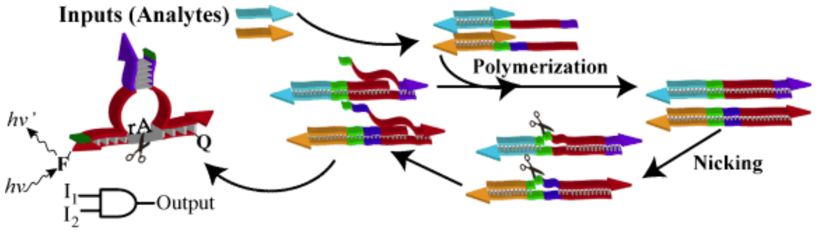
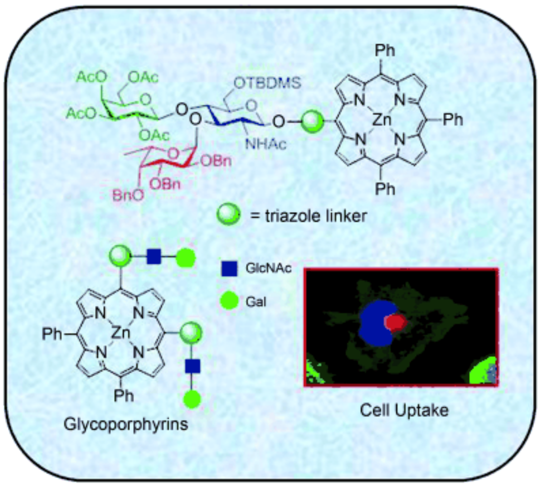
- Nucleic Acid Driven DNA Machineries Synthesizing Mg^{2+}-Dependent DNAzymes: An Interplay between DNA Sensing and Logic-Gate Operations
  Orbach, R.; Mostinski, L.; Wang, F.; Willner, I. *Chem. Eur. J.* **2012**, *18*, 14689–14694.
  Abstract:



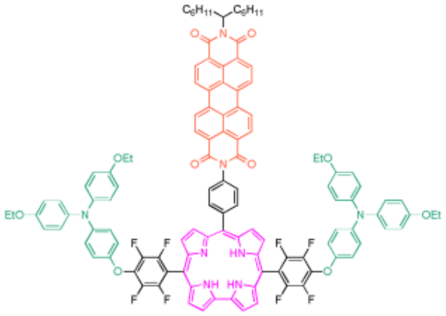
Polymerase/nicking enzymes and nucleic-acid scaffolds are implemented as DNA machines for the development of amplified DNA-detection schemes, and for the design of logic gates. The analyte nucleic acid target acts, also, as input for the logic gates. In the presence of two DNA targets, acting as inputs, and appropriate DNA scaffolds, the polymerase-induced replication of the scaffolds, followed by the nicking of the replication products, are activated, leading to the autonomous synthesis of the Mg^{2+}-dependent DNAzyme or the Mg^{2+}-dependent DNAzyme subunits. These biocatalysts cleave a fluorophore/quencher-functionalized nucleic-acid substrate, thus providing fluorescence signals for the sensing events or outputs for the logic gates. The systems are used to develop OR, AND, and Controlled-AND gates, and the DNA-analyte targets represent two nucleic acid sequences of the smallpox viral genome.

- A New Mussel-Inspired Polydopamine Sensitizer for Dye-Sensitized Solar Cells: Controlled Synthesis and Charge Transfer
  Daly, R.; Vaz, G.; Davies, A. M.; Senge, M. O.; Scanlan; E. M. *Chem. Eur. J.* **2012**, *18*, 14671–14679.
  Abstract:



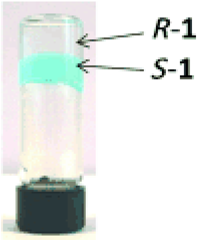
A library of glycosylated porphyrins (glycoporphyrins) was prepared and the compounds were evaluated for their photodynamic therapy (PDT) activity against the oesophageal squamous-cell carcinoma cell line OE21 in vitro. A synthetic methodology was developed to allow incorporation of biologically active carbohydrates, including the histo-blood-group antigen trisaccharide Lewis^{X}, onto the porphyrin backbone. The effect of the carbohydrate group and substitution pattern on the PDT activity, cell uptake and subcellular localisation of the glycoporphyrin compounds is reported.

- Photoinduced Electron Transfer in an Amine–Corrole–Perylene Bisimide Assembly: Charge Separation over Terminal Components Favoured by Solvent Polarity.
  Voloshchuk, R.; Gryko, D. T.; Chotkowski, M.; Ciuciu, A. I.; Flamigni, L. *Chem. Eur. J.* **2012**, *18*, 14845–14859.
  Abstract:



An assembly has been synthesised that consists of four units: a *meso*-substituted corrole (C3), perylene bisimide (PI), and two electron-rich triphenylamine (DPA) units. PI is connected through a 1,4-phenylene bridge to C3, whereas the two DPA units are linked to C3 through a diphenyl ether linkage, which is used for the first time to connect the various moieties. Various synthetic strategies were elaborated, and the chosen one afforded the final system in six steps in an overall yield of 6 %. The resulting assembly, made of three different units, was named a “triad”. Excitation of the corrole (C3) or perylene bisimide (PI) units led to the charge-separated state DPA-C3$^+$-PI$^-$ with a rate k>10^{11} s^{-1} in benzonitrile and dichloromethane (CH_2Cl_2) or with k of the order of 10^{10} s^{-1} in toluene. The latter charge-separated state decayed to the ground state with a rate k=1.8×10^9 s^{-1} in toluene. In the polar solvents benzonitrile and dichloromethane, recombination to the ground state competes with a charge shift to form the distal charge-separated state, DPA$^+$-C3-PI$^-$, the formation of which occurs with a yield of 50 %. Recombination to the ground state of DPA$^+$-C3-PI$^-$ occurs with a rate k=5×10^7 s^{-1} in CH_2Cl_2 and k=2×10^7 s^{-1} in benzonitrile.

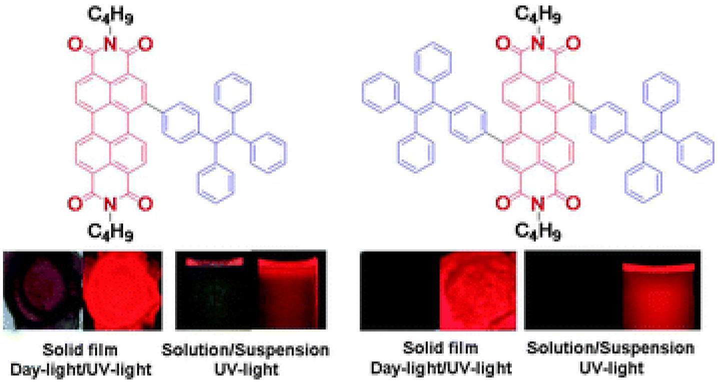
- Self-Assembly Studies of a Chiral Bisurea-Based Superhydrogelator
  Rodríguez-Llansola, F.; Hermida-Merino, D.; Nieto-Ortega, B.; Ramírez, F. J.; Navarrete, J. T. L.; Casado, J.; Hamley, I. W.; Escuder, B.; Hayes, W.; Miravet, J. F. *Chem. Eur. J.* **2012**, *18*, 14725–14731.
  Abstract:



A chiral bisurea-based superhydrogelator that is capable of forming supramolecular hydrogels at concentrations as low as 0.2 mM is reported. This soft material has been characterized by thermal studies, rheology, X-ray diffraction analysis, transmission electron microscopy (TEM), and by various spectroscopic techniques (electronic and vibrational circular dichroism and by FTIR and Raman spectroscopy). The expression of chirality on the molecular and supramolecular levels has been studied and a clear amplification of its chirality into the achiral analogue has been observed. Furthermore, thermal analysis showed that the hydrogelation of compound **1** has a high response to

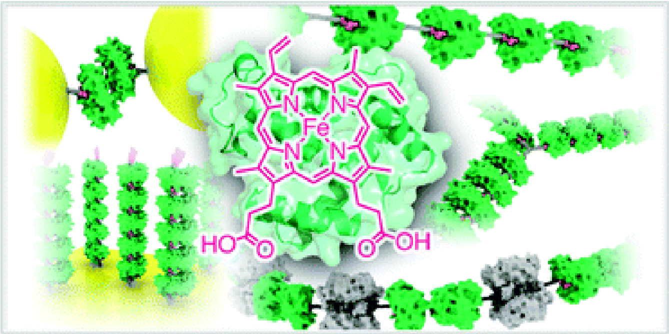
temperature, which corresponds to an enthalpy-driven self-assembly process. These particular thermal characteristics make these materials easy to handle for soft-application technologies.

- Tetraphenylethene modified perylene bisimide: effect of the number of substituents on AIE performance
  Zhao, Q.; Zhang, X. A.; Wei, Q.; Wang, J.; Shen, X. Y.; Qin, A.; Sun, J. Z. ; Tang, B. Z. *Chem. Commun.* **2012,** *48,* 11671–11673.
  Abstract:



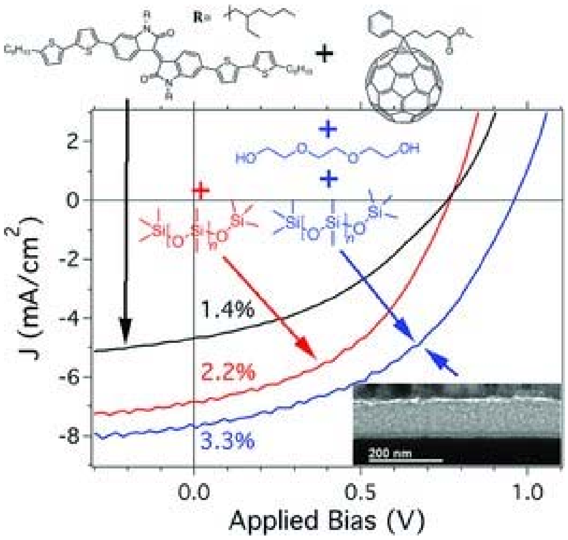
Perylene bisimide derivatives substituted with one and two tetraphenylethene moieties at 1 and 1,7-postions show distinct optical properties. The former displays characteristic emission features of perylene bisimides in solution and red emission in the aggregate state, while the latter is nonemissive in solution but highly red-emissive in the aggregate state.

- Supramolecular assembling systems formed by heme–heme pocket interactions in hemoproteins
  Oohora, K.; Onoda, A.; Hayashi T. *Chem. Commun.* **2012,** *48,* 11714–11726.
  Abstract:



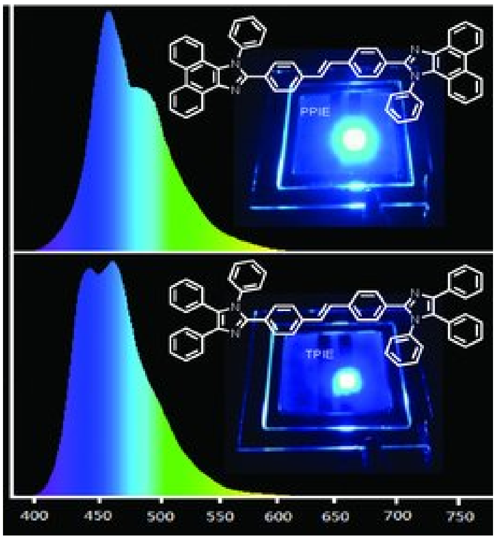
A native protein in a biological system spontaneously produces large and elegant assemblies *via*self-assembly or assembly with various biomolecules which provide non-covalent interactions. In this context, the protein plays a key role in construction of a unique supramolecular structure operating as a functional system. Our group has recently highlighted the structure and function of hemoproteins reconstituted with artificially created heme analogs. The heme molecule is a replaceable cofactor of several hemoproteins. Here, we focus on the successive supramolecular protein assemblies driven by heme–heme pocket interactions to afford various examples of protein fibers, networks and three-dimensional clusters in which an artificial heme moiety is introduced onto the surface of a hemoprotein *via* covalent linkage and the native heme cofactor is removed from the heme pocket. This strategy is found to be useful for constructing hybrid materials with an electrode or with nanoparticles. The new systems described herein are expected to lead to the generation of various biomaterials with functions and characteristic physicochemical properties similar to those of hemoproteins.

- Improved Performance of Molecular Bulk-Heterojunction Photovoltaic Cells through Predictable Selection of Solvent Additives
  Graham, K. R.; Wieruszewski, P. M.; Stalder, R.; Hartel, M. J.; Mei, J.; So, F.; Reynolds, J. R. *Adv. Funct. Mater.* **2012**, *22*, 4801–4813.
  Abstract:



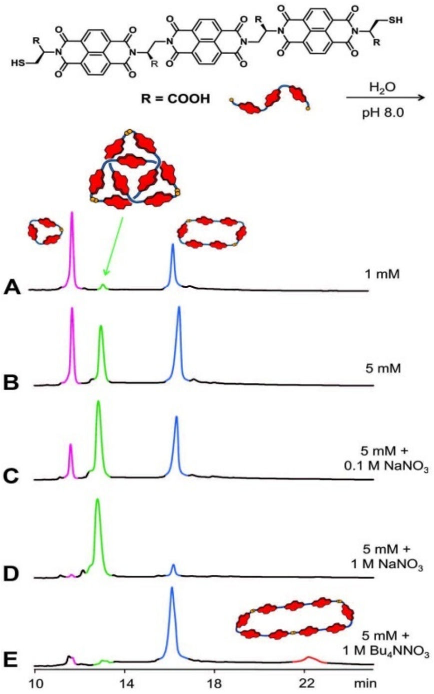
Solvent additives provide an effective means to alter the morphology and thereby improve the performance of organic bulk-heterojunction photovoltaics, although guidelines for selecting an appropriate solvent additive remain relatively unclear. Here, a family of solvent additives spanning a wide range of Hansen solubility parameters is applied to a molecular bulk-heterojunction system consisting of an isoindigo and thiophene containing oligomer as the electron donor and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) as the electron acceptor. Hansen solubility parameters are calculated using the group contribution method and compared with the measured solubilities for use as a screening method in solvent additive selection. The additives are shown to alter the morphologies in a semipredictable manner, with the poorer solvents generally resulting in decreased domain sizes, increased hole mobilities, and improved photovoltaic performance. The additives with larger hydrogen bonding parameters, namely triethylene glycol (TEG) and *N*-methyl-2-pyrrolidone (NMP), are demonstrated to increase the open circuit voltage by ~0.2 V. Combining a solvent additive observed to increase short circuit current, poly(dimethylsiloxane), with TEG results in an increase in power conversion efficiency from 1.4 to 3.3%.

- Synthesis of Diimidazolylstilbenes as n-Type Blue Fluorophores: Alternative Dopant Materials for Highly Efficient Electroluminescent Devices
  Chou, H.-H.; Chen, Y.-H.; Hsu, H.-P.; Chang, W.-H.; Chen, Y.-H.; Cheng, C.-H. *Adv. Mater.* **2012**, *24*, 5867–5871.
  Abstract:



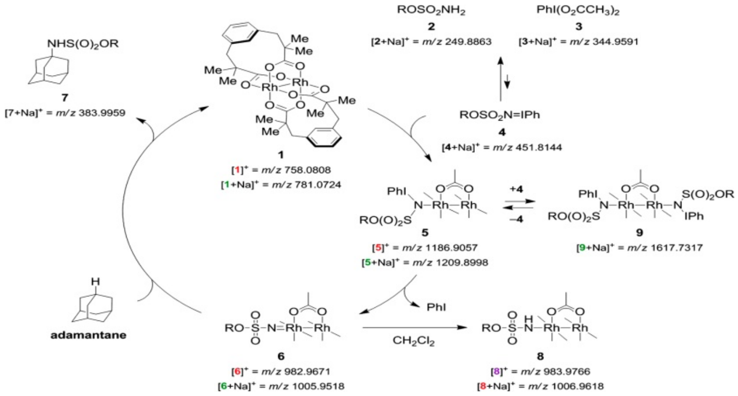
Two new n-type diimidazolylstilbenes as blue-fluorescent dopant materials are synthesized and characterized. Blue-fluorescent devices based on these two compounds as the dopants reveal outstanding external quantum efficiencies (EQEs) (current efficiencies) of 7.8% (10.4 cd A^{-1}) and 7.7% (7.9 cd A^{-1}) with Commission internationale de l'Eclairage (CIE) co-ordinates of (0.14, 0.15) and (0.15, 0.11).

- Discovery of an Organic Trefoil Knot
  Ponnuswamy, N.; Cougnon, F. B. L.; Clough, J. M.; Dan Pantos, G.; Sanders, J. K. M. *Science* **2012**, *338*, 783-785.
  <u>Abstract:</u>



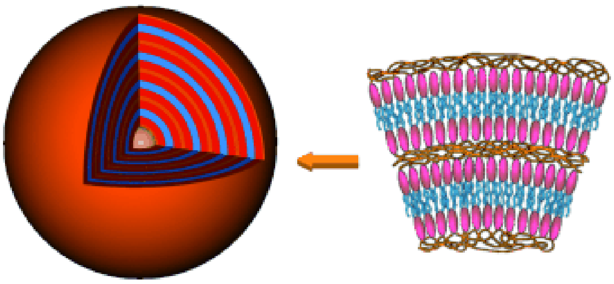
Molecular knots remain difficult to produce using the current synthetic methods of chemistry because of their topological complexity. We report here the near-quantitative self-assembly of a trefoil knot from a naphthalenediimide-based aqueous disulfide dynamic combinatorial library. The formation of the knot appears to be driven by the hydrophobic effect and leads to a structure in which the aromatic components are buried while the hydrophilic carboxylate groups remain exposed to the solvent. Moreover, the building block chirality constrains the topological conformation of the knot and results in its stereoselective synthesis. This work demonstrates that the hydrophobic effect provides a powerful strategy to direct the synthesis of entwined architectures.

- Capturing fleeting intermediates in a catalytic C-H amination reaction cycle
  Perry, R. H.; Cahill III, T. J.; Roizen, J. L.; Du Bois, J.; Zare, R. N. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 18295-18299.
  Abstract:



We have applied an ambient ionization technique, desorption electrospray ionization MS, to identify transient reactive species of an archetypal C-H amination reaction catalyzed by a dirhodium tetracarboxylate complex. Using this analytical method, we have detected previously proposed short-lived reaction intermediates, including two nitrenoid complexes that differ in oxidation state. Our findings suggest that an Rh-nitrene oxidant can react with hydrocarbon substrates through a hydrogen atom abstraction pathway and raise the intriguing possibility that two catalytic C-H amination pathways may be operative in a typical bulk solution reaction. As highlighted by these results, desorption electrospray ionization MS should have broad applicability for the mechanistic study of catalytic processes.

- Light-Switchable Vesicles from Liquid-Crystalline Homopolymer–Surfactant Complexes
  Li, L.; Rosenthal, M.; Zhang, H.; Hernandez, J. J.; Drechsler, M.; Phan, K. H.; Rütten, S.; Zhu, X.; Ivanov, D. A.; Möller, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 11616–11619.
  Abstract:

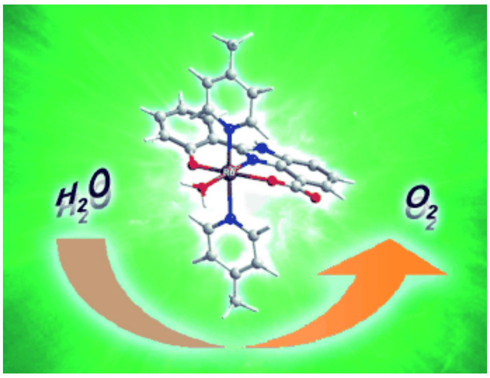


Polymeric onions: A concept of vesicle fabrication based on nonstoichiometric complexation of a polybase with an amphiphilic ligand bearing a sulfonic acid group is developed (see picture). In contrast to conventional polymersomes, the polymer backbones are oriented mainly parallel to the vesicle walls. The vesicles can collapse under UV irradiation because of a UV-triggered *trans–cis* isomerization of the azo-group-containing ligand.

- Water Oxidation by Single-Site Ruthenium Complexes: Using Ligands as Redox and Proton Transfer Mediators

  Kärkäs, M. D.; Åkermark, T.; Johnston, E. V.; Karim, S. R.; Laine, T. M.; Lee, B.-L.; Åkermark, T.; Privalov, T.; Åkermark, B. *Angew. Chem. Int. Ed.* **2012**, *51*, 11589–11593.

  Abstract:

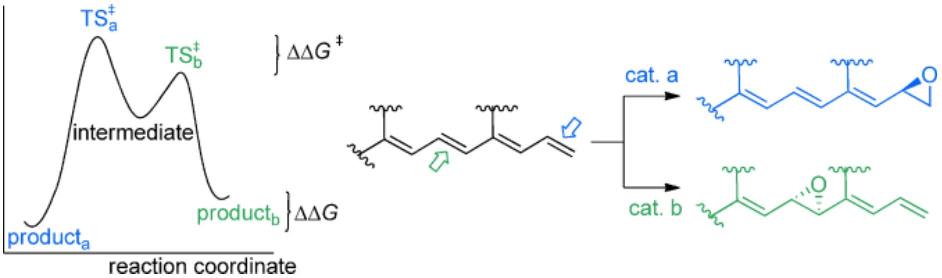


Light me up: Through the use of an imidazole motif it is possible to introduce a combined redox and proton-transfer mediator into single-site ruthenium water-oxidation catalysts. With the complex (see picture), high turnover numbers and high initial turnover frequencies were attained with the mild oxidant $[Ru(bpy)_3]^{3+}$ (bpy=2,2′-bipyridine).

- Catalytic Selective Synthesis

  Mahatthananchai, J.; Dumas, A. M.; Bode, J. W. *Angew. Chem. Int. Ed.* **2012**, *51*, 10954–10990.

  Abstract:

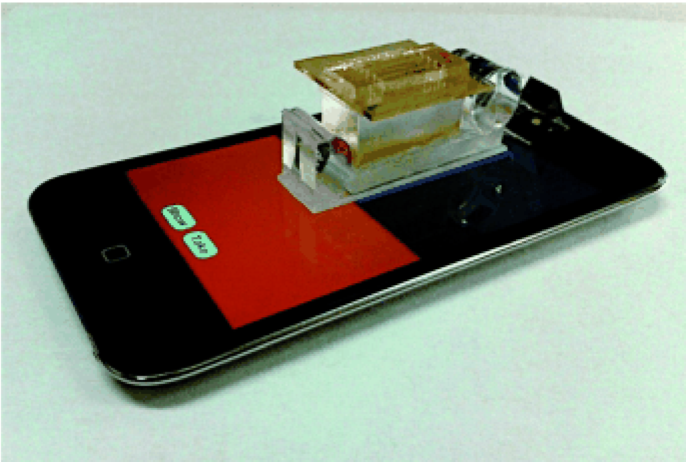


A tale of two catalysts: Catalyst-controlled selectivity is well established for enantioselective catalysis but less formulated for catalytic regio-, chemo,- or product-selective reactions. This Review describes selective transformations of the same starting materials into two or more different products simply by the choice of catalyst even when the reaction conditions are nearly identical.

- Surface Plasmon Resonance Chemical Sensing on Cell Phones

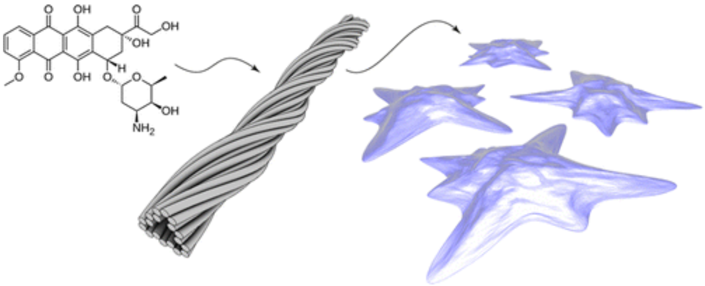
  Preechaburana, P.; Gonzalez, M. C.; Suska, A.; Filippini, D. *Angew. Chem. Int. Ed.* **2012**, *51*, 11585–11588.

  Abstract:



Chemosensing based on angle-resolved surface plasmon resonance is demonstrated on intact cell phones using a disposable optical coupler and software to configure illumination and acquisition. This coupler operates on different cell phones and is applied for classical affinity assays with commercial chips and custom-made tests with embedded calibration. Measured performance (2.14x10−6 refractive index units) is comparable with compact SPR systems.

- DNA Origami Delivery System for Cancer Therapy with Tunable Release Properties
  Zhao, Y.-X.; Shaw, A.; Zeng, X.; Benson, E.; Nyström, A. M.; Högberg, B. *ACS Nano* **2012**, *6*, 8684-8691.
  Abstract:

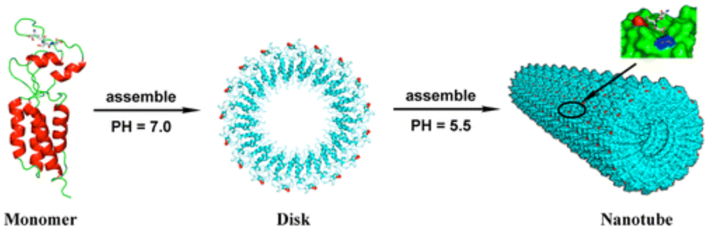


In the assembly of DNA nanostructures, the specificity of Watson–Crick base pairing is used to control matter at the nanoscale. Using this technology for drug delivery is a promising route toward the magic bullet concept, as it would allow the realization of complex assemblies that co-localize drugs, targeting ligands and other functionalities in one nanostructure. Anthracyclines' mechanism of action in cancer therapy is to intercalate DNA, and since DNA nanotechnology allows for such a high degree of customization, we hypothesized that this would allow us to tune the DNA nanostructures for optimal delivery of the anthracycline doxorubicin (Dox) to human breast cancer cells. We have tested two DNA origami nanostructures on three different breast cancer cell lines (MDA-MB-231, MDA-MB-468, and MCF-7). The different nanostructures were designed to exhibit varying degrees of global twist, leading to different amounts of relaxation in the DNA double-helix structure. By tuning the nanostructure design we are able to (i) tune the encapsulation efficiency and the release rate of the drug and (ii) increase the cytotoxicity and lower the intracellular elimination rate when compared to free Dox. Enhanced apoptosis induced by the delivery system in breast cancer cells was investigated using flow cytometry. The findings indicate that DNA origami nanostructures represent an efficient delivery system for Dox, resulting in high degrees of internalization and increased induction of programmed cell death in breast cancer cells. In addition, by designing the structures to exhibit different degrees of twist, we are able to rationally control and tailor the drug release kinetics.

- Construction of GPx Active Centers on Natural Protein Nanodisk/Nanotube: A New Way to Develop Artificial Nanoenzyme

  Hou, C.; Luo, Q.; Liu, J.; Miao, L.; Zhang, C.; Gao, Y.; Zhang, X.; Xu, J.; Dong, Z.; Liu, J. *ACS Nano* **2012**, *6*, 8692-8701.

  <u>Abstract:</u>

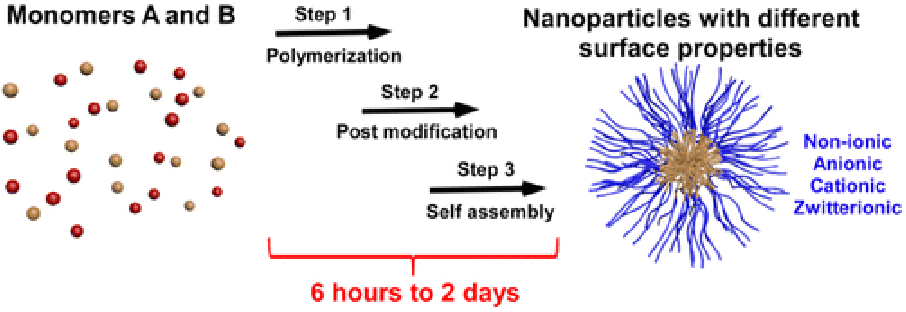


Construction of catalytic centers on natural protein aggregates is a challenging topic in biomaterial and biomedicine research. Here we report a novel construction of artificial nanoenzyme with glutathione peroxidase (GPx)-like function. By engineering the surface of tobacco mosaic virus (TMV) coat protein, the main catalytic components of GPx were fabricated on TMV protein monomers. Through direct self-assembly of the functionalized viral coat proteins, the multi-GPx centers were installed on these well-defined nanodisks or nanotubes. With the help of muti-selenoenzyme centers, the resulting organized nanoenzyme exhibited remarkable GPx activity, even approaching the level of natural GPx. The antioxidation study on subcell mitochondrial level demonstrated that virus-based nanoenzyme exerted excellent capacity for protecting cell from oxidative damage. This strategy represents a new way to develop artificial nanoenzymes.

- Rapid and Versatile Construction of Diverse and Functional Nanostructures Derived from a Polyphosphoester-Based Biomimetic Block Copolymer System

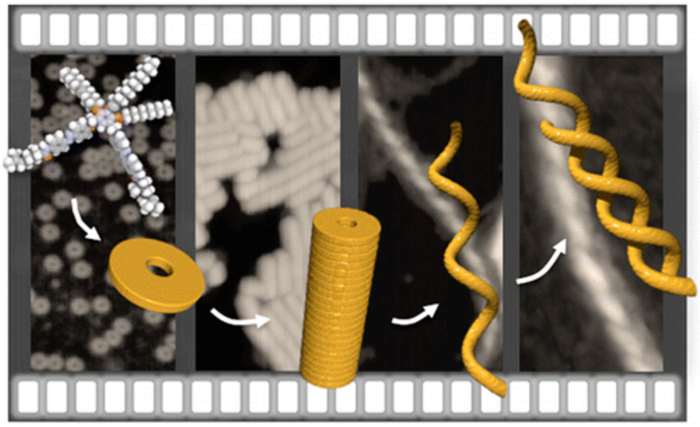
  Zhang, S.; Zou, J.; Zhang, F.; Elsabahy, M.; Felder, S. E.; Zhu, J.; Pochan, D. J.; Wooley K. L. *J. Am. Chem. Soc.* **2012**, *134*, 18467–18474.

  <u>Abstract:</u>



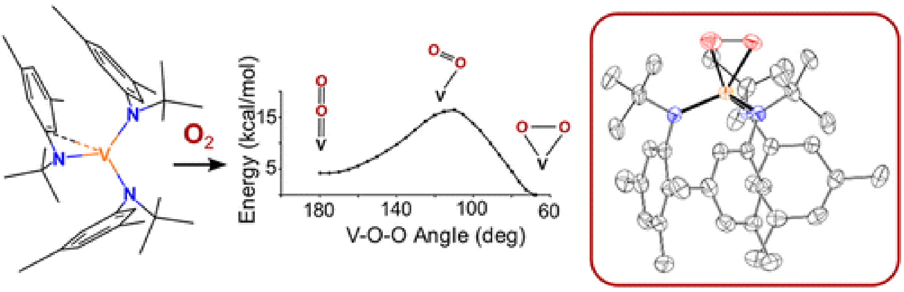
A rapid and efficient approach for the preparation and modification of a versatile class of functional polymer nanoparticles has been developed, for which the entire engineering process from small molecules to polymers to nanoparticles bypasses typical slow and inefficient procedures and rather employs a series of steps that capture fully the “click” chemistry concepts that have greatly facilitated the preparation of complex polymer materials over the past decade. The construction of various nanoparticles with functional complexity from a versatile platform is a challenging aim to provide materials for fundamental studies and also optimization toward a diverse range of applications. In this paper, we demonstrate the rapid and facile preparation of a family of nanoparticles with different surface charges and functionalities based on a biodegradable polyphosphoester block copolymer system. From a retrosynthetic point of view, the nonionic, anionic, cationic, and zwitterionic micelles with hydrodynamic diameters between 13 and 21 nm and great size uniformity were quickly formed by suspending, independently, four amphiphilic diblock polyphosphoesters into water, which were functionalized from the same parental hydrophobic-functional AB diblock polyphosphoester by click-type thiol–yne reactions. The well-defined (PDI < 1.2) hydrophobic-functional AB diblock polyphosphoester was synthesized by an ultrafast (<5 min) organocatalyzed ring-opening polymerization in a two-step, one-pot manner with the quantitative conversions of two kinds of cyclic phospholane monomers. The whole programmable process starting from small molecules to nanoparticles could be completed within 6 h, as the most rapid approach for the anionic and nonionic nanoparticles, although the cationic and zwitterionic nanoparticles required ca. 2 days due to purification by dialysis. The micelles showed high biocompatibility, with even the cationic micelles exhibiting a 6-fold lower cytotoxicity toward RAW 264.7 mouse macrophage cells, as compared to the commercial transfection agent Lipofectamine.

- Control over Hierarchy Levels in the Self-Assembly of Stackable Nanotoroids
  Yagai, S.; Yamauchi, M.; Kobayashi, A.; Karatsu, T.; Kitamura, A.; Ohba, T.; Kikkawa, Y. *J. Am. Chem. Soc.* **2012**, *134*, 18205–18208.
  Abstract:



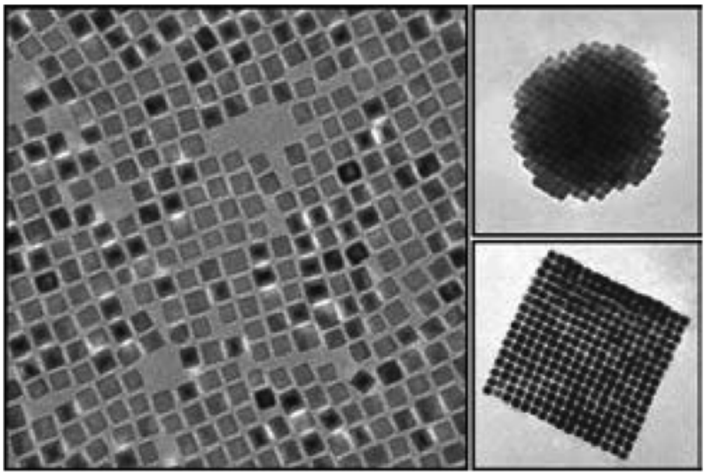
We report a precise control over the hierarchy levels in the outstanding self-organization process shown by chiral azobenzene dimer **1**. This compound forms uniform toroidal nanostructures that can hierarchically organize into chiral nanotubes under the control by temperature, concentration, or light. The nanotubes further organized into supercoiled fibrils, which finally intertwined to form double helices with one-handed helical sense.

- Two-Step Binding of O_2 to a Vanadium(III) Trisanilide Complex To Form a Non-Vanadyl Vanadium(V) Peroxo Complex
  Cozzolino, A. F.; Tofan, D.; Cummins, C. C.; Temprado, M.; Palluccio, T. D.; Rybak-Akimova, E. V.; Majumdar, S.; Cai, X.; Captain, B.; Hoff, C. D. *J. Am. Chem. Soc.* **2012**, *134*, 18249–18252.
  Abstract:



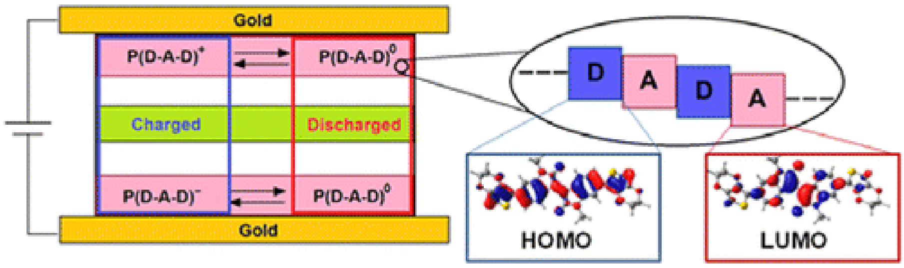
Treatment of V(N[^{t}Bu]Ar)$_3$ (**1**) (Ar = 3,5-Me$_2$C$_6$H$_3$) with O$_2$ was shown by stopped-flow kinetic studies to result in the rapid formation of (η^1-O$_2$)V(N[^{t}Bu]Ar)$_3$ (**2**) ($\Delta H^{\ddagger}$ = 3.3 ± 0.2 kcal/mol and $\Delta S^{\ddagger}$ = −22 ± 1 cal mol^{-1} K^{-1}), which subsequently isomerizes to (η^2-O$_2$)V(N[^{t}Bu]Ar)$_3$ (**3**) ($\Delta H^{\ddagger}$ = 10.3 ± 0.9 kcal/mol and $\Delta S^{\ddagger}$ = −6 ± 4 cal mol^{-1} K^{-1}). The enthalpy of binding of O$_2$ to form **3** is −75.0 ± 2.0 kcal/mol, as measured by solution calorimetry. The reaction of **3** and **1** to form 2 equiv of O≡V(N[^{t}Bu]Ar)$_3$ (**4**) occurs by initial isomerization of **3** to **2**. The results of computational studies of this rearrangement (ΔH = 4.2 kcal/mol; $\Delta H^{\ddagger}$ = 16 kcal/mol) are in accord with experimental data (ΔH = 4 ± 3 kcal/mol; $\Delta H^{\ddagger}$ = 14 ± 3 kcal/mol). With the aim of suppressing the formation of **4**, the reaction of O$_2$ with **1** in the presence of ^{t}BuCN was studied. At −45 °C, the principal products of this reaction are **3** and ^{t}BuC(═O)N═V(N[^{t}Bu]Ar)$_3$ (**5**), in which the bound nitrile has been oxidized. Crystal structures of **3** and **5** are reported.

- Shape-Controlled Synthesis of Colloidal Superparticles from Nanocubes
  Wang, T.; Wang, X.; LaMontagne, D.; Wang, Z.; Wang, Z.; Cao, Y. C. *J. Am. Chem. Soc.* **2012**, *134*, 18225–18228.
  Abstract:



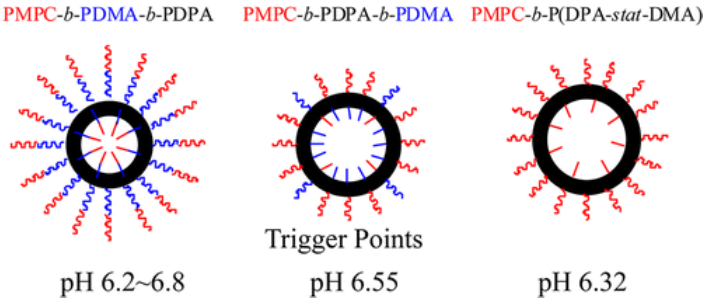
This communication reports a shape-controlled synthesis of colloidal superparticles (SPs) from iron oxide nanocubes. Our results show that the formation of SPs is under thermodynamic control and that their shape is determined by Gibbs free energy minimization. The resulting SPs adopt a simple-cubic superlattice structure, and their shape can be tuned between spheres and cubes by varying the relative free energy contributions from the surface and bulk free energy terms. The formation of sphere-shaped SPs from nanocubes suggests that the size-dependent hydration effect predicted by the Lum–Chandler–Weeks theory plays a very important role in the self-assembly of nano-objects. In addition, the iron oxide SPs exhibit shape-dependent therapeutic effects in magnetomechanical treatments of cancer cells in vitro.

- Poly[Bis-EDOT-Isoindigo]: An Electroactive Polymer Applied to Electrochemical Supercapacitors
  Estrada, L. A.; Liu, D. Y. ; Salazar, D. H. ; Dyer, A. L.; Reynolds, J. R. *Macromolecules* **2012**, *45*, 8211–8220.
  Abstract:



Poly[6,6′-bis(ethylene-3,4-dioxythien-2-yl)]-*N*,*N*′-dialkylisoindigo (PBEDOT-iI) was synthesized and incorporated as an electroactive material into electrochemical supercapacitors (ESCs) in type I and type III configurations. In type I ESCs, PBEDOT-iI provides a specific power of ~360 W/kg and specific energy of ~0.5 Wh/kg, while retaining about 80% of its electroactivity over 10 000 cycles. In addition, we report on the use of PBEDOT-iI in type III supercapacitors where operating voltages as high as 2.5 V were achieved with specific energies of ca. 15 Wh/kg, albeit with limited stability.

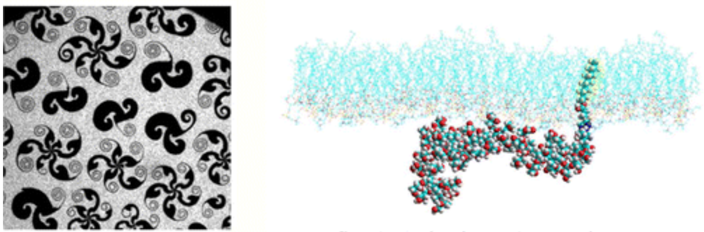
- pH-Sensitive Block Copolymer Vesicles with Variable Trigger Points for Drug Delivery
  Du, J.; Fan, L.; Liu, Q. *Macromolecules* **2012**, *45*, 8275–8283.
  Abstract:



We have previously reported the preparation of a novel pH-sensitive and biocompatible polymer vesicle in pure water based on the spontaneous self-assembly of a diblock copolymer, PMPC-*b*-PDPA, where PMPC is poly[2-(methacryloyloxy)ethyl phosphorylcholine] and PDPA is poly[2-(diisopropylamino)ethyl methacrylate] (*J. Am. Chem. Soc.* 2005, *127*, 17982). Herein, we intend to report the strategy for controlling the pH trigger points of association/dissociation of pH-responsive polymer vesicles for anticancer drug delivery. We introduced a reactive block, poly[2-(dimethylamino)ethyl methacrylate] (PDMA) into the above diblock copolymer to form reactive PMPC-*b*-PDMA-*b*-PDPA and PMPC-*b*-PDPA-*b*-PDMA triblock copolymers, as well as PMPC-*b*-P(DMA-*stat*-DPA) block-statistical copolymer by atom transfer radical polymerization (ATRP) in methanol at room temperature. As a result of different block length of PDPA, the introduction of PDMA chain at different positions, and different initial copolymer concentrations, those block copolymer vesicles showed tunable pH trigger points and various isoelectric points (IEPs) in aqueous solution. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) studies confirmed that the block copolymers with relatively long PDPA block form polymer vesicles by simply tuning the solution pH in pure water. Above pH 6.2, the PDPA block becomes hydrophobic so it forms the vesicle membrane. In all cases, the hydrophilic PMPC chains form the vesicle coronas. The PDMA

chains are designed in three different positions. In PMPC-*b*-PDMA-*b*-PDPA vesicles, the PDMA chains form the middle shell between the PDPA vesicle membrane and the PMPC vesicle corona. In PMPC-*b*-PDPA-*b*-PDMA vesicles, the PDMA can mix with PMPC to serve as mixed coronas. In PMPC-*b*-P(DMA-*stat*-DPA) vesicles, the reactive PDMA chains can be incorporated into the vesicle membrane, which provides an effective strategy regarding the immobilization of vesicles by selective quaternization of PDMA with a bifunctional cross-linker, such as 1,2-bis(2-iodoethoxy)ethane (BIEE). The degree of cross-linking can be tuned by varying the molar ratio of PDMA to BIEE, which was further investigated by ^{1}H NMR, DLS, and TEM, suggesting tunable permeability of vesicle membrane. The triblock copolymer vesicles were able to encapsulate anticancer drugs such as DOX, exhibiting obviously retarded release profile at physiological conditions.

- Interactions of DPPC with Semitelechelic Poly(glycerol methacrylate)s with Perfluoroalkyl End Groups
  Scholtysek, P.; Li, Z.; Kressler, J.; Blume, A. *Langmuir* **2012**, *28*, 15651–15662.
  Abstract:

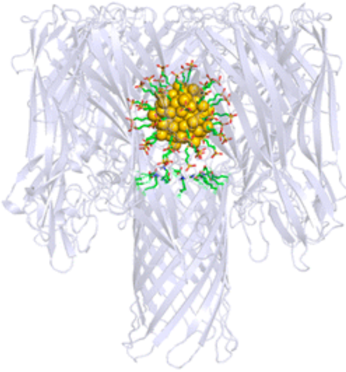

DPPC LC-domains
fluorinated polymer in monolayer

Semitelechelic poly(glycerol methacrylate)s having a perfluoroalkyl end group (PGMA(n)-F(9)) were synthesized by ATRP. The interactions of these polymers with different degrees of polymerization with chiral or racemic dipalmitoylphosphatidylcholine (l-DPPC, d-DPPC, or rac-DPPC) monolayers at the air/water interface were studied. Langmuir trough measurements coupled with epifluorescence microscopy allowed for the observation of domain formation within the coexistence region of liquid-expanded (LE) and liquid-condensed (LC) states of DPPC in mixed DPPC-polymer films prepared by spreading a solution of both compounds in the same organic solvent (cospread films). Because of the incorporation of PGMA(n)-F(9) polymers into the LE phase and their line-active behavior, a formation of novel types of domains could be observed. During compression, a thinning out of the tips of two- to six-lobed flowerlike domain structures and consecutive spiral formation appeared for l- and d-DPPC within the two-phase coexistence region (LE/LC) of the monolayer. When rac-DPPC was used, symmetrical stripe formation was induced at the vertices of the domains and fingerprint-like structures were created by convection-inducing movements of the domains at the air/water interface. Additional investigations of the interaction of PGMA(n)-F(9) with DPPC vesicles using differential scanning calorimetry (DSC) supported the finding on the monolayer system that the incorporation of the polymers into the lipid monolayers is not solely driven by the perfluoroalkyl chain but significantly by the hydrophilic polymer part. Apparently, interactions of the PGMA chain with the lipid headgroups are important as the interactions increase with the elongation of the polymer chain, indicating that the polymer also has hydrophobic character.

- The Role of Lys147 in the Interaction between MPSA-Gold Nanoparticles and the α-Hemolysin Nanopore

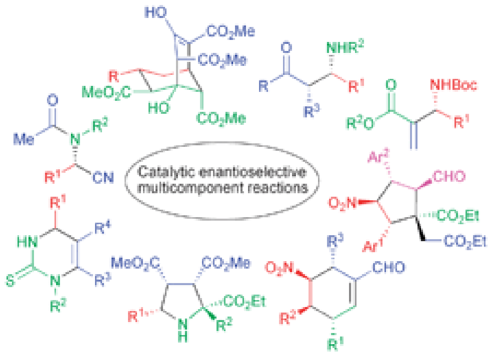
Campos, E.; Asandei, A.; McVey, C. E.; Dias, J. C.; Oliveira, A. S. F.; Soares, C. M.; Luchian, T.; Astier, Y. *Langmuir* **2012**, *28*, 15643–15650.

Abstract:



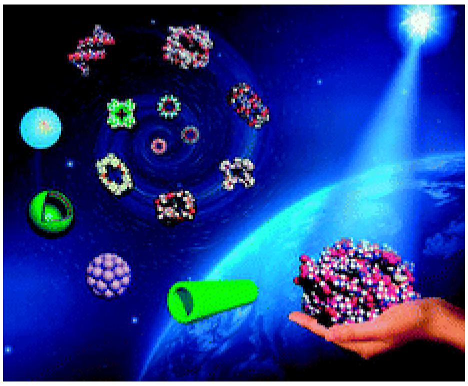
Single channel recordings were used to determine the effect of direct electrostatic interactions between sulfonate-coated gold nanoparticles and the constriction of the *Staphylococcus aureus* α-hemolysin protein channel on the ionic current amplitude. We provide evidence that Lys147 of α-hemolysin can interact with the sulfonate groups at the nanoparticle surface, and these interactions can reversibly block 100% of the residual ionic current. Lys147 is normally involved in a salt bridge with Glu111. The capture of a nanoparticle leads to a partial current block at neutral pH values, but protonation of Glu111 at pH 2.8 results in a full current block when the nanoparticle is captured. At pH 2.8, we suggest that Lys147 is free to engage in electrostatic interactions with sulfonates at the nanoparticle surface. To verify our results, we engineered a mutation in the α-hemolysin protein, where Glu111 is substituted by Ala (E111A), thus removing Glu111–Lys147 interactions and facilitating Lys147–sulfonate electrostatic interactions. This mutation leads to a 100% current block at pH 2.8 and a 92% block at pH 8.0, showing that electrostatic interactions are formed between the nanopore and the nanoparticle surface. Besides demonstrating the effect of electrostatic interactions on cross channel ionic current, this work offers a novel approach to controlling open and closed states of the α-hemolysin nanopore as a function of external gears.

- Multicomponent and sequential organocatalytic reactions: diversity with atom-economy and enantiocontrol
  Marson, C. M. *Chem. Soc. Rev.* **2012**, *41*, 7712-7722.
  Abstract:



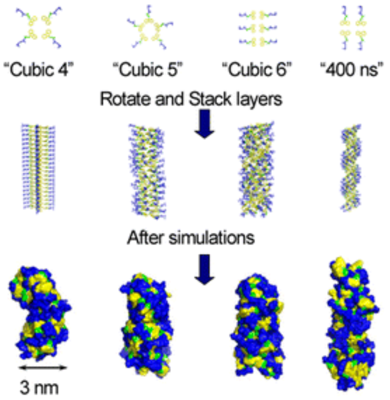
Reactions in which several components are combined in sequence, and without isolation of intermediates, are greatly sought because of the inherent molecular diversity, efficiency, and atom-economy. However, organocatalytic reactions, employing an organic catalyst to assemble products of high enantiomeric excess (a single optical isomer), are also cutting-edge methodology. This *tutorial* *review* covers the overlap of these two areas, outling the structural diversity and stereocontrol arising from one-pot combinations of at least three components, powerful approaches with great potential that minimise formation of by-products and operating costs.

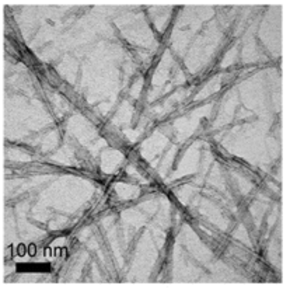
- Artificial enzymes based on supramolecular scaffolds
  Dong, Z.; Luo, Q.; Liu, J. *Chem. Soc. Rev.* **2012**, *41*, 7890-7908.
  <u>Abstract:</u>



Enzymes are nanometer-sized molecules with three-dimensional structures created by the folding and self-assembly of polymeric chain-like components through supramolecular interactions. They are capable of performing catalytic functions usually accompanied by a variety of conformational states. The conformational diversities and complexities of natural enzymes exerted in catalysis seriously restrict the detailed understanding of enzymatic mechanisms in molecular terms. A supramolecular viewpoint is undoubtedly helpful in understanding the principle of enzyme catalysis. The emergence of supramolecular artificial enzymes therefore provides an alternative way to approach the structural complexity and thus to unravel the mystery of enzyme catalysis. This *critical review* covers the recent development of artificial enzymes designed based on supramolecular scaffolds ranging from the synthetic macrocycles to self-assembled nanometer-sized objects. Such findings are anticipated to facilitate the design of supramolecular artificial enzymes as well as their potential uses in important fields, such as manufacturing and food industries, environmental biosensors, pharmaceutics and so on.

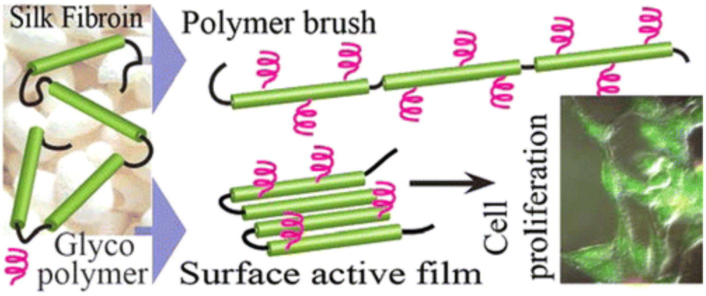
- Experimental and Computational Studies Reveal an Alternative Supramolecular Structure for Fmoc-Dipeptide Self-Assembly
  Mu, X.; Eckes, K. M.; Nguyen M. M.; Suggs L. J.; Ren, P. *Biomacromolecules* **2012**, *13*, 3562–3571.
  <u>Abstract:</u>





We have investigated the self-assembly of fluorenylmethoxycarbonyl-conjugated dialanine (Fmoc-AA) molecules using combined computational and experimental approaches. Fmoc-AA gels were characterized using transmission electron microscopy (TEM), circular dichroism (CD), Fourier transform infrared (FTIR), and wide-angle X-ray scattering (WAXS). Computationally, we simulated the assembly of Fmoc-AA using molecular dynamics techniques. All simulations converged to a condensed fibril structure in which the Fmoc groups stack mostly within in the center of the fibril. However, the Fmoc groups are partially exposed to water, creating an amphiphilic surface, which may be responsible for the aggregation of fibrils into nanoscale fibers observed in TEM. From the fibril models, radial distribution calculations agree with *d*-spacings observed in WAXS for the fibril diameter and π-stacking interactions. Our analyses show that dialanine, despite its short length, adopts a mainly extended polyproline II conformation. In contrast to previous hypotheses, these results indicate that β-sheet-like hydrogen bonding is not prevalent. Rather, stacking of Fmoc groups, inter-residue hydrogen bonding, and hydrogen bonding with water play the important roles in stabilizing the fibril structure of supramolecular assemblies of short conjugated peptides.

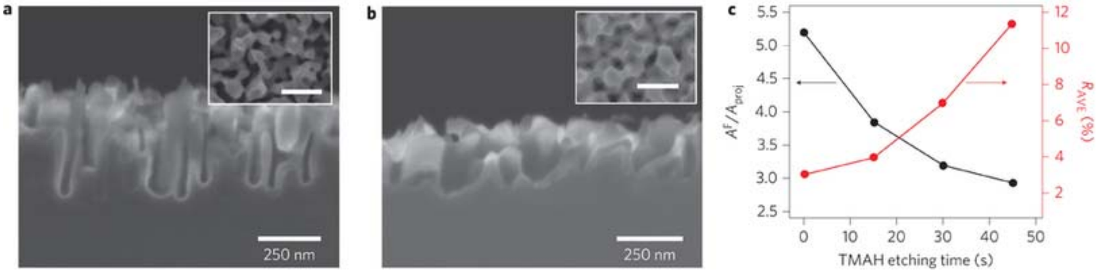
- Synthesis of Silk Fibroin–Glycopolypeptide Conjugates and Their Recognition with Lectin
  Das, S.; Pati, D.; Tiwari, N.; Nisal, A.; Gupta, S. S. *Biomacromolecules* **2012**, *13*, 3695–3702.
  Abstract:



Silk fibroin (SF), the natural fibrous protein created by the *Bombyx mori* silk worm, is being increasingly explored as a biomaterial for tissue engineering due to its excellent mechanical strength, high oxygen/water permeability, and biocompatibility. It is also well known that surface modification of SF with organic ligands such as the extracellular protein binding Arg-Gly-Asp (RGD) peptides help adhesion and proliferation of cells better—a key requirement for it to function as extracellular matrices. In this work, we have conjugated synthetic glycopolypeptides (GPs) that were synthesized by controlled ring-opening polymerization of α-*manno*-lys *N*-carboxyanhydrides (NCAs) onto SF by using Cu catalyzed click reaction to synthesize a new hybrid material (SF–GP), which we believe will have both the mechanical properties of native SF and the molecular recognition property of the carbohydrates in the GP. By controlling the amount of GP grafted onto SF, we have made three SF–GP conjugates that differ in their ability to assemble into films. SF–GP conjugates having a very high content of GP formed completely water-soluble brush-like polymer that displayed very high affinity toward the lectin concanavalin-A (Con-A). Films cast from SF–GP conjugates using lower amounts of grafted GP were more stable in water, and the stability can be modulated by varying the amount of GP grafted. The water-insoluble film SF–GP_{25} was also found to bind to fluorescently labeled Con-A, as was seen by confocal microscopy. Such SF–GP hybrid films may be useful as mimics of extracellular matrices for tissue engineering.

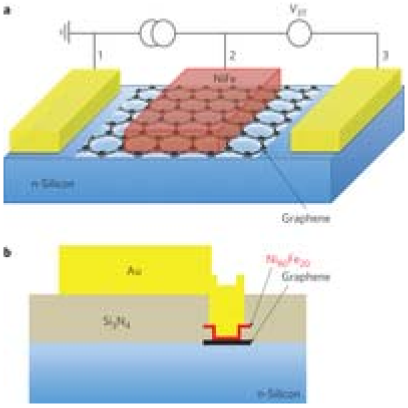
- An 18.2%-efficient black-silicon solar cell achieved through control of carrier recombination in nanostructures

Oh, J.; Yuan, H-C.; Branz, H. M. *Nature Nanotechnology* **2012**, *7*, 743–748.
Abstract:



Silicon nanowire and nanopore arrays promise to reduce manufacturing costs and increase the power conversion efficiency of photovoltaic devices. So far, however, photovoltaic cells based on nanostructured silicon exhibit lower power conversion efficiencies than conventional cells due to the enhanced photocarrier recombination associated with the nanostructures. Here, we identify and separately measure surface recombination and Auger recombination in wafer-based nanostructured silicon solar cells. By identifying the regimes of junction doping concentration in which each mechanism dominates, we were able to design and fabricate an independently confirmed 18.2%-efficient nanostructured 'black-silicon' cell that does not need the antireflection coating layer(s) normally required to reach a comparable performance level. Our results suggest design rules for efficient high-surface-area solar cells with nano- and microstructured semiconductor absorbers.

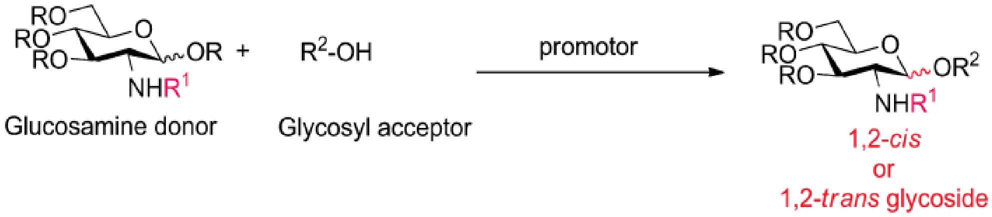
- Low-resistance spin injection into silicon using graphene tunnel barriers
  van 't Erve, O. M. J.; Friedman, A. L.; Cobas, E.; Li, C. H.; Robinson, J. T.; Jonker, B. T. *Nature Nanotechnology* **2012**, *7*, 737–742.
  Abstract:



Spin manipulation in a semiconductor offers a new paradigm for device operation beyond Moore's law. Ferromagnetic metals are ideal contacts for spin injection and detection, but the intervening tunnel barrier required to accommodate the large difference in conductivity introduces defects, trapped charge and material interdiffusion, which severely compromise performance. Here, we show that single-layer graphene successfully circumvents the classic issue of conductivity mismatch between a metal and a semiconductor for electrical spin injection and detection, providing a highly uniform, chemically inert and thermally robust tunnel barrier. We demonstrate electrical generation and detection of spin accumulation in silicon above room temperature, and show that the contact resistance–area products are two to three orders of magnitude lower than those achieved with oxide tunnel barriers on silicon substrates with identical doping levels. Our results identify a new route to low resistance–area product spin-polarized contacts, a key requirement for semiconductor spintronic

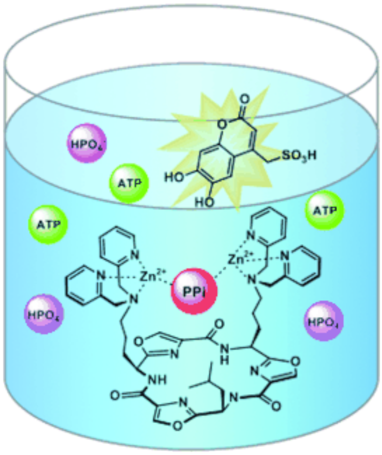
devices that rely on two-terminal magnetoresistance, including spin-based transistors, logic and memory.

- Stereoselective Glycosylation of Glucosamine: The Role of the *N*-Protecting Group
  Enugala, R.; Carvalho, L. C. R.; Dias Pires, M. J.; Marques, M. M. B. *Chem. Asian J.* **2012**, *7,* 2482–2501.
  Abstract:



Oligosaccharides and glycoconjugates play an important role in biological processes. The use of these complex polymers as biocompatible materials for medicinal applications as well as therapeutic agents for the treatment of several diseases has attracted considerable interest. However, these investigations require large and pure amounts of glycostructures. Glucosamine is one of the major building blocks of these highly important glycoconjugates. Recently, considerable synthetic efforts have been devoted to improving stereoselective glycosylation. In this Focus review, the role of the amine protecting group in the outcome of the glucosamine glycosylation reaction is highlighted.

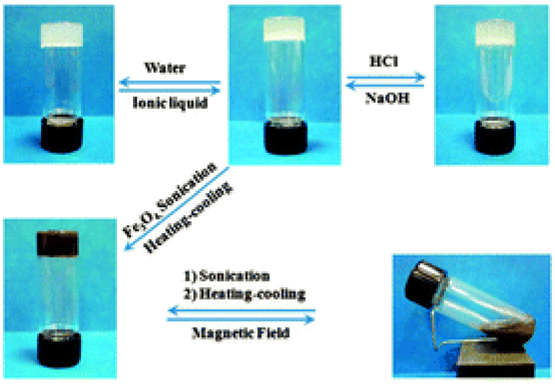
- Selective Pyrophosphate Recognition by Cyclic Peptide Receptors in Physiological Saline
  Butler, S. J.; Jolliffe, K. A. *Chem. Asian J.* **2012**, *7,* 2621–2628
  Abstract:



The anion binding ability of a family of bis(ZnII-Dpa) functionalized cyclic peptides has been investigated using displacement assays with a fluorescent coumarin indicator in water, saline solution, and Krebs buffer. Non-binding side-chain steric bulk, the relative position of binding sites, and the scaffold size were all found to affect the ability of these receptors to discriminate between polyphosphate ions. Most receptors showed some selectivity for pyrophosphate over ATP and ADP in water and saline, and this selectivity was significantly enhanced in the biologically relevant Krebs buffer giving chemosensing ensembles capable of selective recognition of pyrophosphate in the presence of excess ATP.

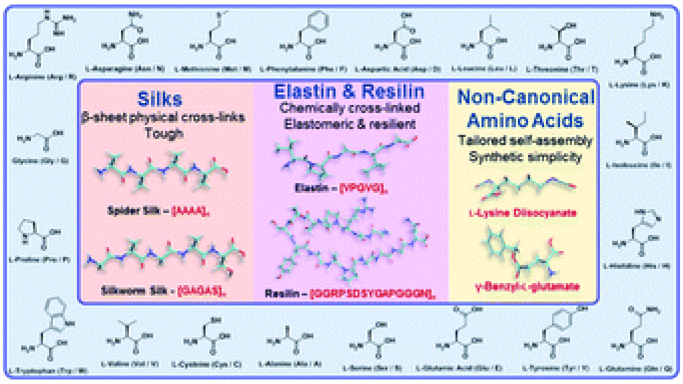
- Cholesterol-based low-molecular mass gelators towards smart ionogels
  Yan, J.; Liu, J.; Jing, P.; Xu, C.; Wu, J.; Gao, D.; Fang, Y. *Soft Matter* **2012**, *8*, 11697-11703.

Abstract:



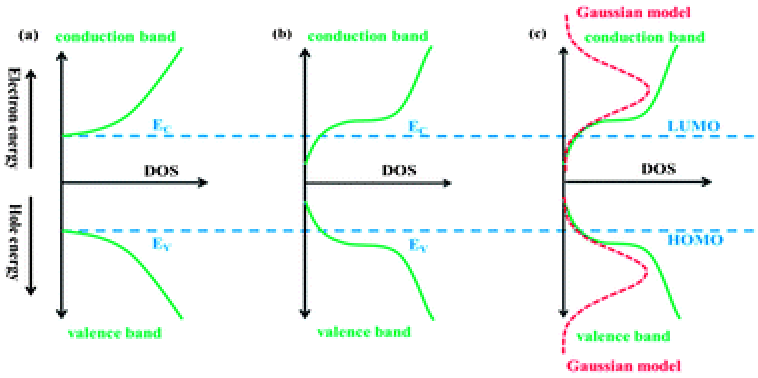
Ionic liquids are solvents of future. One of the promising methods to boost their uses is to solidify them in a physical way but with little interruption of their properties. It is therefore of interest to create gels of ionic liquids by using low-molecular mass compounds as gelators (LMMGs). Herein, we report a number of ionic liquid gels (ionogels) of which specially designed and synthesized cholesteryl derivatives were employed as gelators. The ionogels as obtained are thermo-reversible. In particular, the one with 1-butyl-3-methylimidazolium tetrafluoroborate (IL2) as solvent and a cholesteryl derivative containing a D-phenylalanine residue (1D) as a gelator is very stable both in neutral and acidic mediums as demonstrated by a yield stress of 76 Pa for a self-standing cylinder of the ionogel. Furthermore, the ionogel can be easily converted into a hydrogel *via* simple replacement of the solvent with water *in situ*. More interestingly, the conversion is reversible, a phenomenon never reported before. At the same time, the critical gelation concentration (CGC) of 1D for IL2 is only 0.06%, w/w, which is almost the lowest value reported for ionogels till now, and falls into the category of "super-gelator". Magnetization of the ionogel has been realized by introduction of micro-/nano-Fe_3O_4 particles. As expected, the magnetic gel as obtained is responding to external magnetic field. Specifically, it changes into fluid with the presence of a magnetic field exceeding certain strength, and retains to gel upon removing the magnetic field and with a treatment of sonication and heating–cooling cycle. SEM and TEM observations revealed the continuous fibrous network structures of the molecules of the gelator in the ionogels. To the best of our knowledge, this is the first report on ionogels possessing stimulus-responsive properties, good mechanical strength, and super-gelation talent.

- Enhanced mechanical pathways through nature's building blocks: amino acids
  Johnson, J. C.; Korley, L. T. K. *Soft Matter* **2012**, *8*, 11431-11442.
  Abstract:



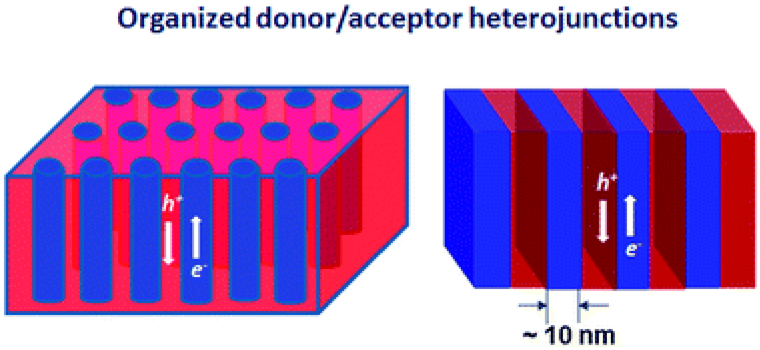
Amino acids are the core building blocks of nature's mechanically robust proteins. Their innate ability to self-assemble into well-ordered secondary structures, such as the α-helix and β-sheet, coupled with unique load-bearing characteristics, has sparked considerable interest in their use in innovative engineering materials. Biomimickry and bioinspired approaches to materials design can be utilized to facilitate the conception of these peptidic-based materials by introducing principles proven by the demanding conditions of nature. In this review, we will explore the design process of tailored mechanics through the examination of research that has employed amino acid sequences inspired by silks, elastin, and resilin to construct hybrid functional polymeric materials as well as polymeric materials exploiting non-canonical or non-native amino acids as building blocks. We foresee the next generation of nature-inspired materials finding widespread use, not only in biomedical and bioengineering applications, but also in roles that require tailored and functional coatings, films and fibers.

- Open-circuit voltage in organic solar cells
  Qi, B.; Wang, J. *J. Mater. Chem.* **2012**, *22*, 24315–24325.
  Abstract:



Open-circuit voltage (V_{OC}) is the maximum voltage a solar cell can provide to an external circuit, which is derived from the splitting of hole and electron quasi-Fermi levels. In crystalline Si solar cells, the effective density of states at the bottom (top) of the conduction (valence) band is constant, and the quasi-Fermi level can be directly calculated *via* the Fermi–Dirac distribution. However, in organic materials, similar to amorphous Si, disorder induces gap tail states. Relaxation of carriers into these tail states brings the electron quasi-Fermi level down and the hole quasi-Fermi level up, and hence reduces V_{OC}. Furthermore, carrier recombination of various kinds can cause additional loss of V_{OC}. This article reviews the research progress in understanding the origin of V_{OC} in organic solar cells. In particular, the dependence of V_{OC} on four important factors, namely temperature, light intensity, work function of the electrode and material microstructure are discussed based on the model of density of states. Techniques to enhance V_{OC} are also briefly introduced and their mechanisms are analysed.

- Top-down meets bottom-up: organized donor–acceptor heterojunctions for organic solar cells
  Wang, M.; Wudl, F. *J. Mater. Chem.* **2012**, *22*, 24297–24314.
  Abstract:



Solar cells involving organic small molecules and polymers have attracted intense attention from chemists, physicists and materials scientists in the past decade. Efforts in materials synthesis and device processing have led to significant improvement of the power conversion efficiency, approaching 10%. In organic solar cells (OSCs), the morphology and the interface of the donor–acceptor (D–A) heterojunctions play a critical role in determining the device efficiency. In this article, we highlight recent progress on both materials synthesis and self-assembly and lithography techniques toward ordered nanostructures and well-defined D/A interfaces that are expected to enhance the performance of OSCs.