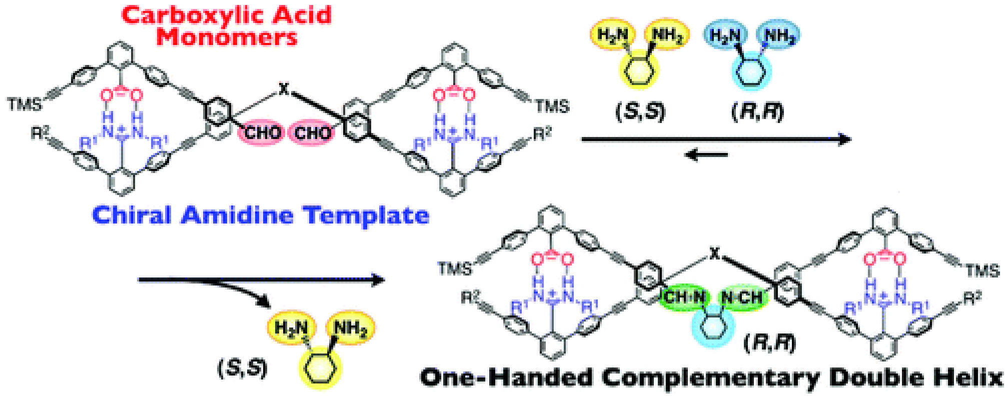
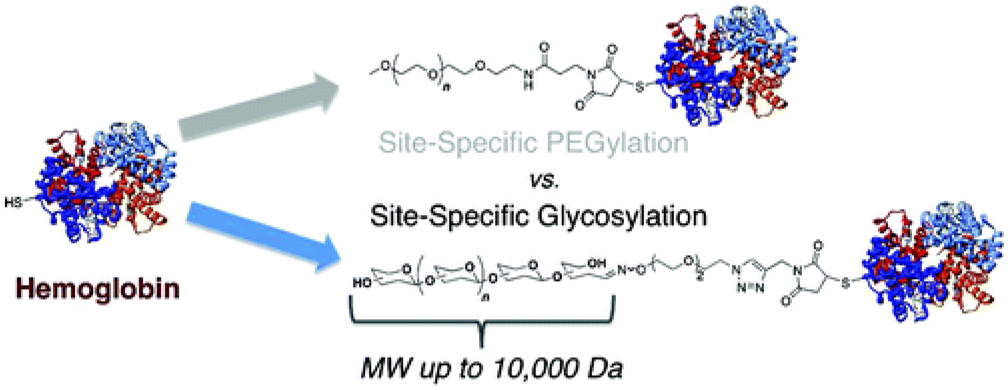
- Diastereoselective Imine-Bond Formation through Complementary Double-Helix Formation
  Yamada, H.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2012**, *134*, 7250–7253.
  Abstract:



Optically active amidine dimer strands having a variety of chiral and achiral linkers with different stereostructures are synthesized and used as templates for diastereoselective imine-bond formations between two achiral carboxylic acid monomers bearing a terminal aldehyde group and racemic 1,2-cyclohexanediamine, resulting in a preferred-handed double helix stabilized by complementary salt bridges. The diastereoselectivity of the racemic amine is significantly affected by the chirality of the amidine residues along with the rigidity and/or chirality of the linkers in the templates. NMR and kinetic studies reveal that the present imine-bond formation involves a two-step reversible reaction. The second step involves formation of a preferred-handed complementary double helix assisted by the chiral amidine templates and determines the overall reaction rate and diastereoselectivity of the amine.

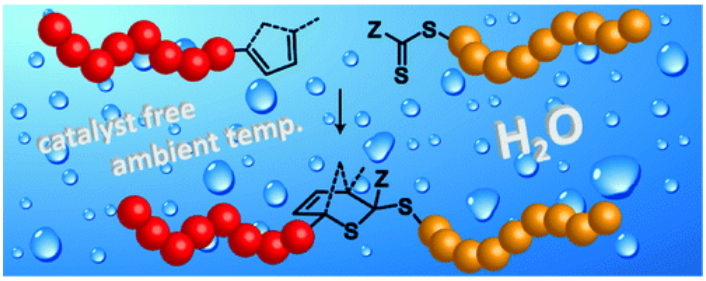
- Site-Selective Glycosylation of Hemoglobin with Variable Molecular Weight Oligosaccharides: Potential Alternative to PEGylation
  Styslinger, T. J.; Zhang, N.; Bhatt, V. S.; Pettit, N.; Palmer, A. F.; Wang, P. G. *J. Am. Chem. Soc.* **2012**, *134*, 7507–7515.
  Abstract:



Poly(ethylene glycol) (PEG) conjugation (i.e., PEGylation) is a commonly used strategy to increase the circulatory half-life of therapeutic proteins and colloids; however, few viable alternatives exist to replicate its functions. Herein, we report a method for the rapid site-selective glycosylation of proteins with variously sized carbohydrates, up to a molecular weight (MW) of 10□000, thus serving as a potential alternative for PEGylation. More importantly, the method developed has two unique features. First, traditional protecting group strategies that typically accompany the modification of the carbohydrate fragments are circumvented, allowing for the facile site-selective glycosylation of a

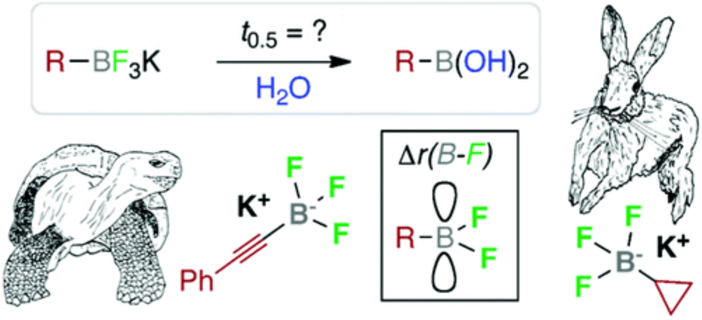
desired protein with variously sized glycans. Second, the methodology employed is not limited by oligosaccharide size; consequently, glycans of MW similar to that of PEG, used in the PEGylation of therapeutic proteins, can be employed. To demonstrate the usefulness of this technology, hemoglobin (Hb) was site-selectively glycosylated with a series of carbohydrates of increasing MW (from 504 to ~10 000). Hb was selected on the basis of the vast wealth of biochemical and biophysical knowledge present in the literature and because of its use as a precursor in the synthesis/formulation of artificial red blood cell substitutes. Following the successful site-selective glycosylation of Hb, the impact of increasing the glycan MW on Hb's biophysical properties was investigated in vitro.

- (Ultra)Fast Catalyst-Free Macromolecular Conjugation in Aqueous Environment at Ambient Temperature
  Glassner, M.; Delaittre, G.; Kaupp, M.; Blinco, J. P.; Barner-Kowollik, C. *J. Am. Chem. Soc.* **2012**, *134*, 7274–7277.
  Abstract:



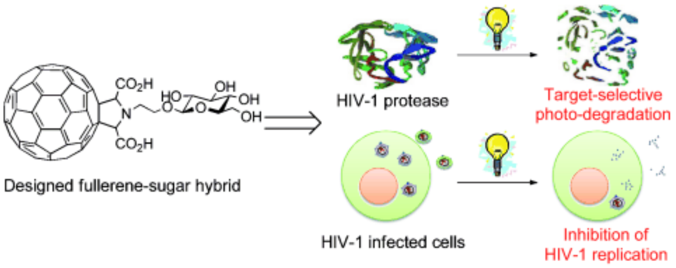
Tailor-made water-soluble macromolecules, including a glycopolymer, obtained by living/controlled RAFT-mediated polymerization are demonstrated to react in water with diene-functionalized poly(ethylene glycol)s without pre- or post-functionalization steps or the need for a catalyst at ambient temperature. As previously observed in organic solvents, hetero-Diels–Alder (HDA) conjugations reached quantitative conversion within minutes when cyclopentadienyl moieties were involved. However, while catalysts and elevated temperatures were previously necessary for open-chain diene conjugation, additive-free HDA cycloadditions occur in water within a few hours at ambient temperature. Experimental evidence for efficient conjugations is provided via unambiguous ESI-MS, UV/vis, NMR, and SEC data.

- Organotrifluoroborate Hydrolysis: Boronic Acid Release Mechanism and an Acid–Base Paradox in Cross-Coupling
  Lennox, A. J. J.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 7431–7441.
  Abstract:



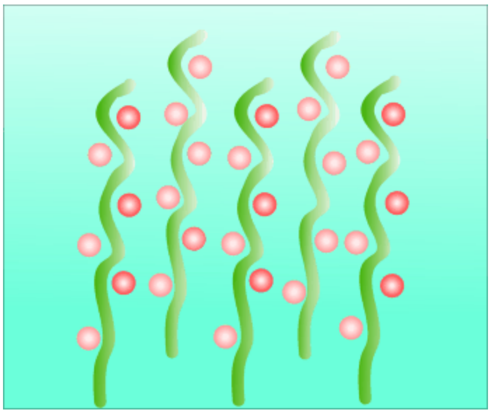
The hydrolysis of potassium organotrifluoroborate (RBF_3K) reagents to the corresponding boronic acids ($RB(OH)_2$) has been studied in the context of their application in Suzuki–Miyaura coupling. The "slow release" strategy in such SM couplings is only viable if there is an appropriate gearing of the hydrolysis rate of the RBF_3K reagent with the rate of catalytic turnover. In such cases, the boronic acid $RB(OH)_2$ does not substantially accumulate, thereby minimizing side reactions such as oxidative homocoupling and protodeboronation. The study reveals that the hydrolysis rates (THF, H_2O, Cs_2CO_3, 55 °C) depend on a number of variables, resulting in complex solvolytic profiles with some RBF_3K reagents. For example, those based on *p*-F-phenyl, naphthyl, furyl, and benzyl moieties are found to require *acid* catalysis for efficient hydrolysis. This acid–base paradox assures their slow hydrolysis under *basic* Suzuki–Miyaura coupling conditions. However, partial phase-splitting of the THF/H_2O induced by the Cs_2CO_3, resulting in a lower pH in the bulk medium, causes the reaction vessel shape, material, size, and stirring rate to have a profound impact on the hydrolysis profile. In contrast, reagents bearing, for example, isopropyl, β-styryl, and anisyl moieties undergo efficient "direct" hydrolysis, resulting in fast release of the boronic acid while reagents bearing, for example, alkynyl or nitrophenyl moieties, hydrolyze extremely slowly. Analysis of B–F bond lengths (DFT) in the intermediate difluoroborane, or the Swain–Lupton resonance parameter ($\mathscr{R}$) of the R group in RBF_3K, allows an a priori evaluation of whether an RBF_3K reagent will likely engender "fast", "slow", or "very slow" hydrolysis. An exception to this correlation was found with vinyl-BF_3K, this reagent being sufficiently hydrophilic to partition substantially into the predominantly aqueous minor biphase, where it is rapidly hydrolyzed.

- Target-Selective Photodegradation of HIV-1 Protease and Inhibition of HIV-1 Replication in Living Cells by Designed Fullerene–Sugar Hybrids
  Tanimoto, S.; Sakai, S.; Kudo, E.; Okada, S.; Matsumura, S.; Takahashi, D.; Toshima, K. *Chem. Asian J.* **2012**, *7*, 911–914.
  Abstract:



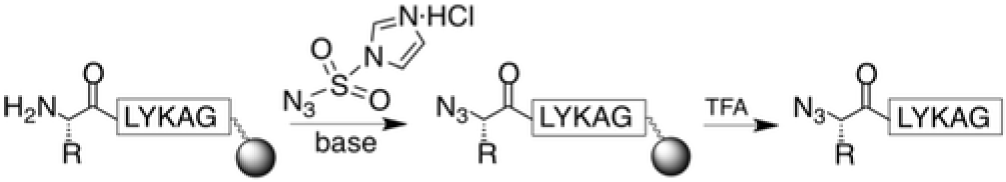
Sweet degradation: A designed fullerene–sugar hybrid selectively caused the degradation of HIV-1 protease, an important target of anti-HIV therapy. Degradation was achieved at irradiation with long-wavelength UV (365 nm) or visible light (diffuse sunlight) in the absence of any additives and under neutral conditions. Moreover, the hybrid inhibited HIV-1 replication in living cells infected with HIV-1.

- Surface-Grafted Polymer-Assisted Electroless Deposition of Metals for Flexible and Stretchable Electronics
  Liu, X.; Zhou, X.; Li, Y.; Zheng, Z. *Chem. Asian J.* **2012**, *7*, 862–870.
  Abstract:



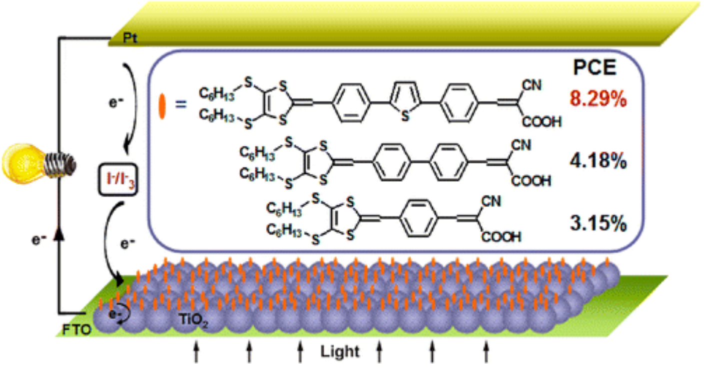
Surface-grafted polymers, that is, ultrathin layers of polymer coating covalently tethered to a surface, can serve as a particularly promising nanoplatform for electroless deposition (ELD) of metal thin films and patterned structures. Such polymers consist of a large number of well-defined binding sites for highly efficient and selective uptake of ELD catalysts. Moreover, the polymer chains provide flexible 3D network structures to trap the electrolessly deposited metal particles, leading to strong metal–substrate adhesion. In the past decade, surface-grafted polymers have been demonstrated as efficient nanoplatforms for fabricating durable and high-performance metal coatings by ELD on plastic substrates for applications in flexible and stretchable electronics. This focus review summarizes these recent advances, with a particular focus on applications in polymeric flexible and stretchable substrates. An outlook on the future challenges and opportunities in this field is given at the end of this paper.

- Simple and Efficient Solid-Phase Preparation of Azido-peptides
  Hansen, M. B.; van Gurp, T. H. M.; van Hest, J. C. M.; Löwik, D. W. P. M. *Org. Lett.* **2012**, *14*, 2330-2333.
  Abstract:



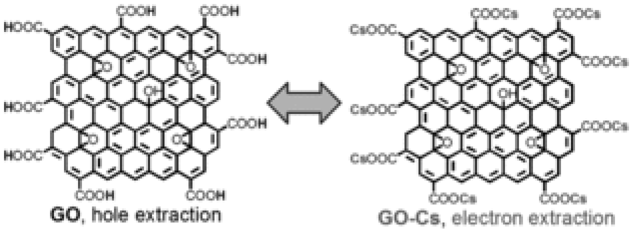
A shelf-stable and easily prepared diazotransfer reagent, imidazole-1-sulfonyl azide hydrochloride, was used to transform the N-terminus of a model peptide on solid phase into an azide moiety. It is demonstrated that this conversion was accomplished within 30 min with high efficiency under aqueous conditions on a NovaPEG resin or in DMF on polystyrene beads.

- Dithiafulvenyl Unit as a New Donor for High-Efficiency Dye-Sensitized Solar Cells: Synthesis and Demonstration of a Family of Metal-Free Organic Sensitizers
  Guo, K.; Yan, K.; Lu, X.; Qiu, Y.; Liu, Z.; Sun, J.; Yan, F.; Guo, W.; Yang, S. *Org. Lett.* **2012**, *14*, 2214-2217.
  Abstract:



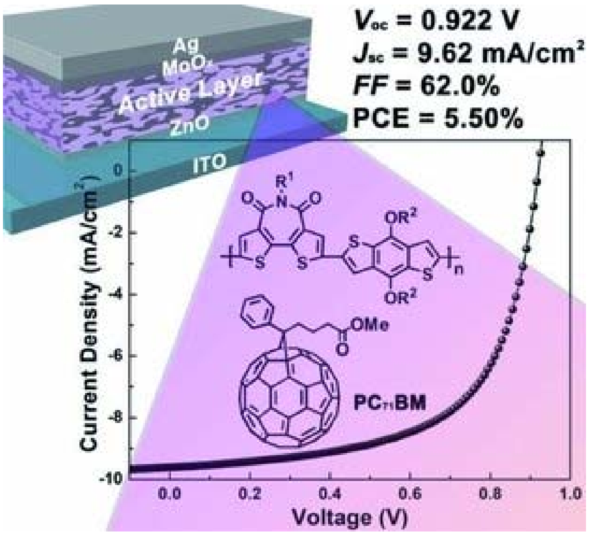
This work identifies the dithiafulvenyl unit as an excellent electron donor for constructing D–π–A-type metal-free organic sensitizers of dye-sensitized solar cells (DSCs). Synthesized and tested are three sensitizers all with this donor and a cyanoacrylic acid acceptor but differing in the phenyl (**DTF-C1**), biphenyl (**DTF-C2**), and phenyl–thiopheneyl–phenyl π-bridges (**DTF-C3**). Devices based on these dyes exhibit a dramatically improved performance with the increasing π-bridge length, culminating with DTF-C3 in η = 8.29% under standard global AM 1.5 illumination.

- Hole and Electron Extraction Layers Based on Graphene Oxide Derivatives for High-Performance Bulk Heterojunction Solar Cells
  Liu, J.; Xue, Y.; Gao, Y.; Yu, D.; Durstock, M.; Dai, L. *Adv. Mater.* **2012**, *24*, 2228–2233.
  Abstract:



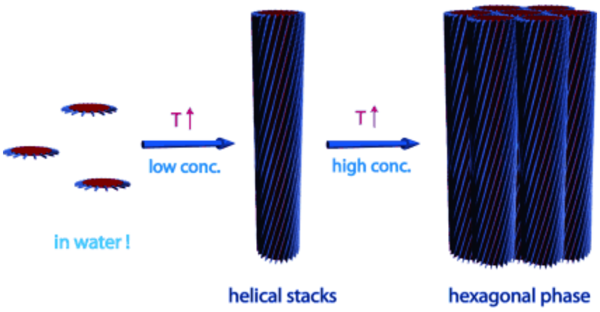
By charge neutralization of carboxylic acid groups in graphene oxide (GO) with Cs_2CO_3 to afford Cesium-neutralized GO (GO-Cs), GO derivatives with appropriate modification are used as both hole- and electron-extraction layers for bulk heterojunction (BHJ) solar cells. The normal and inverted devices based on GO hole- and GO-Cs electron-extraction layers both outperform the corresponding standard BHJ solar cells.

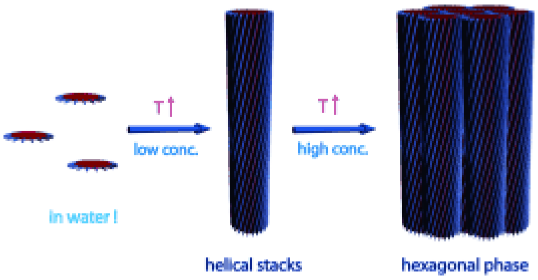
- Bithiophene Imide and Benzodithiophene Copolymers for Efficient Inverted Polymer Solar Cells
  Zhou, N.; Guo, X.; Ortiz, R. P.; Li, S.; Zhang, S.; Chang, R. P. H.; Facchetti, A.; Marks, T. J. *Adv. Mater.* **2012**, *24*, 2242–2248.
  Abstract:



Bithiophene imide (BTI) and benzodithiophene (BDT) copolymers are synthesized for application in organic photovoltaic (OPV) cells. The electron deficiency of the BTI units leads to polymers with a low-lying HOMOs (~-5.6 eV). Inverted solar cells are fabricated to investigate the OPV performance of the BTI-based polymers and achieve power conversion efficiencies up to 5.5%, with substantial V_{oc}s above 0.9 V which are among the highest V_{oc}s reported to date for polymer/PCBM solar cells. The results indicate that the BTI is a promising building block for constructing polymer donors for OPV applications.

- Amphiphilic Folded Dendrimer Discs and Their Thermosensitive Self-Assembly in Water
  El Malah, T.; Rolf, S.; Weidner, S. M.; Thünemann, A. F.; Hecht, S. *Chem. Eur. J.* **2012**, *18*, 5837–5842.
  Abstract:



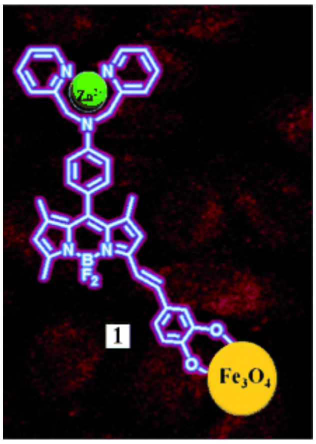


Folded dendrimers with peripheral ether side chains show a thermally induced hierarchical aggregation process, in which the transition temperature and the dimensions of the aggregates can readily be tuned via the generation number (see figure).

- Functionalized Fe_3O_4 Nanoparticles for Detecting Zinc Ions in Living Cells and Their Cytotoxicity

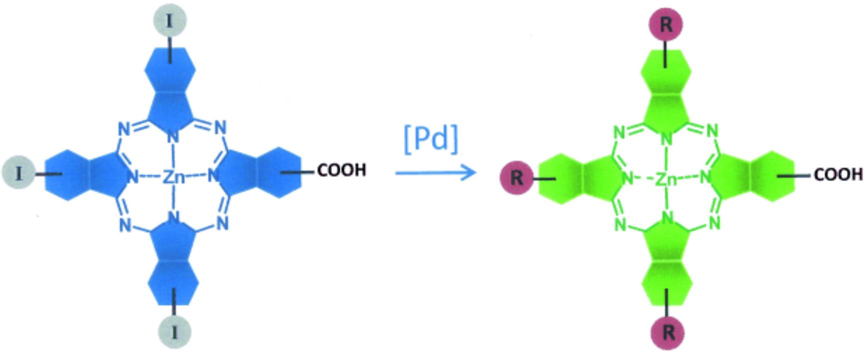
Kang, G.; Son, H.; Lim, J. M.; Kweon, H.-S.; Lee, I. S.; Kang, D.; Jung, J. H. *Chem. Eur. J.* **2012**, *18*, 5843–5847.

Abstract:



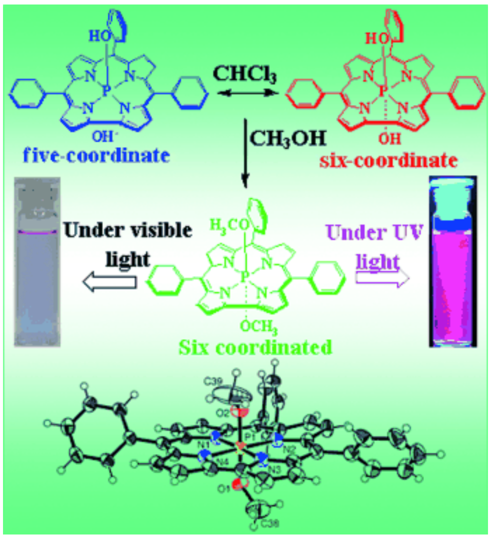
The zinc tank: A new fluoro-chromogenic chemosensor based on BODIPY-functionalized Fe_3O_4 nanoparticles (**1**) has been prepared. Chemoprobe **1** exhibits high selectivity for Zn^{2+} over other competing metal ions tested. Moreover, confocal microscopy experiments established that **1** can be used for detecting Zn^{2+} levels in living cells (see figure).

- Convergent Synthesis of Near-Infrared Absorbing, "Push–Pull", Bisthiophene-Substituted, Zinc(II) Phthalocyanines and their Application in Dye-Sensitized Solar Cells
  Ince, M.; Cardinali, F.; Yum, J.-H.; Martínez-Díaz, M. V.; Nazeeruddin, M. K.; Grätzel, M.; Torres, T. *Chem. Eur. J.* **2012**, *18*, 6343–6348.
  Abstract:



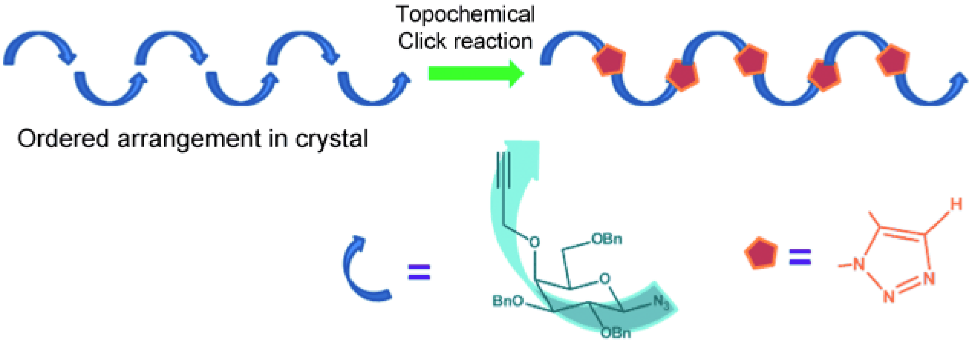
Zinc(II) phthalocyanine dyes that contain triarylamine-terminated bisthiophene and hexylbisthiophene groups have been synthesized by a convergent approach by using carboxytriiodo–ZnPc as a precursor. Further transformation of the iodo groups by a Pd-catalyzed reaction allowed easy preparation of further extended π-conjugated carboxy–ZnPcs. These dyes have been used as sensitizers in dye-sensitized solar cells, which exhibit a panchromatic response and moderate overall efficiencies.

- Synthesis, Structure, Spectroscopic, and Electrochemical Properties of Highly Fluorescent Phosphorus(V)–*meso*-Triarylcorroles
  Ghosh, A.; Ravikanth, M. *Chem. Eur. J.* **2012**, *18*, 6386–6396.
  Abstract:



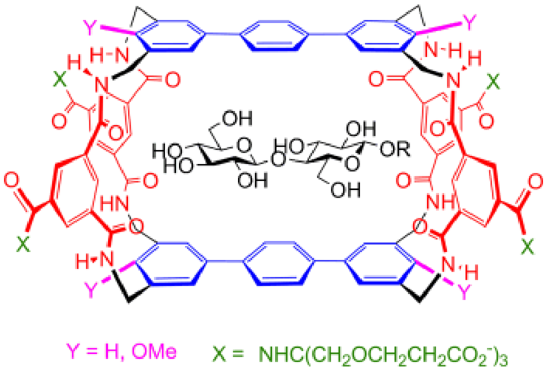
The synthesis, spectroscopic, and electrochemical properties of seven new P^V–*meso*-triarylcorroles (**1**–**7**) are reported. Compounds **1**–**7** were prepared by heating the corresponding free-base corroles with $POCl_3$ at reflux in pyridine. Hexacoordinate P^V complexes of *meso*-triarylcorroles were isolated that contained two axial hydroxy groups, unlike the P^V complex of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole, which was pentacoordinate, or the P^V complex of *meso*-tetraphenylporphyrin, which was hexacoordinate with two axial chloro groups. ^{1}H and ^{31}P NMR spectroscopy in $CDCl_3$ indicated that the hexacoordinated P^V–*meso*-triarylcorroles were prone to axial-ligand dissociation to form pentacoordinated P^V–*meso*-triarylcorroles. However, in the presence of strongly coordinating solvents, such as CH_3OH, THF, and DMSO, the P^V–*meso*-triarylcorroles preferred to exist in a hexacoordinated geometry in which the corresponding solvent molecules acted as axial ligands. X-ray diffraction of two complexes confirmed the hexacoordination environment for P^V–*meso*-triarylcorroles. Their absorption spectra in two coordinating solvents revealed that P^V–*meso*-triarylcorroles showed a strong band at about 600 nm together with other bands, in contrast to P^V–porphyrins, which showed weak bands in the visible region. These compounds were easier to oxidize and more difficult to reduce compared to P^V–porphyrins. These compounds were brightly fluorescent, unlike the weakly fluorescent P^V–porphyrins, and the quantum yields for selected P^V–corroles were as high as Al^{III} and Ga^{III} corroles, which are the best known fluorescent compounds among oligopyrrolic macrocycles.

- Topochemical Click Reaction: Spontaneous Self-Stitching of a Monosaccharide to Linear Oligomers through Lattice-Controlled Azide–Alkyne Cycloaddition
  Pathigoolla, A.; Gonnade, R. G.; Sureshan, K. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 4362-4366.
  Abstract:



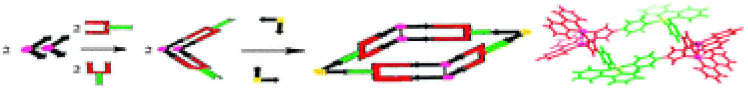
No activation needed: A topochemical click reaction that dispenses with catalyst, solvent, or other modes of activation takes place in crystals of a sugar derivative. The spontaneous, regiospecific azide–alkyne cycloaddition gives linear polymers that are difficult to synthesize by conventional solution-state chemistry (see picture).

- High-Affinity Disaccharide Binding by Tricyclic Synthetic Lectins
  Sookcharoenpinyo, B.; Klein, E.; Ferrand, Y.; Walker, D. B.; Brotherhood, P. R.; Ke, C.; Crump, M. P.; Davis, A. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 4586-4590.
  Abstract:



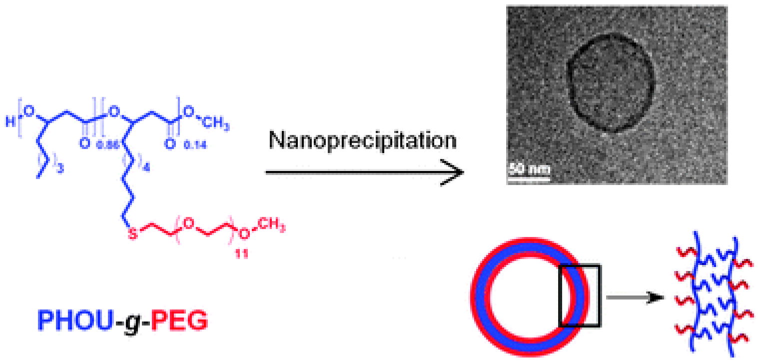
Stay flexible: Rigid preorganization is not always the best approach to molecular recognition. Unlike previous synthetic lectins, new receptors (see picture) were synthesized that possess conformational freedom which allows hydrophobically driven collapse of the cavity. Nonetheless, they bind their carbohydrate targets in water with ground-breaking affinities (up to 4500 m^{-1} for methyl cellobioside, R=Me) and selectivities.

- Programmable self-assembly of homo- or hetero-metallomacrocycles using 4-(1H-pyrazolyl-4-yl)pyridine
  Tong, J.; Yu, S. Y. ; Li, H. *Chem. Commun.* **2012**, *48*, 5343-5345.
  Abstract:



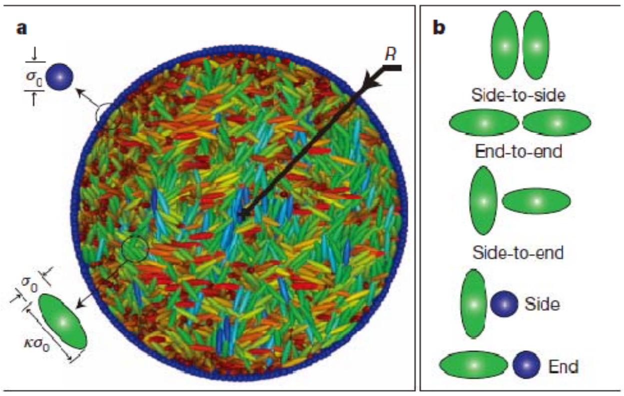
Homo- or hetero-metallomacrocycles are obtained by reacting 4-(1*H*-pyrazolyl-4-yl)pyridine with *cis*-coordinated Pd(II) or Pt(II) complexes through programmable self-assembly processes.

- Poly(3-hydroxyalkanoate)-derived amphiphilic graft copolymers for the design of polymersomes
  Babinot, J.; Guigner, J. M. ; Renard, E. ; Langlois, W. *Chem. Commun.* **2012**, *48*, 5364-5366.
  Abstract:



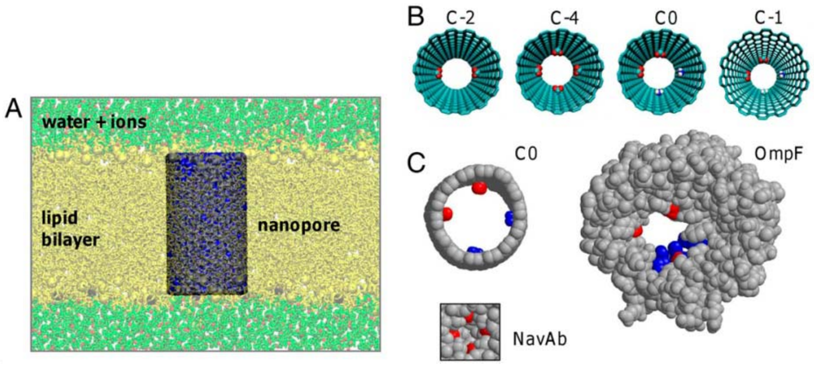
Amphiphilic poly(3-hydroxyalkanoates) are synthesized in a simple and straightforward method using thiol–ene addition. The graft copolymers are proved to form stable and well-defined polymersomes in water.

- Liquid-crystal-mediated self-assembly at nanodroplet interfaces
  Moreno-Razo, J. A.; Sambriski, E. J.; Abbott, N. L.; Hernández-Ortiz, J. P.; de Pablo, J. J. *Nature* **2012**, *485*, 86-89.
  Abstract:



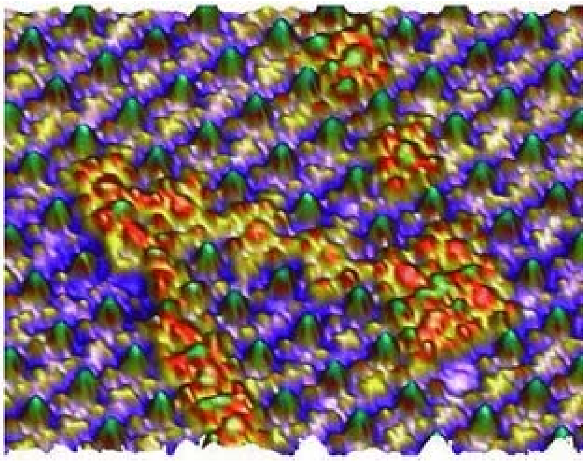
Technological applications of liquid crystals have generally relied on control of molecular orientation at a surface or an interface. Such control has been achieved through topography, chemistry and the adsorption of monolayers or surfactants. The role of the substrate or interface has been to impart order over visible length scales and to confine the liquid crystal in a device. Here, we report results from a computational study of a liquid-crystal-based system in which the opposite is true: the liquid crystal is used to impart order on the interfacial arrangement of a surfactant. Recent experiments on macroscopic interfaces have hinted that an interfacial coupling between bulk liquid crystal and surfactant can lead to a two-dimensional phase separation of the surfactant at the interface, but have not had the resolution to measure the structure of the resulting phases. To enhance that coupling, we consider the limit of nanodroplets, the interfaces of which are decorated with surfactant molecules that promote local perpendicular orientation of mesogens within the droplet. In the absence of surfactant, mesogens at the interface are all parallel to that interface. As the droplet is cooled, the mesogens undergo a transition from a disordered (isotropic) to an ordered (nematic or smectic) liquid-crystal phase. As this happens, mesogens within the droplet cause a transition of the surfactant at the interface, which forms new ordered nanophases with morphologies dependent on surfactant concentration. Such nanophases are reminiscent of those encountered in block copolymers, and include circular, striped and worm-like patterns.

- Designing biomimetic pores based on carbon nanotubes
  García-Fandiño, R.; Sansoma, M. S. P. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 6939-6944.
  Abstract:



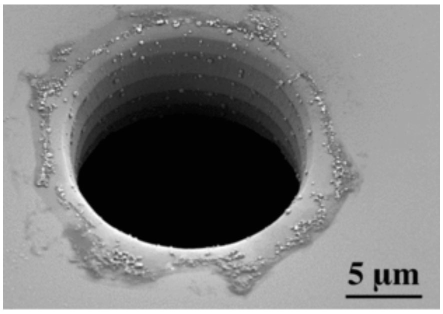
Biomimetic nanopores based on membrane-spanning singlewalled carbon nanotubes have been designed to include selectivityfilters based on combinations of anionic and cationic groups mimicking those present in bacterial porins and in voltage-gated sodium and calcium channels. The ion permeation and selectivity properties of these nanopores when embedded in a phospholipid bilayer have been explored by molecular dynamics simulations and free energy profile calculations. The interactions of the nanopores with sodium, potassium, calcium, and chloride ions have been explored as a function of the number of anionic and cationic groups within the selectivity filter. Unbiased molecular dynamics simulations show that the overall selectivity is largely determined by the net charge of the filter. Analysis of distribution functions reveals considerable structuring of the distribution of ions and water within the nanopores. The distributions of ions along the pore axisreveal local selectivity for cations around filter, even in those nanopores (C0) where the net filter charge is zero. Single ion free energy profiles also reveal clear evidence for cation selectivity, even in the C0 nanopores. Detailed analysis of the interactions of the C0 nanopore with Ca^{2+} ions reveals that local interactions with the anionic (carboxylate) groups of the selectivity filter lead to (partial) replacement of solvating water as the ion passes through the pore. These studies suggest that a computational biomimetic approach can be used to evaluate our understanding of the design principles of nanopores and channels.

- Reversible Single-Molecule Switching in an Ordered Monolayer Molecular Dipole Array
  Li Huang, Y.; Lu, Y.; Niu, T. C.; Huang, H.; Kera, S.; Ueno, N.; Wee, A. T. S.; Chen, W. *Small* **2012**, *8*, 1423–1428.
  Abstract:



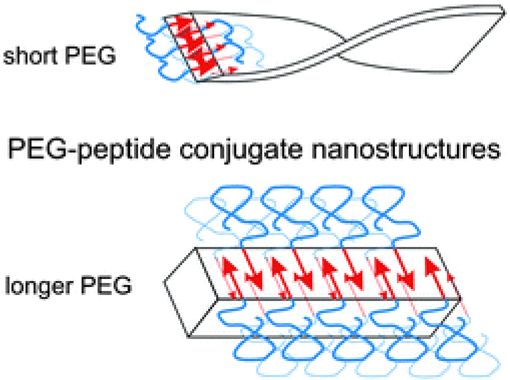
Making electronic devices using a single molecule has been the ultimate goal of molecular electronics. For binary data storage in particular, the challenge has been the ability to switch a single molecule in between bistable states in a simple and repeatable manner. The reversible switching of single molecules of chloroaluminum phthalocyanine (ClAlPc) dipolar molecules within a close-packed monolayer is demonstrated. By pulsing an scanning tunneling microscopy tip, read–write operations of single-molecular binary bits at ~40 Tb/cm^2 (~250 Tb/in^2) are demonstrated.

- Electrochemically Induced Maskless Metal Deposition on Micropore Wall
  Liu, J.; Hébert, C.; Pham, P.; Sauter-Starace, F.; Haguet, V.; Livache, T.; Mailley, P. *Small* **2012**, *8*, 1345–1349.
  Abstract:



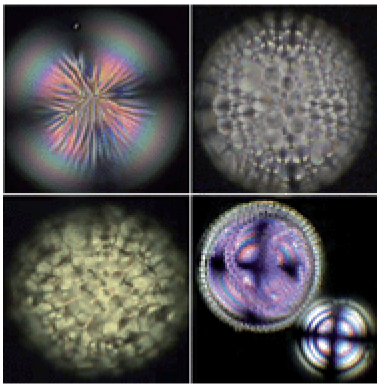
By applying an external electric field across a micropore via an electrolyte, metal ions in the electrolyte can be reduced locally onto the inner wall of the micropore, which was fabricated in a silica-covered silicon membrane. This maskless metal deposition on the silica surface is a result of the pore membrane polarization in the electric field.

- Control of strand registry by attachment of PEG chains to amyloid peptides influences nanostructure
  Castelletto, V.; Cheng, G.; Furzeland, S.; Atkins, D.; Hamley, I. W. *Soft Matter* **2012**, *8*, 5434-5438.
  Abstract:



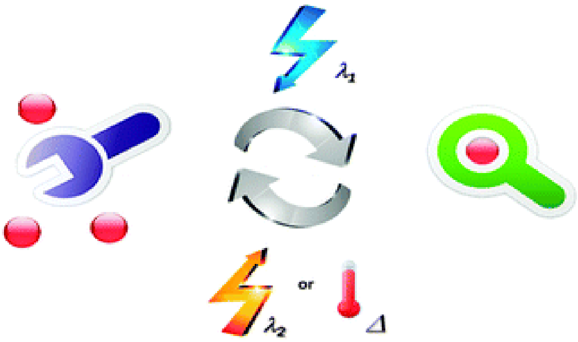
The self-assembly in aqueous solution of PEG-peptide conjugates comprising a model amyloid peptide sequence FFKLVFF that contains the Aβ(16–20) KLVFF motif is investigated. X-ray diffraction reveals different packing motifs dependent on PEG chain length. This is correlated to remarkable differences in self-assembled nanostructures. The control of strand registry points to a subtle interplay between aromatic stacking, electrostatic and amphiphilic interactions.

- Towards tunable defect arrangements in smectic liquid crystal shells utilizing the nematic–smectic transition in hybrid-aligned geometries
  Liang, H.-L.; Zentel, R.; Rudquist, P.; Lagerwall, J. *Soft Matter* **2012**, *8*, 5443-5450.
  Abstract:



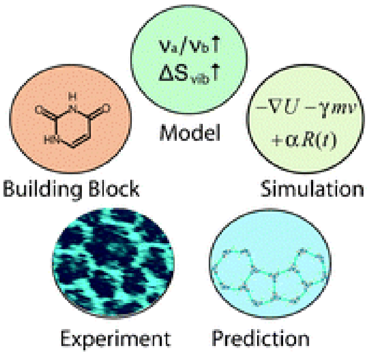
We produce and investigate liquid crystal shells with hybrid alignment—planar at one boundary, homeotropic at the other—undergoing a transition between the nematic (N) and smectic-A (SmA) phases. The shells display a dynamic sequence of patterns, the details depending on the alignment agents and on the diameter and thickness of the shell. In shells of sufficient diameter we typically find a transient striped texture near the N–SmA transition, stabilising into a pattern of tiled, more or less regularly spaced focal conic domains in the SmA phase. The domain size and spacing decrease with reduced shell thickness. In case of strong homeotropic anchoring at one boundary and small shell size, however, the increased curvature favors homeotropic against planar alignment in the smectic phase, and the shell then tends to adapt to complete homeotropic alignment at the final stage of the transition. This is the first study of hybrid-aligned smectic shells and the results constitute a beautiful demonstration of the capacity for dynamic structure formation and reformation *via* self-assembly in soft matter. The new patterns extend the range of arrays of topological defects that can be realised with liquid crystals in spherical morphology and the correlation between the feature arrangements and the variable parameters of the shell and its environment opens a route towards tunability. However, the observed strong impact from increasing curvature, even for these rather large shells, indicates that the choice of alignment agents inducing planar or homeotropic alignment with varying strength will become critical when targeting the most attractive colloidal size scale of about a micron or smaller.

- Molecular switches as photocontrollable “smart” receptors
  Natali, M.; Giordani, S. *Chem. Soc. Rev.* **2012**, *41*, 4010-4029.
  Abstract:



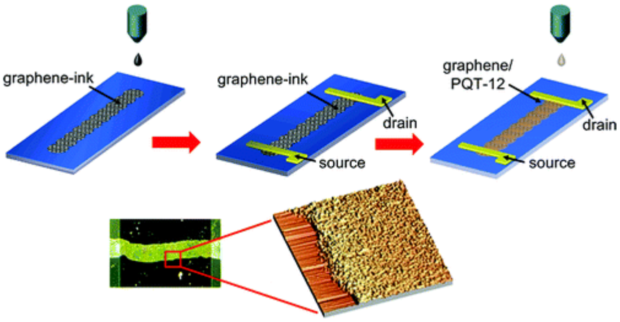
This *critical review* focuses on the development of photochromic compounds as sensors for cations, anions, and biologically important molecules. The review commences with a brief description of photochromism and the strategies to exploit photochromic molecular switches' properties for sensing application. This is followed by a summary of photoswitchable receptors emerged to date and classified according to the photochromic structure they are based on. These include azobenzenes, fulgides, dithienylethenes, dihydroindolizines, chromenes and spiropyrans.

- Predicting self-assembly: from empirism to determinism
  Palma, C.-A.; Cecchini, M.; Samorì, P. *Chem. Soc. Rev.* **2012**, *41*, 3713-3730.
  Abstract:



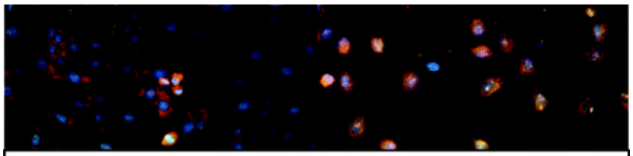
Self-assembly is one of the most important concepts of the 21st century. Strikingly, despite the rational design of molecules for biological and pharmaceutical applications is rather well established, only few are the attempts to formally refine predictions of self-assembly in material science. In the present *tutorial review*, we encompass some of the most significant efforts towards the systematic study of (thermodynamically stable) self-assembly. We discuss experimental and computer-simulated self-assembly events in hard-matter, soft-matter and higher symmetry architectures under the common framework of partition functions. In this framework, we endeavor to correlate state-of-the-art chemical design, programming and/or engineering of reversible (thermal and chemical equilibrium) self-assembly with knowledge of the underlying partition function landscape in a step towards quantitative predictions and *ab initio* molecular design.

- Inkjet-Printed Graphene Electronics
  Torrisi, F.; Hasan, T.; Wu, W.; Sun, A.; Lombardo, A.; Kulmala, T. S.; Hsieh, G.-W.; Jung, S.; Bonaccorso, F.; Paul, P. J.; Chu, D.; Ferrari, A. C. *ACS Nano* **2012**, *6*, 2992-3006.
  Abstract:



We demonstrate inkjet printing as a viable method for large-area fabrication of graphene devices. We produce a graphene-based ink by liquid phase exfoliation of graphite in *N*-methylpyrrolidone. We use it to print thin-film transistors, with mobilities up to ~95 $cm^2\ V^{-1}\ s^{-1}$, as well as transparent and conductive patterns, with ~80% transmittance and ~30 kΩ/□ sheet resistance. This paves the way to all-printed, flexible, and transparent graphene devices on arbitrary substrates.

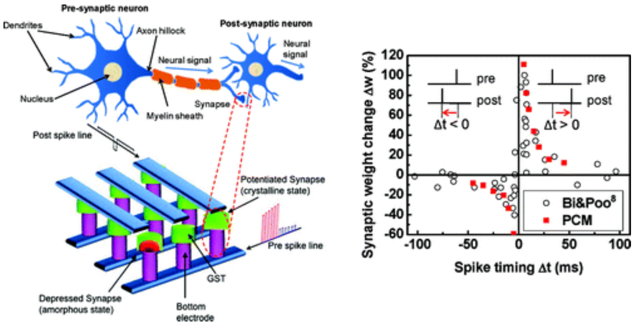
- Antibody-Targeted Nanovectors for the Treatment of Brain Cancers
  Sharpe, M. A.; Marcano, D. C.; Berlin, J. M.; Widmayer, M. A.; Baskin, D. S.; Tour, J. M. *ACS Nano* **2012,** *6*, 3114-3120.
  Abstract:



GBM cells treated with 0.5 μM Vinblastine/PEG-HCCs, in the absence (left) and presence (right) of anti-EGFR IgG. Dead and dying GBM cells are RBG labeled with *dd*TUNEL (red) and viability dyes Dead Green and Hoechst (blue).

Introduced here is the hydrophilic carbon clusters (HCCs) antibody drug enhancement system (HADES), a methodology for cell-specific drug delivery. Antigen-targeted, drug-delivering nanovectors are manufactured by combining specific antibodies with drug-loaded poly(ethylene glycol)–HCCs (PEG–HCCs). We show that HADES is highly modular, as both the drug and antibody component can be varied for selective killing of a range of cultured human primary glioblastoma multiforme. Using three different chemotherapeutics and three different antibodies, without the need for covalent bonding to the nanovector, we demonstrate extreme lethality toward glioma, but minimal toxicity toward human astrocytes and neurons.

- Nanoelectronic Programmable Synapses Based on Phase Change Materials for Brain-Inspired Computing
  Kuzum, D.; Jeyasingh, R. G. D.; Lee, B.; Wong, H.-S. P. *Nano Letters* **2012,** *12*, 2179-2186.
  Abstract:

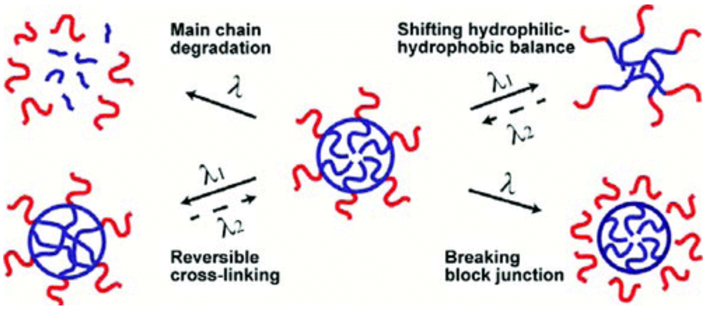


Brain-inspired computing is an emerging field, which aims to extend the capabilities of information technology beyond digital logic. A compact nanoscale device, emulating biological synapses, is needed as the building block for brain-like computational systems. Here, we report a new nanoscale electronic synapse based on technologically mature phase change materials employed in optical data storage and nonvolatile memory applications. We utilize continuous resistance transitions in phase change materials to mimic the analog nature of biological synapses, enabling the implementation of a synaptic learning rule. We demonstrate different forms of spike-timing-dependent plasticity using the same nanoscale synapse with picojoule level energy consumption.

- Light-Responsive Block Copolymer Micelles

Zhao, Y. *Macromolecules* **2012**, *45*, 3647–3657.

Abstract:

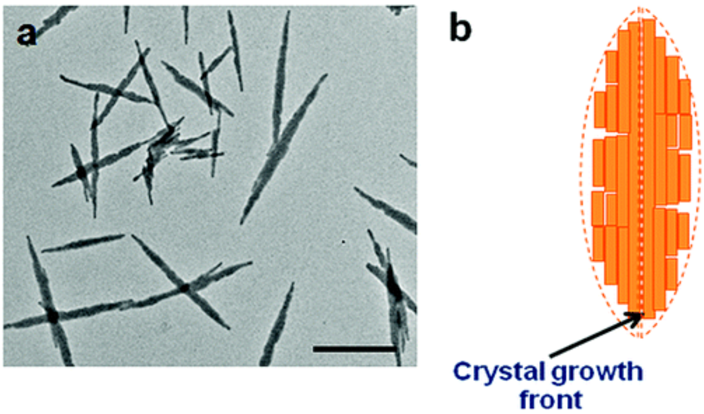


The association state of light-responsive block copolymer (BCP) micelles in aqueous solution can be altered, often reversibly, by light. Driven by the potential application in controlled drug delivery, this type of stimuli-responsive polymer micelles has received increasing attention. This Perspective highlights the progress achieved in recent years. On the one hand, we discuss the different approaches of rational BCP design, making use of various photochromic moieties and photochemical reactions, and the underlying mechanisms leading to photoinduced disruption of BCP micelles. On the other hand, we suggest possible future directions in this area, including exploration of new mechanisms and chemistry and solutions to the excitation wavelength problem crucial for biomedical applications.

- Formation of Lenticular Platelet Micelles via the Interplay of Crystallization and Chain Stretching: Solution Self-Assembly of Poly(ferrocenyldimethylsilane)-*block*-poly(2-vinylpyridine) with a Crystallizable Core-Forming Metalloblock

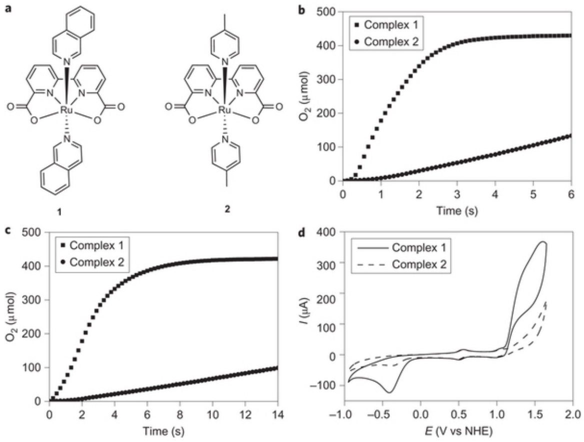
  Yusoff, S. F. M.; Hsiao, M.-S.; Schacher, F. H.; Winnik, M. A.; Manners, I. *Macromolecules* **2012**, *45*, 3883–3891.

  Abstract:



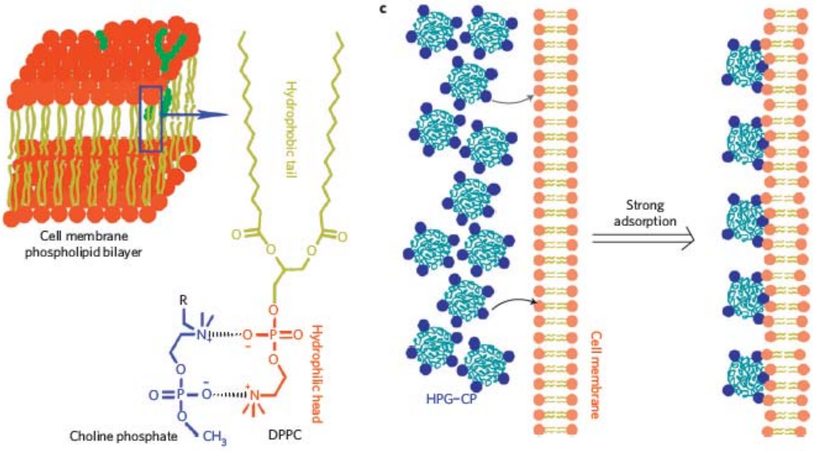
The influence of solvent composition on micelle morphology has been investigated for two crystalline-coil poly(ferrocenyldimethylsilane-*block*-2-vinylpyridine) (PFS-*b*-P2VP) diblock copolymers with different block ratios (5:1 and 1:1). The solution self-assembly of these materials was explored in solvent mixtures containing different ratios of a good solvent for both blocks (THF) and a selective solvent for the P2VP block (isopropanol). Various micellar morphologies such as spheres and platelets were characterized using transmission electron microscopy (TEM), selected area electron diffraction (SAED), dynamic light scattering (DLS), wide-angle X-ray scattering (WAXS), and atomic force microscopy (AFM). The results showed that the solution self-assembly of PFS-*b*-P2VP block copolymers (5:1, 1:1) gave spherical micelles with an amorphous PFS core at low THF content (10 vol %). Subsequently, the amorphous spheres were slowly transformed into platelet micelles with a lenticular shape that consisted of a crystalline PFS core sandwiched by two coronal P2VP layers. This indicated that the amorphous spherical micelles were in a metastable state. The transformation of spheres into platelets was significantly slower for the 5:1 block copolymer with the longer PFS core-forming segment presumably due to a lower rate of crystallization of the metalloblock. Platelets were found to be dominant for both block copolymers at higher THF content (THF ≥ 30 vol %). The formation of lenticular rather than regular platelets was attributed to a poisoning effect whereby interference of the P2VP corona-forming blocks in the growth of the crystalline PFS core leads to the creation of defects in the crystal growth fronts.

- A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II
  Duan,L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. *Nature Chemistry* **2012**, *4*, 418–423.
  Abstract:



Across chemical disciplines, an interest in developing artificial water splitting to O2 and H2, driven by sunlight, has been motivated by the need for practical and environmentally friendly power generation without the consumption of fossil fuels. The central issue in light-driven water splitting is the efficiency of the water oxidation, which in the best-known catalysts falls short of the desired level by approximately two orders of magnitude. Here, we show that it is possible to close that 'two orders of magnitude' gap with a rationally designed molecular catalyst [Ru(bda)(isoq)2] (H2bda = 2,2′-bipyridine-6,6′-dicarboxylic acid; isoq = isoquinoline). This speeds up the water oxidation to an unprecedentedly high reaction rate with a turnover frequency of >300 s−1. This value is, for the first time, moderately comparable with the reaction rate of 100–400 s−1 of the oxygen-evolving complex of photosystem II in vivo.

- Polyvalent choline phosphate as a universal biomembrane adhesive
  Yu, X.; Liu, Z.; Janzen, J.; Chafeeva, I.; Horte, S.; Chen, W.; Kainthan, R. K.; Kizhakkedathu, J. N.; Brooks, D. E. *Nature Materials* **2012**, *11*, 468–476.
  Abstract:



Phospholipids in the cell membranes of all eukaryotic cells contain phosphatidyl choline (PC) as the headgroup. Here we show that hyperbranched polyglycerols (HPGs) decorated with the ’PC-inverse’ choline phosphate (CP) in a polyvalent fashion can electrostatically bind to a variety of cell membranes and to PC-containing liposomes, the binding strength depending on the number density of CP groups per macromolecule. We also show that HPG–CPs can cause cells to adhere with varying affinity to other cells, and that binding can be reversed by subsequent exposure to low molecular weight HPGs carrying small numbers of PCs. Moreover, PC-rich membranes adsorb and rapidly internalize fluorescent HPG–CP but not HPG–PC molecules, which suggests that HPG–CPs could be used as drug-delivery agents. CP-decorated polymers should find broad use, for instance as tissue sealants and in the self-assembly of lipid nanostructures.