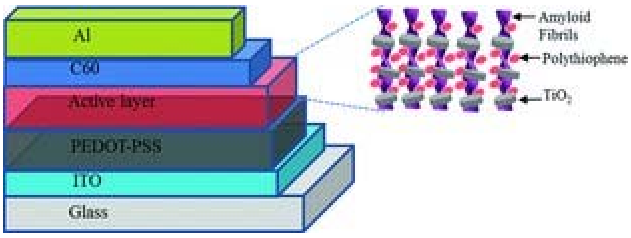
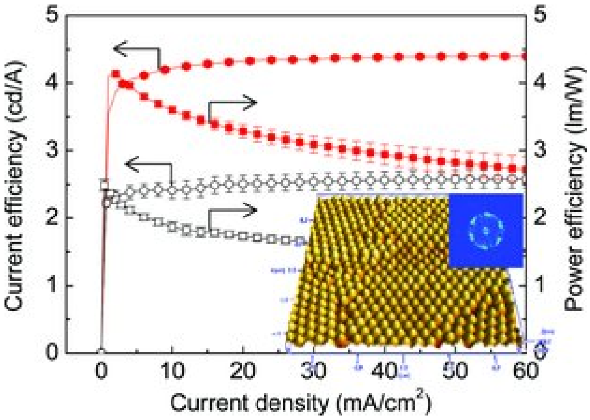
- Amyloid Directed Synthesis of Titanium Dioxide Nanowires and Their Applications in Hybrid Photovoltaic Devices
  Bolisetty, S.; Adamcik, J.; Heier, J.; Mezzenga, R. *Adv. Funct. Mater.* **2012**, *22*, 3424–3428.
  Abstract:



This paper reports β-lactoglobulin amyloid protein fibrils directed synthesis of Titanium Dioxide (TiO_2) hybrid nanowires. Protein fibrils act as templates to generate closely packed TiO_2 nanoparticles on the surface of the fibrils using titanium (IV) bis (ammonium lactato) dihydroxide (TiBALDH) as precursor, resulting in the TiO_2–coated amyloid hybrid nanowires. These amyloid fibrils also exhibit complexation with a luminescent water-soluble semiconductive polythiophene (P3HT). TiO_2 nanowires behave as electron acceptor while, P3HT as electron donor. In this way, amyloid-TiO_2 hybrid nanowires can serve in heterojunction photovoltaic devices. To demonstrate this, a photovoltaic active layer is prepared by spin coating the blended mixture of polythiophene-coated fibrils and amyloid-TiO_2 hybrid nanowires. The current–voltage characteristics of these photovoltaic devices exhibit excellent fill factor of 0.53, photovoltaic current density of 3.97 $mA \cdot cm^{-2}$ and power conversion efficiency of 0.72%, highlighting a possible future role for amyloid-based templates in donor–acceptor devices, organic electronics and hybrid solar cells.

- Light Extraction of Organic Light Emitting Diodes by Defective Hexagonal-Close-Packed Array
  Koo, W. H.; Youn, W.; Zhu, P.; Li, X.-H.; Tansu, N.; So, F. *Adv. Funct. Mater.* **2012**, *22*, 3454–3459.
  Abstract:

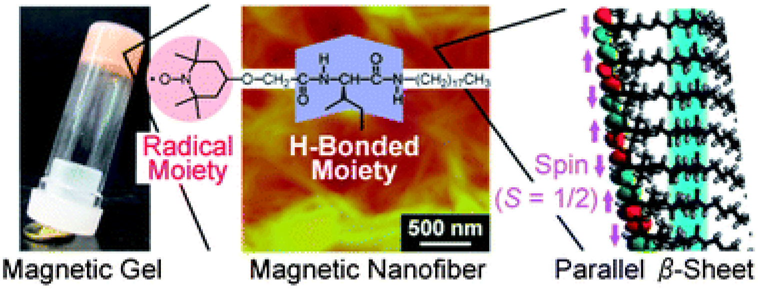


Defective silica sphere arrays having locally hexagonal-closed-packed structure but lack of long range ordering were incorporated into organic light emitting diodes as grating to extract the waveguided light trapped in the indium tin oxide/organic layers and the glass substrate. Using these defective hexagonal-closed-packed gratings for light extraction, broad band lambertian emitters are obtained due to the periodicity broadening and the random orientation in the gratings, resulting in enhancements in current and power efficiencies by a factor of 1.7 and 1.9, respectively.

- Supramolecular approach to the formation of magneto-active physical gels

Wu, Y.; Hirai, Y.; Tsunobuchi, Y.; Tokoro, H.; Eimura, H.; Yoshio, M.; Ohkoshi, S.; Kato, T. *Chem. Sci.* **2012**, *3*, 3007-3010.

Abstract:

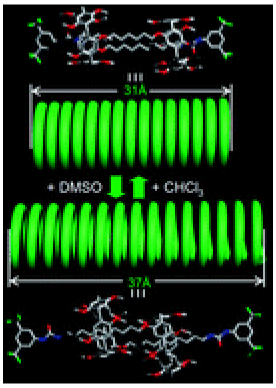


Magnetic nanofibers with one-dimensionally aligned spins were obtained through self-assembly of a nitroxide radical gelator derived from a hydrogen-bonded L-isoleucine-based scaffold.

- A solvent-driven molecular spring

  Zhang, Z.; Han, C.; Yu, G.; Huang, F. *Chem. Sci.* **2012**, *3*, 3026-3031.

  Abstract:

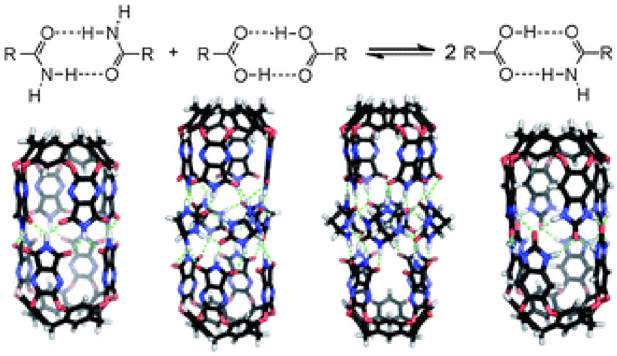


A solvent-driven doubly threaded rotaxane dimer based on an amino-modified copillar[5]arene was prepared using bis(trifluoromethyl)phenyl isocyanate as stoppers.

- Complexes within complexes: hydrogen bonding in capsules

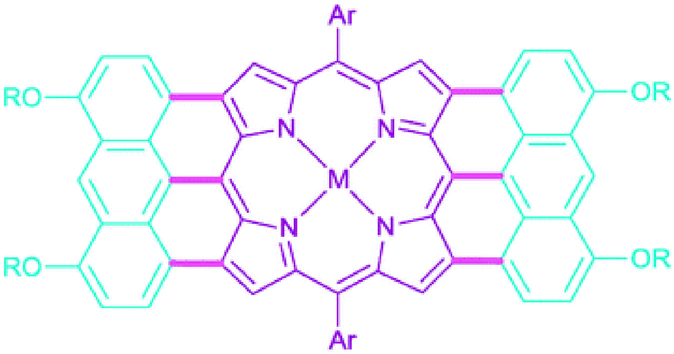
  Jiang, W.; Tiefenbacher , K.; Ajami, D.; Rebek, J. *Chem. Sci.* **2012**, *3,* 3022–3025.

  Abstract:



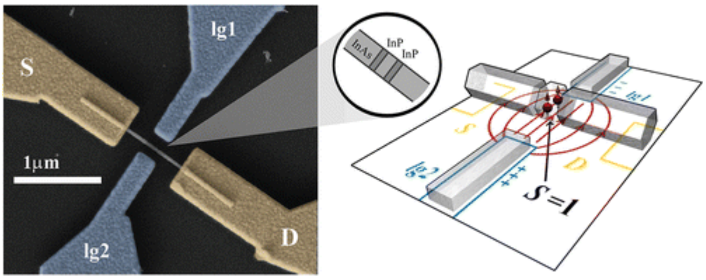
Hydrogen bonds play an important role in molecular recognition, biomolecule stabilization and organocatalysis. Typically, individual hydrogen bonding interactions are weak and short-lived in solution but isolated in capsules the encounters are intense and prolonged. We report here the interactions of carboxylic acids and primary carboxamides in a number of different capsule environments. The preference for hetero- *vs.* homo-dimerization is interpreted in terms of the adaptation of the guests to the hosts' spaces and chemical surfaces.

- Synthesis of π-extended porphyrins *via* intramolecular oxidative coupling
  Lewtak, J. P.; Gryko, D. T. *Chem. Commun.* **2012**, *48,* 10069–10086.
  Abstract:



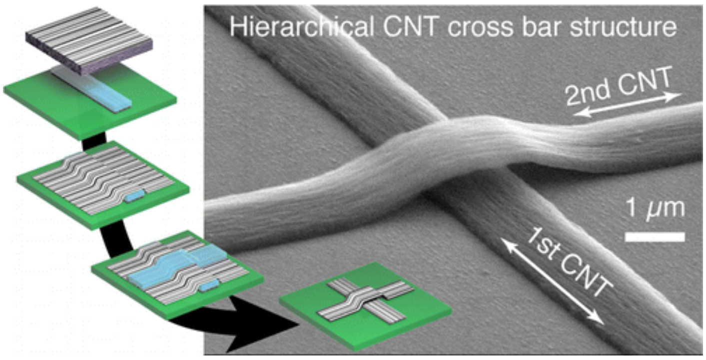
Porphyrins fused with other aromatic units at the *meso*- and β-positions have recently emerged as a hot topic of research. Their synthesis typically starts with preparation of precursors *via* either Suzuki coupling of a *meso*-bromoporphyrin or mixed-aldehyde condensation, and is followed by oxidative aromatic coupling, often using high-valent metal reagents (DDQ/Sc(OTf)$_3$ and Fe(III) salts are among the most popular). In recent years, porphyrins were oxidatively coupled not only with well-known aromatic hydrocarbons such as naphthalene and pyrene, but also with more complex heterocyclic fragments, including indole, phenanthro[1,10,9,8-*cdefg*]carbazole and BODIPY. A subtle relationship exists between the output of intramolecular oxidative coupling and the nature of the second aromatic moiety, cation in the porphyrin cavity, oxidant, and type of remaining *meso*-substituent. The extension of the porphyrin chromophore leads to significant change in linear and non-linear optical properties. Very strong bathochromic shifts of absorption (λ_{max} reaching 1.5–2 microns in some cases) and increases in two-photon absorption cross-sections are typical for these functional dyes.

- Electrostatic Spin Control in InAs/InP Nanowire Quantum Dots
  Romeo, L.; Roddaro, S.; Pitanti, A.; Ercolani, D.; Sorba, L.; Beltram, F. *Nano Letters* **2012,** *12*, 4490-4494.
  Abstract:



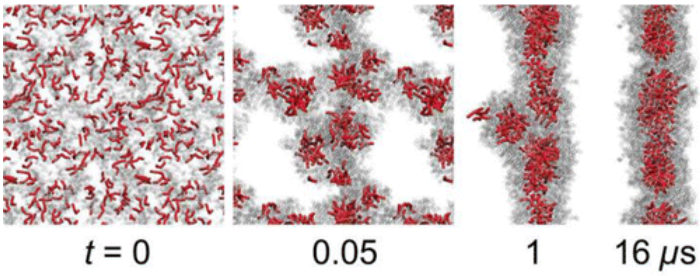
Very robust voltage-controlled spin transitions in few-electron quantum dots are demonstrated. Two lateral-gate electrodes patterned on opposite sides of an InAs/InP nanowire are used to apply a transverse electric field and tune orbital energy separation down to level-pair degeneracy. Transport measurements in this regime allow us to demonstrate the breakdown of the standard alternate up/down spin filling scheme and unambiguously show singlet–triplet spin transitions. The strong confinement of the present devices leads to a large energy gain for the observed anomalous spin configurations that exceeds 4 meV. As a consequence, this behavior is well visible even at temperatures exceeding *T* = 20 K.

- Hierarchical Three-Dimensional Layer-by-Layer Assembly of Carbon Nanotube Wafers for Integrated Nanoelectronic Devices
  Yamada, T.; Makiomoto, N.; Sekiguchi, A.; Yamamoto, Y.; Kobashi, K.; Hayamizu, Y.; Yomogida, Y.; Tanaka, H.; Shima, H.; Akinaga, H.; Futaba, D. N.; Hata, K. *Nano Letters* **2012,** *12*, 4540-4545.
  Abstract:



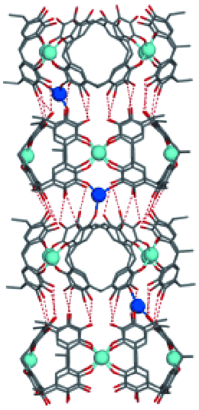
We report a general approach to overcome the enormous obstacle of the integration of CNTs into devices by bonding single-walled carbon nanotubes (SWNTs) films to arbitrary substrates and transferring them into densified and lithographically processable “CNT wafers”. Our approach allows hierarchical layer-by-layer assembly of SWNTs into organized three-dimensional structures, for example, bidirectional islands, crossbar arrays with and without contacts on Si, and flexible substrates. These organized SWNT structures can be integrated with low-power resistive random-access memory.

- Modeling the Self-Assembly of Peptide Amphiphiles into Fibers Using Coarse-Grained Molecular Dynamics
  Lee, O.-S.; Cho, V.; Schatz, G. C. *Nano Letters* **2012,** *12*, 4907-4913.
  Abstract:



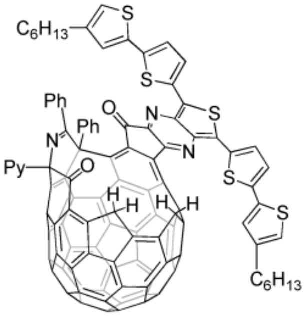
We have studied the self-assembly of peptide amphiphiles (PAs) into a cylindrical micelle fiber starting from a homogeneous mixture of PAs in water using coarse-grained molecular dynamics simulations. Nine independent 16 μs runs all show spontaneous fiber formation in which the PA molecules first form spherical micelles, and then micelles form a three-dimensional network via van der Waals interactions. As the hydrophobic core belonging to the different micelles merge, the three-dimensional network disappears and a fiber having a diameter of ∼80 Å appears. In agreement with atomistic simulation results, water molecules are excluded from the hydrophobic core and penetrate to ∼15 Å away from the axis of fiber. About 66% of the surface of fiber is covered with the IKVAV epitope, and ∼92% of the epitope is exposed to water molecules.

- Solution-Phase and Magnetic Approach towards Understanding Iron Gall Ink-like Nanoassemblies
  Kumari, H.; Kline, S. R.; Dennis, C. L.; Mossine, A. V.; Paul, R. L.; Deakyne, C. A.; Atwood, J. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 9263-9266.
  Abstract:



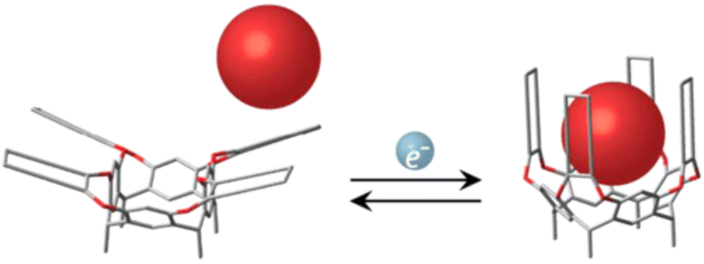
Metal-containing tubes: The structures of several iron-containing C-methylpyrogallol[4]arene (PgC1) nanoassemblies were studied in both the solid and solution phases. The nanoassemblies have a tubular architecture with the iron as part of the framework (see picture; gray C, red O, turquoise/blue Fe), and magnetic analysis suggests a canted or spiral arrangement of the iron centers.

- Absorption into the Near-IR Region by Conjugately Fusing Oligothiophenes
  Xiao, Z.; Ye, G.; Liu, Y.; Chen, S.; Peng, Q.; Zuo, Q.; Ding, L. *Angew. Chem. Int. Ed.* **2012**, *51*, 9038-9041.
  Abstract:



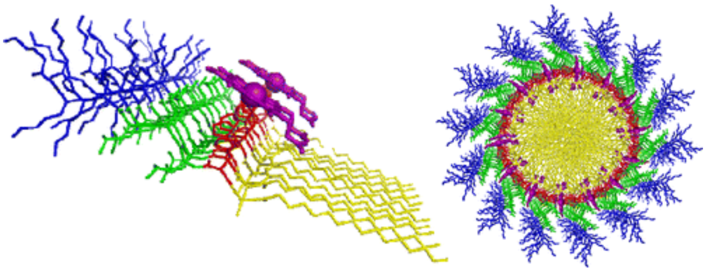
Fusing two in one: The π-electron systems of fullerene and an oligothiophene were conjugately fused by an open-cage process. This led to novel fullerene–oligothiophene chromophores with significantly enhanced light-absorbing capability, which covers a wide spectral range. The fullerene band gap could be tuned to about 1 eV by a chemical approach.

- Redox-Switchable Resorcin[4]arene Cavitands: Molecular Grippers
  Pochorovski, I.; Ebert, M.-O.; Gisselbrecht, J.-P.; Boudon, C.; Schweizer, W. B.; Diederich, F. *J. Am. Chem. Soc.* **2012**, *134*, 14702-14705.
  Abstract:



Diquinone-based resorcin[4]arene cavitands that open to a kite and close to a vase form upon changing their redox state, thereby releasing and binding guests, have been prepared and studied. The switching mechanism is based on intramolecular H-bonding interactions that stabilize the vase form and are only present in the reduced hydroquinone state. The intramolecular H-bonds were characterized using X-ray, IR, and NMR spectroscopies. Guests were bound in the closed, reduced state and fully released in the open, oxidized state

- Self-Assembly of Highly Ordered Peptide Amphiphile Metalloporphyrin Arrays
  Fry, H. C.; Garcia, J. M.; Medina, M. J.; Ricoy, U. M.; Gosztola, D. J.; Nikiforov, M. P.; Palmer, L. C.; Stupp, S. I. *J. Am. Chem. Soc.* **2012**, *134*, 14646-14649.
  Abstract:

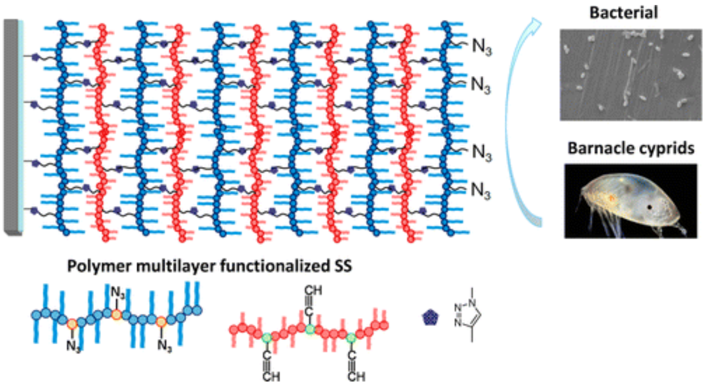


Long fibers assembled from peptide amphiphiles capable of binding the metalloporphyrin zinc protoporphyrin IX ((PPIX)Zn) have been synthesized. Rational peptide design was employed to generate a peptide, c16-AHL$_3$K$_3$-CO$_2$H, capable of forming a β-sheet structure that propagates into larger fibrous structures. A porphyrin-binding site, a single histidine, was engineered into the peptide sequence in order to bind (PPIX)Zn to provide photophysical functionality. The resulting system indicates control from the molecular level to the macromolecular level with a high order of porphyrin organization. UV/visible and circular dichroism spectroscopies were employed to detail molecular organization, whereas electron microscopy and atomic force microscopy aided in macromolecular characterization. Preliminary picosecond transient absorption data are also reported. Reduced hemin, (PPIX)Fe^{II}, was also employed to highlight the material's versatility and tunability.

- REACH Coarse-Grained Simulation of a Cellulose Fiber
  Glass, D. C.; Moritsugu, K.; Cheng, X.; Smith, J. C. *Biomacromol.* **2012**, *13*, 2634-2644.
  Abstract:

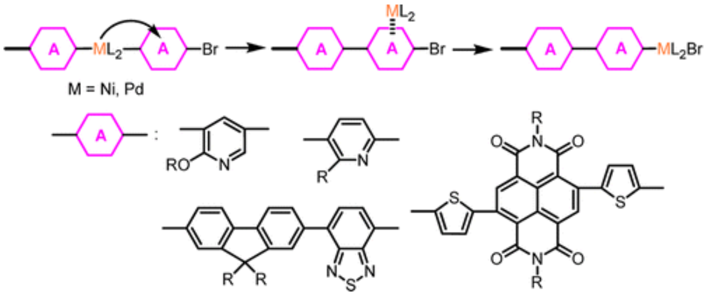
A molecular level understanding of the structure, dynamics and mechanics of cellulose fibers can aid in understanding the recalcitrance of biomass to hydrolysis in cellulosic biofuel production. Here, a residue-scale REACH (Realistic Extension Algorithm via Covariance Hessian) coarse-grained force field was derived from all-atom molecular dynamics (MD) simulations of the crystalline Iβ cellulose fibril. REACH maps the atomistic covariance matrix onto coarse-grained elastic force constants. The REACH force field was found to reproduce the positional fluctuations and low-frequency vibrational spectra from the all-atom model, allowing elastic properties of the cellulose fibril to be characterized using the coarse-grained force field with a speedup of >20 relative to atomistic MD on systems of the same size. The calculated longitudinal/transversal Young's modulus and the velocity of sound are in agreement with experiment. The persistence length of a 36-chain cellulose microcrystal was estimated to be ~380 μm. Finally, the normal-mode analysis with the REACH force field suggests that intrinsic dynamics might facilitate the deconstruction of the cellulose fibril from the hydrophobic surface.

- Layer-by-Layer Click Deposition of Functional Polymer Coatings for Combating Marine Biofouling
  Yang, W. J.; Pranantyo, D.; Neoh, K.-G.; Kang, E.-T.; Lay-Ming Teo, S.; Rittschof, D. *Biomacromol.* **2012**, *13*, 2769-2780.
  <u>Abstract:</u>



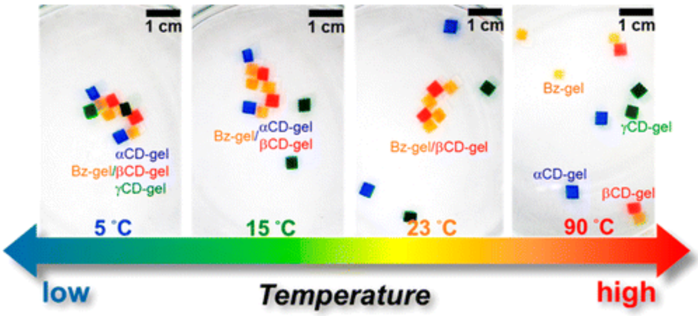
"Click" chemistry-enabled layer-by-layer (LBL) deposition of multilayer functional polymer coatings provides an alternative approach to combating biofouling. Fouling-resistant *azido*-functionalized poly(ethylene glycol) methyl ether methacrylate-based polymer chains (*azido*-poly(PEGMA)) and antimicrobial *alkynyl*-functionalized 2-(methacryloyloxy)ethyl trimethyl ammonium chloride-based polymer chains (*alkynyl*-poly(META)) were click-assembled layer-by-layer via alkyne–azide 1,3-dipolar cycloaddition. The polymer multilayer coatings are resistant to bacterial adhesion and are bactericidal to marine Gram-negative *Pseudomonas sp.* NCIMB 2021 bacteria. Settlement of barnacle (*Amphibalanus* (=*Balanus*) *amphitrite*) cyprids is greatly reduced on the multilayer polymer-functionalized substrates. As the number of the polymer layers increases, efficacy against bacterial fouling and settlement of barnacle cyprids increases. The LBL-functionalized surfaces exhibit low toxicity toward the barnacle cyprids and are stable upon prolonged exposure to seawater. LBL click deposition is thus an effective and potentially environmentally benign way to prepare antifouling coatings.

- Precision Synthesis of n-Type π-Conjugated Polymers in Catalyst-Transfer Condensation
  Yokozawa, T.; Nanashima, Y.; Ohta, Y. *ACS Macro Lett.*, **2012**, *1*, 862–866.
  <u>Abstract:</u>



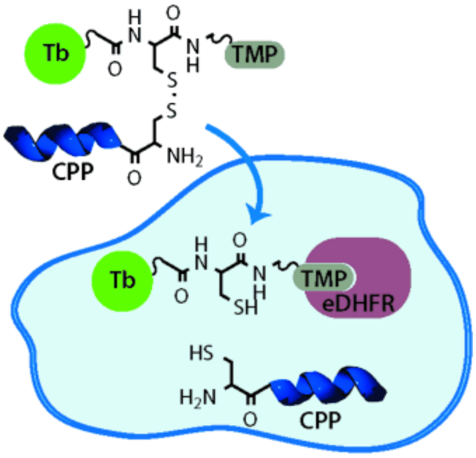
Recent developments in catalyst-transfer condensation polymerization, which proceeds in a chain-growth polymerization manner, have made it possible to synthesize well-defined π-conjugated polymers with controlled molecular weight and low polydispersity, as well as block copolymers and gradient copolymers. However, catalyst-transfer condensation polymerization has been limited to the polymerization of donor monomers (such as thiophene) for the synthesis of p-type π-conjugated polymers. Here, we highlight several recent advances in catalyst-transfer condensation polymerization leading to n-type π-conjugated polymers. The Kumada–Tamao coupling polymerization of Grignard pyridine monomers yields well-defined poly(pyridine-3,5-diyl) and poly(pyridine-2,5-diyl) with a broad molecular weight distribution. Monomers consisting of strong acceptor and weak donor moieties also undergo catalyst-transfer polymerization; well-defined poly(fluorene benzothiaziazole) was obtained by Suzuki–Miyaura coupling polymerization and poly(bithiophene naphthalene diimide) was obtained by an unusual Ni-catalyzed coupling polymerization of an anion radical generated from a bromothiophene naphathalene diimide bromothiophene monomer and activated zinc.

- Temperature-Sensitive Macroscopic Assembly Based on Molecular Recognition
  Zheng, Y.; Hashidzume, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *ACS Macro Lett.*, **2012**, *1*, 1083–1085.
  Abstract:



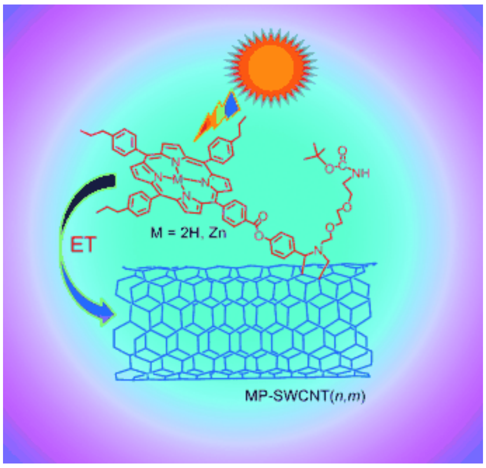
The interaction of polyacrylamide(pAAm)-based gel modified with benzyl (Bz) moiety (Bz(*x*)-gel, where *x* denotes the mol % content of Bz moiety) with a pAAm-based gel possessing cyclodextrin (CD) moieties (αCD-gel, βCD-gel, and γCD-gel) was investigated at various temperatures to elucidate the effect of temperature on the formation of macroscopic assembly. The interaction of Bz(*x*)-gel with CD-gels was stronger at a lower temperature, consistent with the binding constants for the model system of pAAm modified with 1 mol % Bz moiety and native CDs. Bz(15)-gel interacted only with βCD-gel at a higher temperature (<ca. 90 °C), with αCD-gel at a temperature ≤15 °C, and with γCD-gel at 5 °C to form gel assemblies. The formation of gel assemblies depending on temperature showed a good reversibility. On the basis of these observations, it is concluded that temperature is also an important stimulus for macroscopic assembly based on molecular recognition.

- Cell-Penetrating Peptides as Delivery Vehicles for a Protein-Targeted Terbium Complex
  Mohandessi, S.; Rajendran, M.; Magda, D.; Miller, L. W. *Chem. Eur. J.* **2012**, *18*, 10825–10829.
  Abstract:



Release after transmission: Arginine-rich, cell-penetrating peptides (CPPs) mediate cytoplasmic delivery of trimethoprim (TMP)–terbium complex conjugates and selective, intracellular labeling of *E. coli* dihydrofolate reductase (eDHFR) fusion proteins. A disulfide bond linking CPP and cargo is reduced following uptake (see picture). CPP conjugation can be used to deliver otherwise cell-impermeable, ligand–fluorophore conjugates.

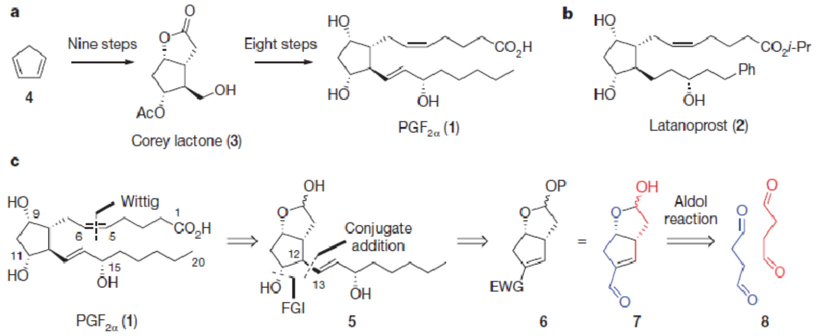
- Functionalization of Diameter-Sorted Semiconductive SWCNTs with Photosensitizing Porphyrins: Syntheses and Photoinduced Electron Transfer
  Das, S. K.; Sandanayaka, A. S. D.; Subbaiyan, N. K.; Zandler, M. E.; Ito, O.; D'Souza, F. *Chem. Eur. J.* **2012**, *18*, 11388–11398.
  Abstract:



Covalent functionalization of diameter sorted SWCNTs with porphyrins (MP), and photochemistry to establish nanotube diameter-dependent charge separation efficiencies are reported. The MP–SWCNT(*n*,*m*) [M=2 H or Zn, and (*n*,*m*)=(7,6) or (6,5)] nanohybrids are characterized by a variety of spectroscopic, thermogravimetric, TEM imaging techniques, and also by DFT MO calculations. The thermogravimetric, Raman and fluorescence studies reveal the presence of a moderate number of porphyrins on the SWCNT surface. The MO results suggest charge separation (CS) via the excited state of MP. Time-resolved fluorescence studies reveal quenching of the singlet excited state of the MP with SWCNT(*n*,*m*), giving the rate constants of charge separation (k_{CS}) in the range of (4–5)×10^9 s^{-1}. Nanosecond transient absorption measurements confirm the charge-separated radical cation and

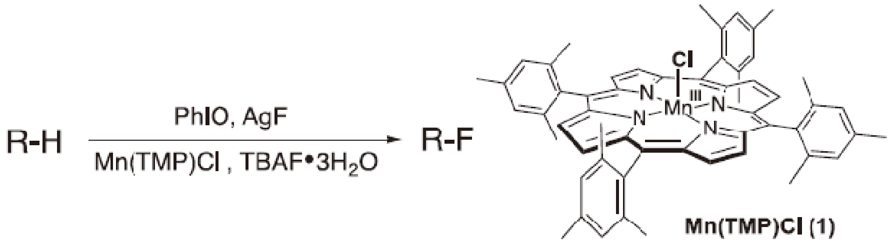
the radical anion as [MP$^{\cdot+}$–SWCNT$^{\cdot-}$] with their characteristic absorption bands in the visible and near-IR regions. The charge separated states persist for about 70–100 ns thus giving an opportunity to utilize them to build photoelectrochemical cells, which allowed us to derive the structure–reactivity relationship between the nature of porphyrin and diameter of the employed nanotubes.

- Stereocontrolled organocatalytic synthesis of prostaglandin PGF$_{2\alpha}$ in seven steps
  Coulthard, G.; Erb, W.; Aggarwal, V. K. *Nature* **2012**, *489*, 278-281.
  Abstract:



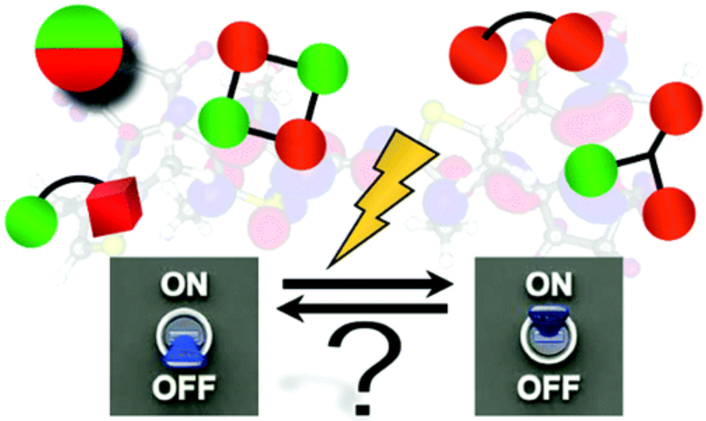
Prostaglandins are hormone-like chemical messengers that regulate a broad range of physiological activities, including blood circulation, digestion and reproduction. Their biological activities and their complex molecular architectures have made prostaglandins popular targets for synthetic organic chemists for over 40 years. Prostaglandin analogues are widely used as pharmaceuticals and some, such as latanoprost, which is used to treat glaucoma, have become billion-dollar drugs. Previously reported syntheses of these compounds are quite lengthy, and every chemical step costs time and energy, generates waste and is accompanied by material losses. Using a new bond disconnection, here we report a concise synthesis of the most complex prostaglandin, PGF$_{2\alpha}$, with high levels of control of relative and absolute stereochemistry, and fewer steps. The key step is an aldol cascade reaction of succinaldehyde using proline organocatalysis to create a bicyclic enal in one step and an enantiomeric excess of 98 %. This intermediate bicyclic enal is fully primed with the appropriate functionality for attachment of the remaining groups. Access to this bicyclic enal will not only render existing prostaglandin-based drugs more affordable, but will also facilitate the rapid exploration of related chemical structures around the ubiquitous five-membered ring motif, such as potentially therapeutic prostaglandin analogues.

- Oxidative Aliphatic C-H Fluorination with Fluoride Ion Catalyzed by a Manganese Porphyrin
  Liu, W.; Huang, X.; Cheng, M.-J.; Nielsen, R. J.; Goddard III, W. A.; Groves, J. T. *Science* **2012**, *337*, 1322-1325.
  Abstract:



Despite the growing importance of fluorinated organic compounds in drug development, there are no direct protocols for the fluorination of aliphatic C-H bonds using conveniently handled fluoride salts. We have discovered that a manganese porphyrin complex catalyzes alkyl fluorination by fluoride ion under mild conditions in conjunction with stoichiometric oxidation by iodosylbenzene. Simple alkanes, terpenoids, and even steroids were selectively fluorinated at otherwise inaccessible sites in 50 to 60 % yield. Decalin was fluorinated predominantly at the C2 and C3 methylene positions. Bornyl acetate was converted to exo-5-fluoro-bornyl acetate, and 5α-androstan-17-one was fluorinated selectively in the A ring. Mechanistic analysis suggests that the regioselectivity for C-H bond cleavage is directed by an oxomanganese(V) catalytic intermediate followed by F delivery via an unusual manganese(IV) fluoride that has been isolated and structurally characterized.

- Single Molecule Multiphotochromism with Diarylethenes
  Perrier, A.; Maurel, F.; Jacquemin, D. *Acc. Chem. Res.* **2012**, *45*, 1173-1182.
  Abstract:



In single photochromes, the two isomers that are interconverted in photoinduced reactions can serve as *on* and *off* states in a molecular switching device. The addition of several photochromic moieties onto a single molecule can allow the processing of more complex logical patterns. For example, an asymmetric triad could, in principle, store a byte, rather than a bit, of data. Because of the potential impact of multiphotochromic molecules in many research areas, over the past decade several groups have synthesized these coupled structures. The targets are easily addressable molecules that display increased contrast between the *on* and *off* states and in which all isomers have significantly distinguishable optical signatures.

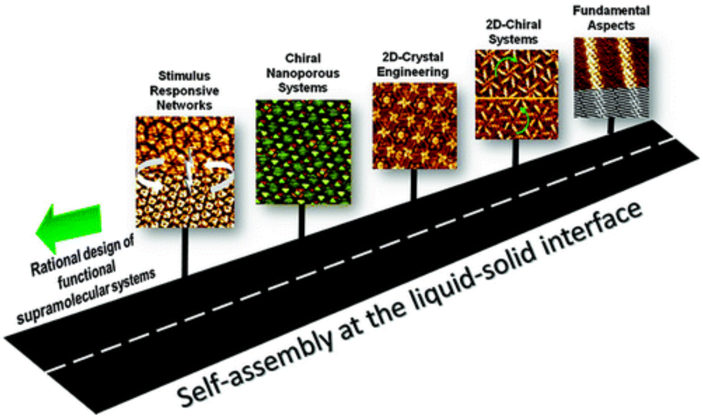
In this Account, we provide an overview of the multiswitchable molecular systems that incorporate at least one diarylethene group, which is the most successful thermally stable (P-type) organic photochrome. Up to this point, most systems have presented significant limitations. First of all, the reversibility of the processes is hindered by several side reactions more frequently than for single photochromes. Second, switching one part of the compound impedes the photoreactivity of other fragments in approximately 50% of the cases, and maximizing the electronic communication increases the probability of partial activity. In addition, most of the few synthesized operative systems only demonstrate cumulative absorption spectra rather than new features. Finally, it is impossible to selectively induce a chosen conversion because one wavelength might trigger several processes. We also emphasize the promising successes of asymmetric diarylethene dimers and trimers and molecules that combine two families of photochromes, such as diarylethene added to fulgimide or phenoxy-naphthacenequinone.

In that framework, theoretical simulations offer complementary tools to investigate these structures, both to obtain structure/property relationships and to propose paths for the design of more efficient molecules. However, due to the size of the systems, researchers can only apply semiquantitative models. The investigation of the absorption spectra of the photochromes with time-dependent density functional theory (TD-DFT), the analysis of the topology of the LUMO + n (typically n = 1) of the closed–open hybrid, and an estimate of the steric stress in the hypothetical (ground-state) closed–closed structure serve as a useful combination of parameters to obtain initial insights regarding the photocyclization of the different open diarylethene groups. Nevertheless, because a first-order qualitative approach does not explore the potential energy surface of the photoexcited states, it remains inadequate for the investigation of some molecules.

- Exploring the Complexity of Supramolecular Interactions for Patterning at the Liquid–Solid Interface

  Mali, K. S.; Adisoejoso, J.; Ghijsens, E.; De Cat, I.; De Feyter, S. *Acc. Chem. Res.* **2012**, *45*, 1309-1320.

  Abstract:

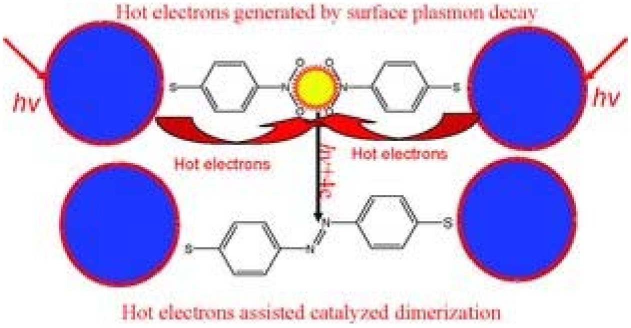


The use of self-assembly to fabricate surface-confined adsorbed layers (adlayers) from molecular components provides a simple means of producing complex functional surfaces. The molecular self-assembly process relies on supramolecular interactions sustained by noncovalent forces such as van der Waals, electrostatic, dipole–dipole, and hydrogen bonding interactions. Researchers have exploited these noncovalent bonding motifs to construct well-defined two-dimensional (2D) architectures at the liquid–solid interface. Despite myriad examples of 2D molecular assembly, most of these early findings were serendipitous because the intermolecular interactions involved in the process are often numerous, subtle, cooperative, and multifaceted. As a consequence, the ability to tailor supramolecular patterns has evolved slowly. Insight gained from various studies over the years has contributed significantly to the knowledge of supramolecular interactions, and the stage is now set to systematically engineer the 2D supramolecular networks in a “preprogrammed” fashion.

The control over 2D self-assembly of molecules has many important implications. Through appropriate manipulation of supramolecular interactions, one can “encode” the information at the molecular level via structural features such as functional groups, substitution patterns, and chiral centers which could then be retrieved, transferred, or amplified at the supramolecular level through well-defined molecular recognition processes. This ability allows for precise control over the nanoscale structure and function of patterned surfaces. A clearer understanding and effective use of these interactions could lead to the development of functional surfaces with potential applications in molecular electronics, chiral separations, sensors based on host–guest systems, and thin film materials for lubrication.

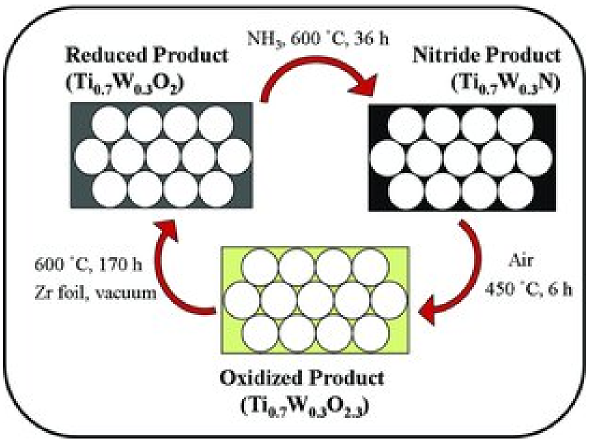
In this Account, we portray our various attempts to achieve rational design of self-assembled adlayers by exploiting the aforementioned complex interactions at the liquid–solid interface. The liquid–solid interface presents a unique medium to construct flawless networks of surface confined molecules. The presence of substrate and solvent provides an additional handle for steering the self-assembly of molecules. Scanning tunneling microscopy (STM) was used for probing these molecular layers, a technique that serves not only as a visualization tool but could also be employed for active manipulation of molecules. The supramolecular systems described here are only weakly adsorbed on a substrate, which is typically highly oriented pyrolytic graphite (HOPG). Starting with fundamental studies of substrate and solvent influence on molecular self-assembly, this Account describes progressively complex aspects such as multicomponent self-assembly via 2D crystal engineering, emergence, and induction of chirality and stimulus responsive supramolecular systems.

- A Novel Application of Plasmonics: Plasmon-Driven Surface-Catalyzed Reactions
  Sun, M.; Xu, H. *Small* **2012**, *8*, 2777–2786.
  Abstract:



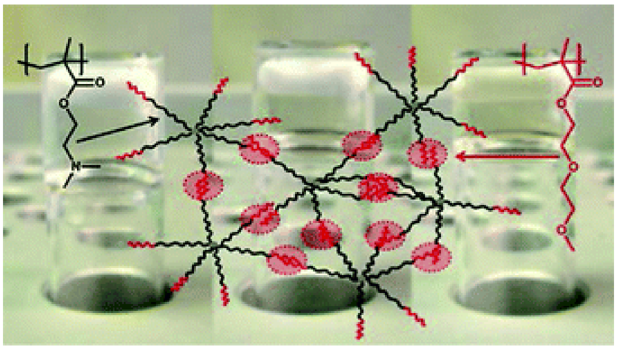
The first experimental and theoretical evidence of the surface-catalyzed reaction of p,p’-dimercaptoazobenzene (DMAB) produced from para-aminothiophenol (PATP) by local surface plasmons was reported in 2010, and since that time a series of investigations have supported these findings using different experimental and theoretical methods. Recent work has also found that local plasmons can drive a surface-catalyzed reaction of DMAB converted from 4-nitrobenzenethiol (4NBT), assisted by local surface plasmons. There are at least three important discoveries in these investigations: 1) in the field of surface-enhanced Raman scattering (SERS) the widely accepted misinterpretation (since 1994) that the chemical mechanism resulting in three additional Raman peaks of PATP in Ag or Au solutions has been corrected with a new mechanism; 2) it is confirmed that SERS is not always a noninvasive technique, and under certain conditions cannot always obtain the vibrational fingerprint information of the original surface species; 3) a novel method to synthesize new molecules, induced by local surface plasmons or plasmon waveguides on the nanoscale, has been found. This Review considers recent novel applications of plasmonics to chemical reactions, especially to plasmon-driven surface-catalyzed reactions.

- Interconversion of Inverse Opals of Electrically Conducting Doped Titanium Oxides and Nitrides
  Subban, C. V.; Smith, I. C.; DiSalvo, F. J. *Small* **2012**, *8*, 2824–2832.
  Abstract:



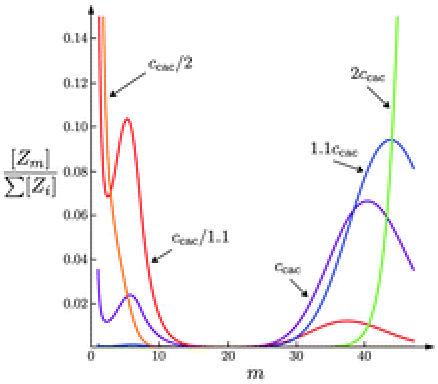
There is a need for conducting, porous, and chemically stable materials for technologies including, but not limited to, fuel cells, solar cells, and batteries. The need for catalyst support materials that are more durable than carbon black in fuel cells motivated previous studies of the synthesis, characterization, and corrosion resistance of $Ti_{0.7}W_{0.3}O_2$ nanoparticles. However, because even higher porosity and increased electrical conductivity are desired, processes were developed to prepare rutile phase $Ti_{0.7}W_{0.3}O_2$ and cubic $Ti_{0.7}W_{0.3}N$ in inverse opal morphologies from a precursor inverse opal of very poorly conducting, amorphous $Ti_{0.7}W_{0.3}O_{2.3}$. Inverse opals have been explored for a variety of applications from catalysis to photonics, and inverse opals of both oxides and nitrides have been reported. By synthesizing highly conducting mixed-metal oxides and mixed-metal nitrides, the applications of inverse opals can be broadened. Herein, the synthesis and characterization of polystyrene-templated, single-phase, crystalline inverse opals of $Ti_{0.7}W_{0.3}O_2$ are reported. These conducting inverse opals can subsequently be converted to inverse opals of $Ti_{0.7}W_{0.3}N$ and then fully oxidized back to inverse opals of the original insulating, amorphous $Ti_{0.7}W_{0.3}O_{2.3}$. Such changes in composition and crystal structure, while successfully retaining the inverse opal morphology without the use of a supporting template during the conversion, have not been previously reported.

- Smart hydrogels based on responsive star-block copolymers
  Schmalz, A.; Schmalz, H.; Müller, A. H. E. *Soft Matter* **2012**, *8*, 9436-9445.
  Abstract:



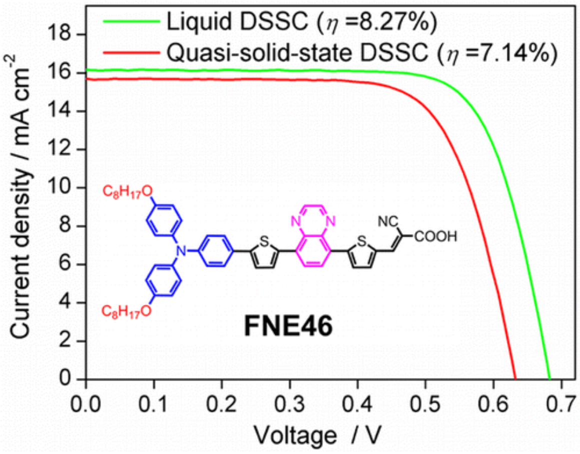
A series of smart hydrogels based on dual stimuli responsive star-block copolymers responding to pH and temperature were prepared *via* atom transfer radical polymerization (ATRP) employing the core-first method. They consist of poly(2-(dimethylamino)ethyl methacrylate) (PDMA) inner blocks and outer blocks comprised of poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA). The aggregation behavior of these block copolymer stars is analyzed by dependence on block length and arm number. The dual stimuli responsiveness of the stars is demonstrated by turbidity as well as dynamic light scattering on dilute aqueous solution, and the gelation behavior of concentrated aqueous solutions is studied by rheology. Above the transition temperature of the PDEGMA outer blocks the stars form flower-like aggregates in dilute solution or free-standing gels at higher concentrations. When the temperature is increased further above the transition temperature of the PDMA inner block, the aggregates start to contract and a weakening was observed for soft gels, whereas for strong gels no influence on the moduli was detected. The behavior is controlled by both concentration and pH value. In addition, we show that the minimum polymer concentration for gel formation can be lowered by quaternizing the inner block of the stars, but a second response to stimuli is lost during the procedure.

- Theory of DNA–cationic micelle complexation
  Schiessel, H.; Correa-Rodríguez, M. D.; Rudiuk, S.; Baigl D.; Yoshikawa, K. *Soft Matter* **2012**, *8*, 9406-9411.
  Abstract:



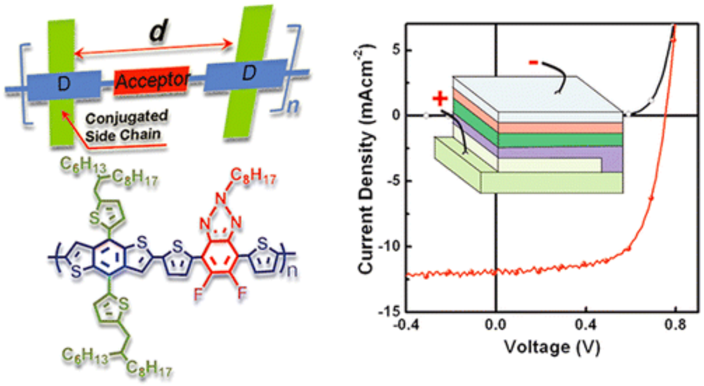
We present a theory of spherical micelle formation from cationic amphiphiles in the absence and in the presence of DNA. The distribution of micelle sizes as well as the critical micelle and aggregation concentrations (cmc and cac) are calculated. Micelle formation is favored by the hydrophobic tails but disfavored by the entropic cost associated with counterion condensation. Counterion release drives the complexation between DNA and amphiphiles and causes micellation at a much smaller concentration than in the absence of DNA. The stiffness of double-stranded DNA favors the formation of large micelles leading to a bimodal distribution of micelle sizes.

- Molecular Engineering of Quinoxaline-Based Organic Sensitizers for Highly Efficient and Stable Dye-Sensitized Solar Cells
  Lu, X.; Feng, Q.; Lan, T.; Zhou, G.; Wang, Z.-S. *Chem. Mater.* **2012**, *24*, 3179–3187.
  Abstract:



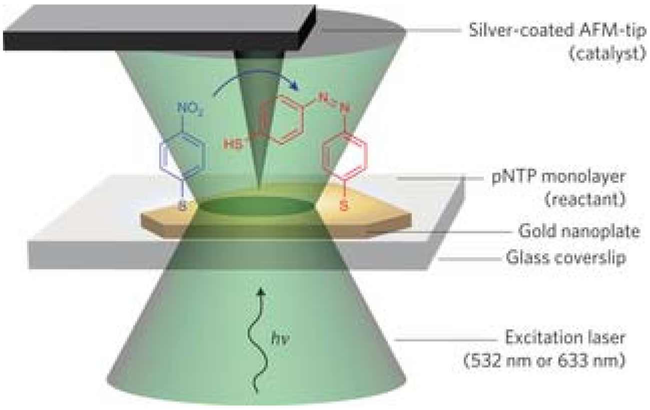
A series of quinoxaline based metal-free organic sensitizers has been designed and synthesized for dye-sensitized solar cells (DSSCs). The absorption, electrochemical, and photovoltaic properties for all sensitizers have been systematically investigated. It is found that the incorporation of quinoxaline unit instead of thienopyrazine unit results in a negative shift of the lowest unoccupied molecular orbital levels for **FNE44**, **FNE45**, **FNE46**, and **FNE47**, in comparison to **FNE32**, which induces a remarkable enhancement of the electron injection driving force from the excited organic sensitizers to the TiO_2 semiconductor. Moreover, when the alkyl substituents are removed from the spacer part in **FNE44** to the donor part in **FNE45** and **FNE46**, a more conjugated system and a bathochromically shifted maximum absorption band can be realized, which consequently results in an increased light harvesting efficiency and photogenerated current. In addition, the length of the alkyl substituents on the donor part has a certain influence on the DSSC performance. Combining the three contributions, **FNE46**-based DSSC with liquid electrolyte displays the highest power conversion efficiency (η) of 8.27%. Most importantly, a η of 7.14% has been achieved for **FNE46** based quasi-solid-state DSSC and remained at 100% of the initial value after continuous light soaking for 1000 h, which indicates that **FNE46** is appropriate for promising commercial application. Our findings will facilitate the understanding of the crucial importance of molecular engineering and pave a new path to design novel metal-free organic dyes for highly efficient and stable DSSCs.

- Conjugated Side-Chain-Isolated D–A Copolymers Based on Benzo[1,2-b:4,5-b′]dithiophene-alt-dithienylbenzotriazole: Synthesis and Photovoltaic Properties
  Min, J.; Zhang, Z.-G.; Zhang, S.; Li, Y. *Chem. Mater.* **2012**, *24*, 3493–3499.
  Abstract:



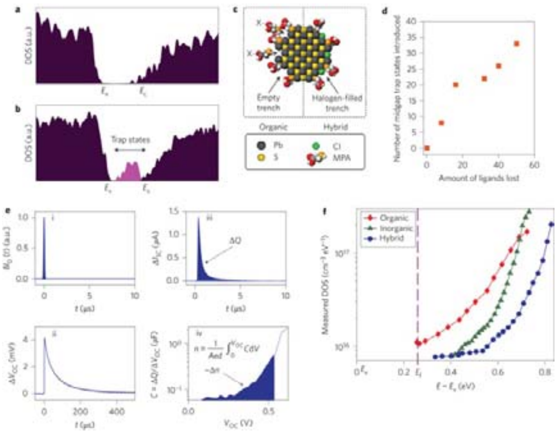
Conjugated side-chain-isolated D–A copolymers, based on the donor unit of benzodithiophene (BDT) with a thiophene-conjugated side chain, thiophene π bridge, and the acceptor unit of benzotriazole (BTA) with or without fluorine substitution (PBDT-FBTA and PBDT-HBTA), were designed and synthesized for elucidating their structure–property relationships. The copolymer films demonstrated well-defined absorption peaks with steep absorption edges, consistent with their rigid and ordered structures in the solid films. The substitution of a thiophene-conjugated side chain on the BDT unit in the copolymers aroused 15-nm red-shifted absorption in comparison with its polymer analogues with alkoxy side chains on the BDT unit. Compared to PBDT-HBTA, PBDT-FBTA with two-fluorine-atom substitution on the BTA unit demonstrated a lower highest occupied molecular orbital energy level, higher hole mobility, and significantly better photovoltaic performance. A polymer solar cell (PSC) based on PBDT-FBTA/$PC_{70}BM$ (1:2, w/w) with a 5% 1,8-diiodooctane additive displayed a power conversion efficiency (PCE) of 6.0% with a J_{sc} of 11.9 mA cm^{-2}, a V_{OC} of 0.75 V, and a fill factor of 67.2%, under the illumination of AM1.5G, 100 mW cm^{-2}. Even at a thicker active layer of 400 nm, the PSC still demonstrated a higher PCE of 4.74%. The results indicate that PBDT-FBTA is a promising polymer donor material for future application of large-area PSCs.

- Catalytic processes monitored at the nanoscale with tip-enhanced Raman spectroscopy
  Lantman, E. M. S.; Deckert-Gaudig, T.; Mank, A. J.G.; Deckert, V.; Weckhuysen, B. M. *Nature Nanotech.* **2012**, *7*, 583–586.
  Abstract:



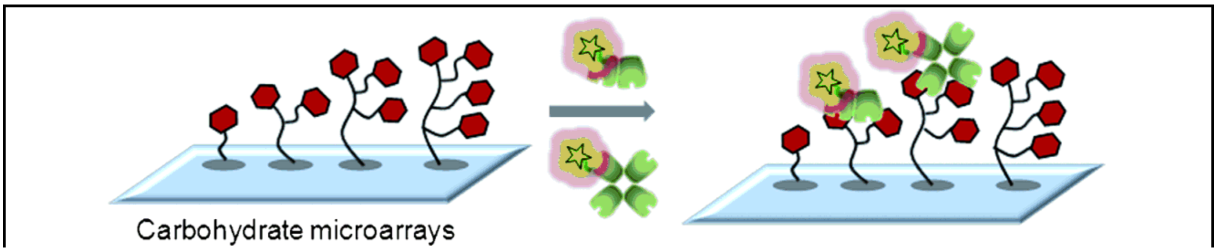
Heterogeneous catalysts play a pivotal role in the chemical industry, but acquiring molecular insights into functioning catalysts remains a significant challenge. Recent advances in micro-spectroscopic approaches have allowed spatiotemporal information to be obtained on the dynamics of single active sites and the diffusion of single molecules. However, these methods lack nanometre-scale spatial resolution and/or require the use of fluorescent labels. Here, we show that time-resolved tip-enhanced Raman spectroscopy can monitor photocatalytic reactions at the nanoscale. We use a silver-coated atomic force microscope tip to both enhance the Raman signal and to act as the catalyst. The tip is placed in contact with a self-assembled monolayer of p-nitrothiophenol molecules adsorbed on gold nanoplates. A photocatalytic reduction process is induced at the apex of the tip with green laser light, while red laser light is used to monitor the transformation process during the reaction. This dual-wavelength approach can also be used to observe other molecular effects such as monolayer diffusion.

- Hybrid passivated colloidal quantum dot solids
  Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; Kemp, K. W.; Kramer, I. J.; Ning, Z.; Labelle, A. J.; Chou, K. W.; Amassian, A., Sargent, E. H. *Nature Nanotech.* **2012**, *7*, 577–582.
  Abstract:



Colloidal quantum dot (CQD) films allow large-area solution processing and bandgap tuning through the quantum size effect. However, the high ratio of surface area to volume makes CQD films prone to high trap state densities if surfaces are imperfectly passivated, promoting recombination of charge carriers that is detrimental to device performance7. Recent advances have replaced the long insulating ligands that enable colloidal stability following synthesis with shorter organic linkers or halide anions, leading to improved passivation and higher packing densities. Although this substitution has been performed using solid-state ligand exchange, a solution-based approach is preferable because it enables increased control over the balance of charges on the surface of the quantum dot, which is essential for eliminating midgap trap states. Furthermore, the solution-based approach leverages recent progress in metal:chalcogen chemistry in the liquid phase. Here, we quantify the density of midgap trap states in CQD solids and show that the performance of CQD-based photovoltaics is now limited by electron–hole recombination due to these states. Next, using density functional theory and optoelectronic device modelling, we show that to improve this performance it is essential to bind a suitable ligand to each potential trap site on the surface of the quantum dot. We then develop a robust hybrid passivation scheme that involves introducing halide anions during the end stages of the synthesis process, which can passivate trap sites that are inaccessible to much larger organic ligands. An organic crosslinking strategy is then used to form the film. Finally, we use our hybrid passivated CQD solid to fabricate a solar cell with a certified efficiency of 7.0%, which is a record for a CQD photovoltaic device.

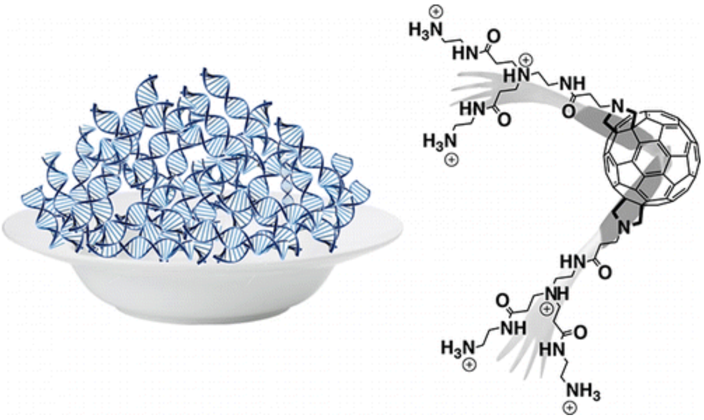
- Analysis of Density-Dependent Binding of Glycans by Lectins Using Carbohydrate Microarrays
  Tian, X.; Pai, J.; Shin, I. *Chem. Asian J.* **2012**, *7*, 2052–2060.
  Abstract:



To investigate the density-dependent binding of glycans by lectins using carbohydrate microarrays, a number of C-terminal hydrazide-conjugated neoglycopeptides with various valences and different spatial arrangements of the sugar ligands were prepared on a solid support. The synthetic strategy includes (1) assembly of alkyne-linked peptides possessing C-terminal hydrazide on a solid support, (2) coupling of azide-linked, unprotected sugars to the alkyne-linked peptides on the solid support utilizing click chemistry, and (3) release of the neoglycopeptides from the solid support. By using this synthetic methodology, sixty five neoglycopeptides with a valency ranging from 1 to 4 and different spatial arrangements of the carbohydrate ligands were generated. Carbohydrate microarrays were constructed by immobilizing the prepared neoglycopeptides on epoxide-derivatized glass slides and were used to analyze the density-dependent binding of glycans by lectins. The results of binding property determinations show that lectin binding is highly dependent on the surface glycan density.

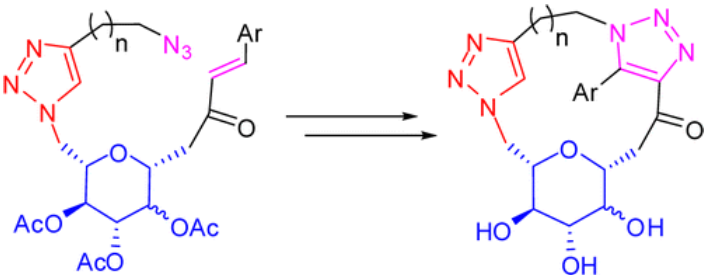
- Synthesis and Characterization of Highly Water-Soluble Dendrofulleropyrrolidine Bisadducts with DNA Binding Activity
  Montellano López, A.; Scarel, F.; Rubio Carrero, N.; Vázquez, E.; Mateo-Alonso, A.; Da Ros, T.; Prato, M. *Org. Lett.* **2012**, *14*, 4450-4453.

Abstract:



The synthesis, characterization and DNA binding studies of a series of polycationic fullerene adducts are reported. These cationic species, exhibiting reasonably high water solubility and a heterogeneous distribution of positive charges, can efficiently complex plasmid DNA. Electrophoresis studies show different DNA binding efficiencies for different adducts, some of which can be considered excellent candidates for DNA binding therapies.

- Diversity Oriented Synthesis of Pyran Based Polyfunctional Stereogenic Macrocyles and Their Conformational Studies
  Ajay, A.; Sharma, S.; Gupt, M. P.; Hamidullah, V. B.; Kumar, B.; Kaushik, M. P.; Konwar, R.; Ampapathi, R. S.; Tripathi, R. P. *Org. Lett.* **2012**, *14*, 4306-4309.
  Abstract:



A new approach to synthesize a homologous series of 14-, 15-, and 16-membered drug-like, macrocyclic glycoconjugates involving TBAHS promoted azide-propenone intramolecular cycloaddition in designed *C*-glycopyranosyl butenones from a simple sugar d-glucose and d-mannose is reported.