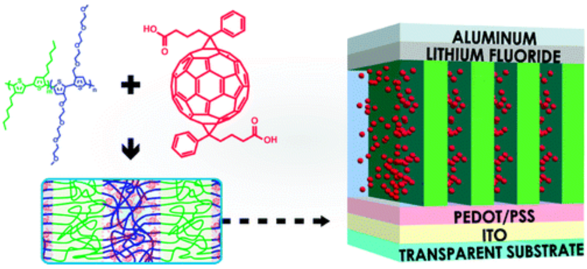
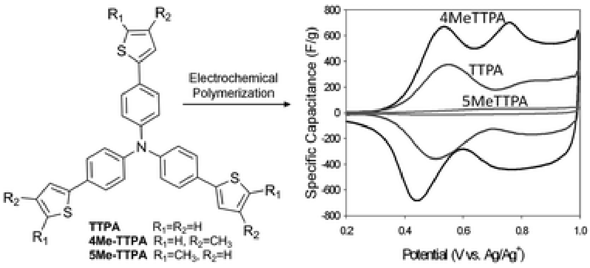
- Cooperative Assembly of Hydrogen-Bonded Diblock Copolythiophene/ Fullerene Blends for Photovoltaic Devices with Well-Defined Morphologies and Enhanced Stability
  Lin, Y.; Lim, J. A.; Wei, Q.; Mannsfeld, S. C. B.; Briseno, A. L.; Watkins, J. J. *Chem. Mater.* **2012,** 24, 622-632.
  Abstract:



We report the cooperative self-assembly of functionalized fullerenes and all conjugated block copolymers (BCPs) containing polythiophene derivatives in both segments to yield solar cells with well-defined nanostructures and enhanced morphological stability. Favorable hydrogen bonding interactions between the COOH-functionalized fullerene, bis-[6, 6]-phenyl C61-butyric acid (bis-PCBA), and the tetraethyleneglycol side chains of poly(3-hexylthiophene)-*block*-poly[3-(2,5,8,11-tetraoxadodecane)thiophene] (P3HT-*b*-P3TODT) allows for high loading of bis-PCBA (up to 40 wt % to the blend) within the P3TODT domains, while preserving the lamellar morphology. Characterization by grazing incidence small-angle X-ray scattering, electron microscopy, and atomic force microscopy indicates that the periods of the structures range between 24 and 29 nm depending on the bis-PCBA loading. The hydrogen bond interactions between bis-PCBA and P3TODT segments further suppress crystallization and macrophase separation of the fullerenes, even under harsh annealing conditions (150 °C for 12 h). Bulk heterojunction solar cells prepared using P3HT-*b*-P3TODT/bis-PCBA exhibit a photoconversion efficiency of 2.04%, which is greater than that of a reference system, P3HT-*b*-P3TODT/bis-PCBM. Accelerated aging experiments reveal enhanced thermal stability as a result of the limited translational mobility of COOH-functionalized fullerene in P3HT-*b*-P3TODT relative to devices prepared using bis-PCBM in P3HT-*b*-P3TODT or P3HT. We believe that cooperative assembly using strong noncovalent interactions is a general approach that can be used to improve the processing, morphological stability, and aging of organic and hybrid photovoltaic devices.

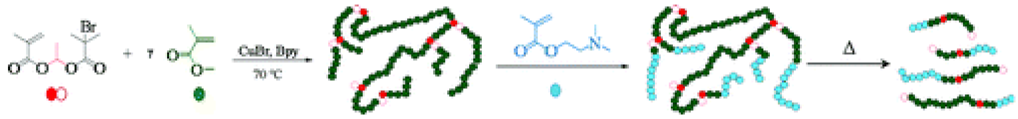
- Enhanced performance of triarylamine redox electrodes through directed electrochemical polymerization
  Kearns, J. T.; Roberts, M. E. *J. Mater. Chem.* **2012**, 22, 2392-2394.
  Abstract:



Molecular variations are incorporated in a triphenylamine-thiophene monomer to direct the polymerization and structure of electro-active polymer electrodes. When methyl groups are inserted at the 4-position of tris(4-(thiophen-2-yl)phenyl)amine, electropolymerization occurs solely at the 5-

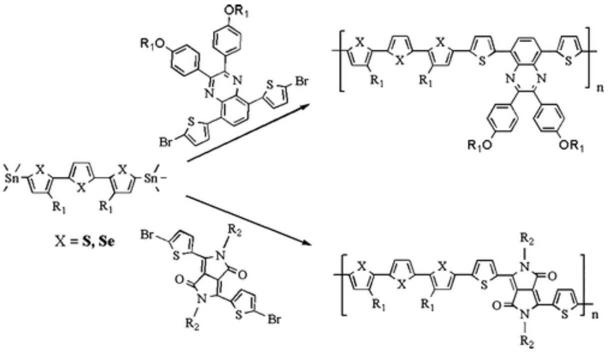
position resulting in a polymer electrode with enhanced Faradaic charge storage over an expanded potential range.

- Synthesis, Characterization and Thermolysis of Hyperbranched Homo- and Amphiphilic Co-Polymers Prepared Using an Inimer Bearing a ThermolyzableAcylal Group
  Rikkou-Kalourkoti, M.; Matyjaszewski, K.; Patrickios, C. S. *Macromolecules* **2012***, 45,* 1313–1320.
  Abstract:



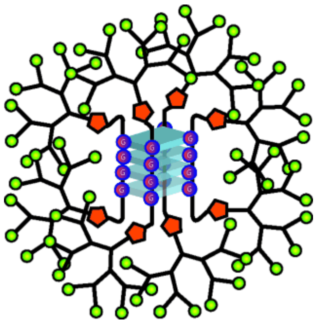
Degradable hyperbranched polymers were synthesized via self-condensing atom transfer radical copolymerization of methyl methacrylate (MMA) with a novel inimer bearing a thermolyzableacylal group. This inimer was 1-(2-bromoisobutyryloxyl)ethyl methacrylate (BIB1EMA) and was synthesized in a one-step reaction between 2-bromoisobutyric acid and vinyl methacrylate at 40% yield. The inimer was subsequently used for the preparation of three degradable hyperbranchedhomopolymers of MMA (monomer conversion 80%) with molecular weights in the range from 36□000 to 51□000 g mol–1 synthesized using initial MMA-to-inimer molar ratios between 25 and 100. The inimer was also used for the preparation of two degradable hyperbranchedamphiphilic copolymers of MMA and 2-(dimethylamino)ethyl methacrylate (DMAEMA) with an MMA hydrophobic hyperbranched core and different compositions, 10 and 38 mol % DMAEMA, afforded by changing the relative loadings in the two comonomers. Both hyperbranchedamphiphilic copolymers were soluble in THF: water mixtures with up to 50% w/w water content, whereas they precipitated at higher water contents. All hyperbranched (co)polymers were thermolyzed in a vacuum oven at 200 °C within 24–56 h. The molecular weights of the thermolysis products were consistent with the inimer content and the complete thermolysis of the hyperbranched (co)polymers. Hyperbranched polymers of MMA, also prepared in this investigation, but using a nondegradableinimer, isomeric to BIB1EMA, 2-(2-bromoisobutyryloxyl)ethyl methacrylate (BIB2EMA), did not present any reduction in their molecular weight when subjected to the same thermolysis conditions as those applied for the degradable hyperbranched polymers (200 °C, 24 h).

- Synthesis and Characterization of New Selenophene-Based Donor–Acceptor Low-Bandgap Polymers for Organic Photovoltaic Cells
  Lee, W. H.; Son, S. K.; Kim, K.; Lee, S. K.; Shin, W. S.; Moon, S-J.; Kang, I-N. *Macromolecules* **2012**, *45,* 1303–1312.
  Abstract:



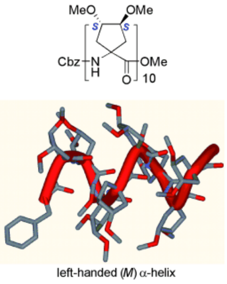
A series of novel thiophene- and selenophene-based low-bandgap polymers were synthesized using a Stille cross-coupling reaction; these polymers contained quinoxaline and diketopyrrolopyrrole as acceptors. Various acceptors were introduced into the selenophene backbones, and the solubility, absorption spectra, energy levels, charge transport, blend film morphology, and photovoltaic properties of the resulting polymers were investigated. The weight-averaged molecular weights (Mw) of P3TDTQ, P3SDTQ, P3TDTDPP, and P3SDTDPP were found to be 12□300, 15□500, 13□300, and 17□200, with polydispersity indices of 1.46, 1.85, 1.58, and 1.63, respectively. Photophysical studies revealed low bandgaps of 1.70 eV for P3TDTQ, 1.63 eV for P3SDTQ, 1.27 eV for P3TDTDPP, and 1.25 eV for P3SDTDPP; the films could harvest a broad solar spectrum, covering the range from 300 to 800 nm (P3TDTQ and P3SDTQ) and from 350 to 950 nm (P3TDTDPP and P3SDTDPP). Solution-processed field-effect transistors fabricated from these polymers had p-type organic thin film transistor characteristics. The field-effect mobilities of P3TDTQ, P3SDTQ, P3TDTDPP, and P3SDTDPP were measured to be 2.8 × 10–5, 5.0 × 10–5, 1.0 × 10–3, and 2.1 × 10–3 cm2 V–1 s–1, respectively. The novel polymers were combined with a PCBM ([6,6]-phenyl C71-butyric acid methyl ester) acceptor to fabricate bulk heterojunction solar cells, which produced power conversion efficiencies of 0.64–3.18% under AM 1.5 G (100 mW/cm2) conditions.

- SupramolecularDendrimers: Convenient Synthesis by Programmed Self-Assembly and Tunable Thermoresponsivity
  Ghosh, P. S.; Hamilton, A. D. *Chem. Eur. J.* **2012**, *18*, 2361-2365.
  Abstract:



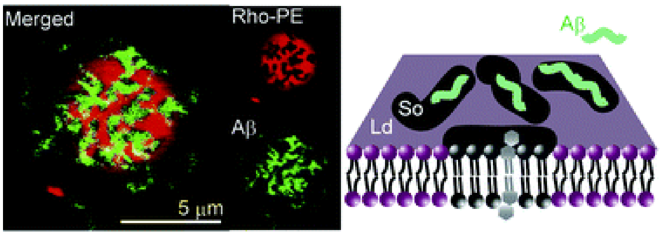
We report here the noncovalent synthesis of thermosensitivedendrimers. Short oligoguanosine strands were linked to the focal point of a dendron by using “click chemistry”, and quadruplex formation was used to drive the self-assembly process in the presence of metal ions. The dynamic nature of these noncovalent assemblies can be exploited to create combinatorial libraries of dendrimers as demonstrated by the co-assembly of two components. These supramoleculardendrimers showed thermoresponsive behavior that can be tuned by varying the templatingcations or the number of guanines in the oligonucleotide strand.

- One-Handed Helical Screw Direction of Homopeptide Foldamer Exclusively Induced by Cyclic α-Amino Acid Side-Chain Chiral Centers
  Demizu, Y.; Doi, M.; Kurihara, M.; Maruyama, T.; Suemune, H.; Tanaka, M. *Chem. Eur. J.* **2012**, *18*, 2430-2439.
  Abstract:



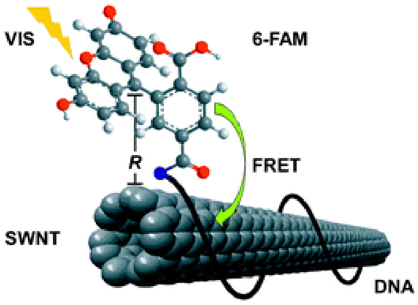
Chiral cyclic α,α-disubstituted amino acids, (3S,4S)- and (3R,4R)-1-amino-3,4-(dialkoxy)cyclopentanecarboxylic acids ((S,S)- and (R,R)-Ac5cdOR; R: methyl, methoxymethyl), were synthesized from dimethyl l-(+)- or d-(−)-tartrate, and their homochiralhomoligomers were prepared by solution-phase methods. The preferred secondary structure of the (S,S)-Ac5cdOMe hexapeptide was a left-handed (M) 310 helix, whereas those of the (S,S)-Ac5cdOMe octa- and decapeptides were left-handed (M) α helices, both in solution and in the crystal state. The octa- and decapeptides can be well dissolved in pure water and are more α helical in water than in 2,2,2-trifluoroethanol solution. The left-handed (M) helices of the (S,S)-Ac5cdOMe homochiralhomopeptides were exclusively controlled by the side-chain chiral centers, because the cyclic amino acid (S,S)-Ac5cdOMe does not have an α-carbon chiral center but has side-chain γ-carbon chiral centers.

- Selective localization of Alzheimer's amyloid beta in membrane lateral compartments
  Morita M.; Hamada T.; Tendo T.; Hata T.; Vestergaard M.C.; Takagi M. *Soft Matter* **2012**, *8*, 2816-2819.
  Abstract:



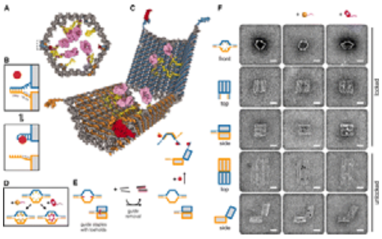
Model membrane systems revealed that lateral heterogeneity of the membrane mediates the localization of amyloid beta peptides in a peptide aggregation-dependent manner.

- Influence of DNA conformation on the dispersion of SWNTs: single-strand DNA *vs.* hairpin DNA
  Hain, T. C.; Kröker, K.; Stich, D. G.; Hertel, T. *Soft Matte*, **2012**, *8*, 2820-2823.
  Abstract:



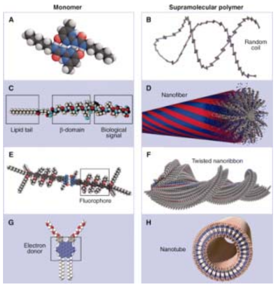
Dispersion of CNTs with single-strand (ss) and hairpin (hp) DNA yields suspensions with varying degree of individualization and selectivity towards specific tube types. Time-resolved fluorescence spectroscopy with dye labelled oligomers is used to investigate structural properties of DNA–SWNT conjugates. hpDNA is found to bind with its loop sideways to the CNT surface.

- A Logic-Gated Nanorobot for Targeted Transport of Molecular Payloads
  Douglas, S. M.; Bachelet, I.; Church, G. M. *Science* **2012,** *335*, 831-834.
  Abstract:



We describe an autonomous DNA nanorobot capable of transporting molecular payloads to cells, sensing cell surface inputs for conditional, triggered activation, and reconfiguring its structure for payload delivery. The device can be loaded with a variety of materials in a highly organized fashion and is controlled by an aptamer-encoded logic gate, enabling it to respond to a wide array of cues. We implemented several different logical AND gates and demonstrate their efficacy in selective regulation of nanorobot function. As a proof of principle, nanorobots loaded with combinations of antibody fragments were used in two different types of cell-signaling stimulation in tissue culture. Our prototype could inspire new designs with different selectivities and biologically active payloads for cell-targeting tasks.

- Functional Supramolecular Polymers
  Aida, T.; Meijer, E. W.; Stupp, S. I. *Science* **2012,** *335*, 813-817.
  Abstract:

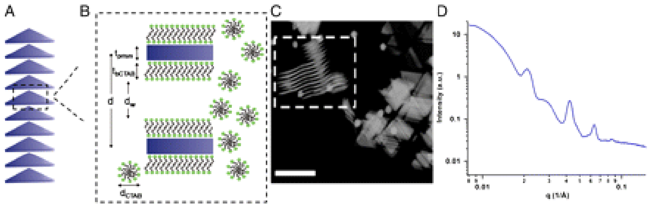


Supramolecular polymers can be random and entangled coils with the mechanical properties of plastics and elastomers, but with great capacity for processability, recycling, and self-healing due to their reversible monomer-to-polymer transitions. At the other extreme, supramolecular polymers can be formed by self-assembly among designed subunits to yield shape-persistent and highly ordered filaments. The use of strong and directional interactions among molecular subunits can achieve not only rich dynamic behavior but also high degrees of internal order that are not known in ordinary polymers. They can resemble, for example, the ordered and dynamic one-dimensional supramolecular assemblies of the cell cytoskeleton and possess useful biological and electronic functions.

- Assembly of reconfigurable one-dimensional colloidal superlattices due to a synergy of fundamental nanoscale forces

Young, K. L.; Jones, M. R.; Zhang, J.; Macfarlane, R. J.; Esquivel-Sirvent, R.; Nap, R. J.; Wu, J.; Schatz, G. C.; Lee, B.; Mirkin, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2012,** *109*, 2240-2245.

Abstract:

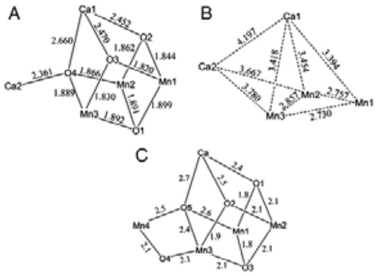


We report that triangular gold nanoprisms in the presence of attractive depletion forces and repulsive electrostatic forces assemble into equilibrium one-dimensional lamellar crystals in solution with interparticle spacings greater than four times the thickness of the nanoprisms. Experimental and theoretical studies reveal that the anomalously large *d* spacings of the lamellar superlattices are due to a balance between depletion and electrostatic interactions, both of which arise from the surfactant cetyltrimethylammonium bromide. The effects of surfactant concentration, temperature, ionic strength of the solution, and prism edge length on the lattice parameters have been investigated and provide a variety of tools for in situ modulation of these colloidal superstructures. Additionally, we demonstrate a purification procedure based on our observations that can be used to efficiently separate triangular nanoprisms from spherical nanoparticles formed concomitantly during their synthesis.

- Synthetic model of the asymmetric [Mn3CaO4] cubane core of the oxygen-evolving complex of photosystem II

  Mukherjee, S.; Stull, J. A.; Yano, J.; Stamatatos, T. C.; Pringouri, K.; Stich, T. A.; Abboud, K. A.; Britt, R. D.; Yachandra, V. K.; Christou, G. *Proc. Natl. Acad. Sci. U. S. A.* **2012,** *109*, 2257-2262.

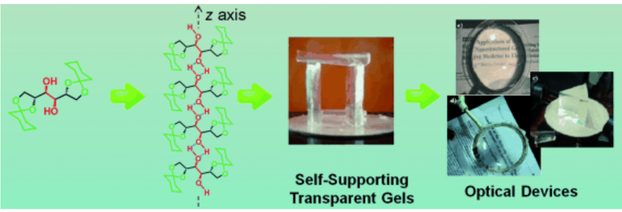
  Abstract:



The laboratory synthesis of the oxygen-evolving complex (OEC) of photosystem II has been the objective of synthetic chemists since the early 1970s. However, the absence of structural information on the OEC has hampered these efforts. Crystallographic reports on photosystem II that have been appearing at ever-improving resolution over the past ten years have finally provided invaluable structural information on the OEC and show that it comprises a [Mn_3CaO_4] distorted cubane, to which is attached a fourth, external Mn atom, and the whole unit attached to polypeptides primarily by aspartate and glutamate carboxylate groups. Such a heterometallic Mn/Ca cubane with an additional metal attached to it has been unknown in the literature. This paper reports the laboratory synthesis of such an asymmetric cubane-containing compound with a bound external metal atom, [$\mathrm{Mn^{IV}}_3\mathrm{Ca_2O_4(O_2CBu^t)_8(Bu^tCO_2H)_4}$(**1**)] . All peripheral ligands are carboxylate or carboxylic acid groups. Variable-temperature magnetic susceptibility data have established **1** to possess an *S* = 9/2 ground state. EPR spectroscopy confirms this, and the Davies electron nuclear double resonance data reveal similar hyperfine couplings to those of other Mn^{IV} species, including the OEC S_2

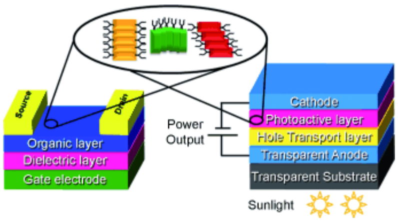
state. Comparison of the X-ray absorption data with those for the OEC reveal **1** to possess structural parameters that make it a close structural model of the asymmetric-cubane OEC unit. This geometric and electronic structural correspondence opens up a new front in the multidisciplinary study of the properties and function of this important biological unit.

- Flexible Optics: Recent Developments in Molecular Gels
  John, G.; Jadhav, S. R.; Menon, V. M.; John, V. T. *Angew. Chem. Int. Ed.* **2012**, *51,* 1760-1762.
  Abstract:



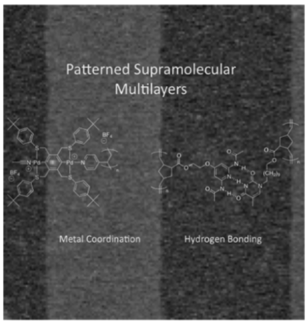
Get smart: Organogels based on sugar ketals have been prepared with a unique combination of properties suitable for the development of flexible optical devices and potential applications as smart materials for the fabrication of microphotonic systems. Key features in the self-assembly of these gelators were conformational restrictions and interaction affinities.

- Self-Assembled Gelators for Organic Electronics
  Babu, S. S.; Prasanthkumar, S.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2012**, *51,* 1766-1776.
  Abstract:



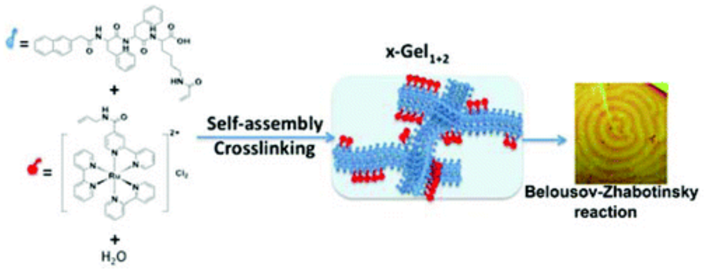
All gelled together: Solvent-assisted gelation of functional organic molecules leading to one-dimensional fibers is an area of great interest. Recent developments in molecular self-assembly-assisted gelation of π systems into soft functional materials and their potential application in organic electronic devices, such as organic field-effect transistors and organic solar cells, are reviewed (see picture).

- Patterned Polymeric Multilayered Assemblies through Hydrogen Bonding and Metal Coordination
  Piñón III, V.; Weck, M. *Langmuir* **2012**, *28*, 3279-3284.
  Abstract:



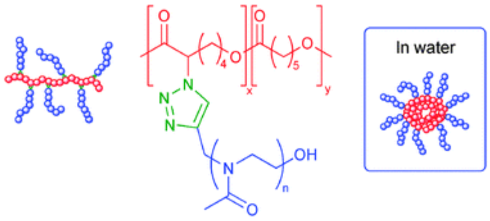
Patterned polymeric multilayered assemblies were formed using a combination of metal coordination and hydrogen bonding interactions. We proved that the hydrogen bonding interaction between diamidopyridine and thymine can be employed for polymeric multilayer assemblies. We then combined this strategy along with a second supramolecular interaction, metal coordination. These interactions proved to be orthogonal to one another on the surface, making each discrete region individually responsive to external stimuli.

- Post-Self-Assembly Cross-Linking of Molecular Nanofibers for Oscillatory Hydrogels
  Zhang, Y.; Li, N.; Delgado, J.; Gao, Y.; Kuang, Y.; Fraden, S.; Epstein, I. R.; Xu, B. *Langmuir* **2012**, *28*, 3063-3066.
  Abstract:



After a polymerizable hydrogelator self-assembles in water to form molecular nanofibers, post-self-assembly cross-linking allows the catalyst of the Belousov–Zhabotinsky (BZ) reaction to be attached to the nanofibers, resulting in a hydrogel that exhibits concentration oscillations, spiral waves, and concentric waves. In addition to the first report of the observation of BZ spiral waves in a hydrogel that covalently integrates the catalyst, we suggest a new approach to developing active soft materials as chemical oscillators and for exploring the correlation between molecular structure and far-from-equilibrium dynamics.

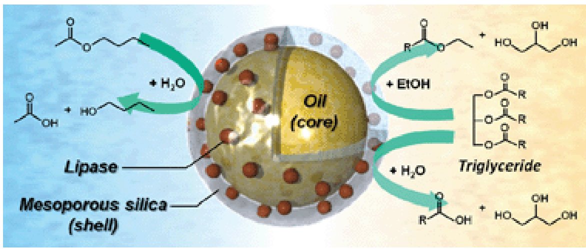
- Synthesis and evaluation of triazole-linked poly(ε-caprolactone)-*graft*-poly(2-methyl-2-oxazoline) copolymers as potential drug carriers
  Guillerm, B.; Darcos, V.; Lapinte , V.; Monge, S.; Coudane, J.; Robin, J.-J. *Chem. Commun.* **2012**, *48*, 2879-2881.
  Abstract:



Well-defined graft copolymers were obtained using a copper-catalysed azide–alkyne Huisgen's cycloaddition click reaction from both biocompatible and non-toxic poly(ε-caprolactone) and poly(2-methyl-2-oxazoline) homopolymers. Resulting amphiphilic copolymers proved to form micelles that could be used as potential drug carriers.

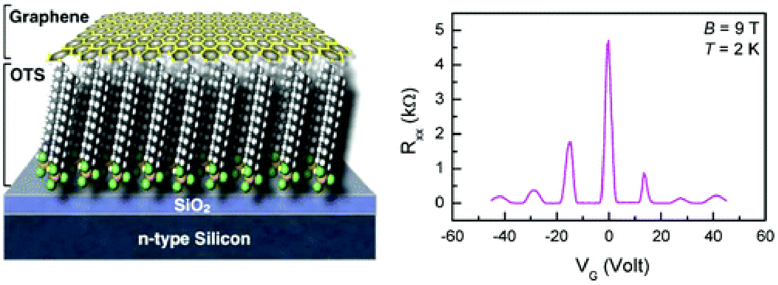
- Lipase-embedded silica nanoparticles with oil-filled core–shell structure: stable and recyclable platforms for biocatalysts
  Kuwahara, Y.; Yamanishi, T.; Kamegawa, T.; Mori, K.; Che, M.; Yamashita, H. *Chem. Commun.* **2012**, *48*, 2882-2884.

Abstract:



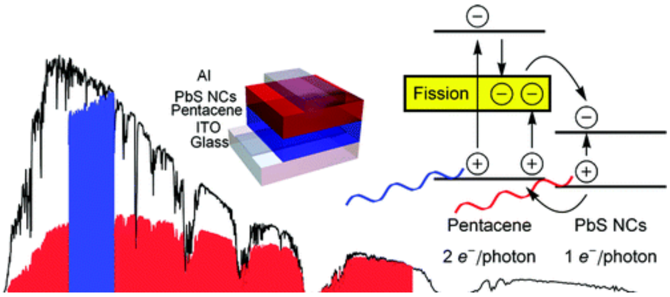
Lipase enzyme was embedded within silica nanoparticles with oil-filled core–shell structure. The enzyme embedded within such architecture retained all of its activity and showed high catalytic performance both in water and in organic media with optimal stability and recyclability.

- Transport/Magnetotransport of High-Performance Graphene Transistors on Organic Molecule-Functionalized Substrates
  Chen, S. Y.; Ho, P. H.; Shiue, R. J.; Chen, C. W.; Wang, W. H. *Nano Lett.* **2012**, *12,* 964–969.
  Abstract:



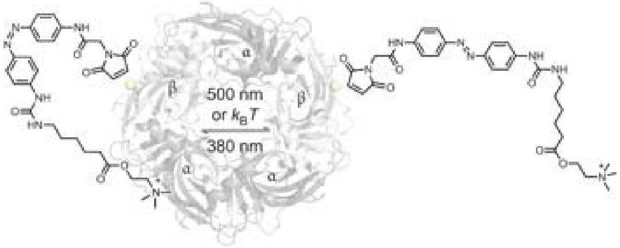
In this article, we present the transport and magnetotransport of high-quality graphene transistors on conventional SiO_2/Si substrates by modification with organic molecule octadecyltrichlorosilane (OTS) self-assembled monolayers (SAMs). Graphene devices on OTS SAM-functionalized substrates with high carrier mobility, low intrinsic doping, suppressed carrier scattering, and reduced thermal activation of resistivity at room temperature were observed. Most interestingly, the remarkable magnetotransport of graphene devices with pronounced quantum Hall effect, strong Shubnikov-de Haas oscillations, a nonzero Berry's phase, and a short carrier scattering time also confirms the high quality of graphene on this ultrasmooth organic SAM-modified platform. The high-performance graphene transistors on the solution-processable OTS SAM-functionalized SiO_2/Si substrates are promising for the future development of large-area and low-cost fabrications of graphene-based nanoelectronics.

- Singlet Exciton Fission-Sensitized Infrared Quantum Dot Solar Cells
  Ehrler, B.; Wilson, M. W. B.; Rao, A.; Friend, R. H.; Greenham, N. C. *Nano Lett.* **2012**, *12*, 1053–1057.
  Abstract:



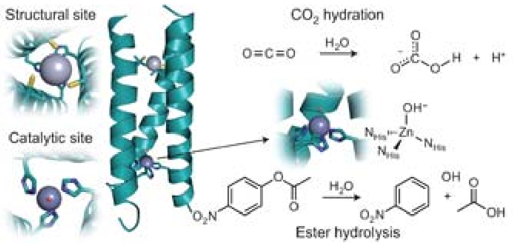
We demonstrate an organic/inorganic hybrid photovoltaic device architecture that uses singlet exciton fission to permit the collection of two electrons per absorbed high-energy photon while simultaneously harvesting low-energy photons. In this solar cell, infrared photons are absorbed using lead sulfide (PbS) nanocrystals. Visible photons are absorbed in pentacene to create singlet excitons, which undergo rapid exciton fission to produce pairs of triplets. Crucially, we identify that these triplet excitons can be ionized at an organic/inorganic heterointerface. We report internal quantum efficiencies exceeding 50% and power conversion efficiencies approaching 1%. These findings suggest an alternative route to circumvent the Shockley-Queisser limit on the power conversion efficiency of single-junction solar cells.

- Optochemical control of genetically engineered neuronal nicotinic acetylcholine receptors
  Tochitsky, I.; Banghart, M. R.; Mourot, A.; Yao, J. Z.;Gaub, B.; Kramer, R. H.; Trauner,D. *Nature Chem.* **2012**, *4*, 105-111.
  Abstract:



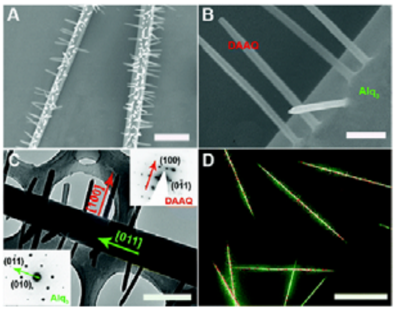
Advances in synthetic chemistry, structural biology, molecular modelling and molecular cloning have enabled the systematic functional manipulation of transmembrane proteins. By combining genetically manipulated proteins with light-sensitive ligands, innately ‘blind’ neurobiological receptors can be converted into photoreceptors, which allows them to be photoregulated with high spatiotemporal precision. Here, we present the optochemical control of neuronal nicotinic acetylcholine receptors (nAChRs) with photoswitchable tethered agonists and antagonists. Using structure-based design, we produced heteromeric α3β4 and α4β2 nAChRs that can be activated or inhibited with deep-violet light, but respond normally to acetylcholine in the dark. The generation of these engineered receptors should facilitate investigation of the physiological and pathological functions of neuronal nAChRs and open a general pathway to photosensitizing pentameric ligand-gated ion channels.

- Hydrolytic catalysis and structural stabilization in a designed metalloprotein
  Zastrow, M. L.; Peacock, A. F. A.; Stuckey, J.A.; Pecoraro, V. L. *Nature Chem.* **2012**, *4*, 118-123.
  Abstract:



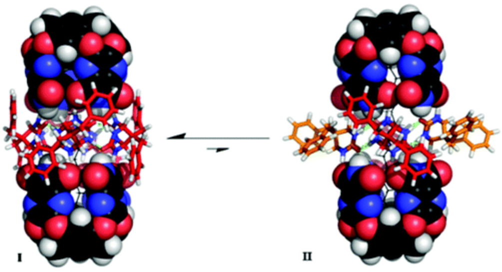
Metal ions are an important part of many natural proteins, providing structural, catalytic and electron transfer functions. Reproducing these functions in a designed protein is the ultimate challenge to our understanding of them. Here, we present an artificial metallohydrolase, which has been shown by X-ray crystallography to contain two different metal ions—a Zn(II) ion, which is important for catalytic activity, and a Hg(II) ion, which provides structural stability. This metallohydrolase displays catalytic activity that compares well with several characteristic reactions of natural enzymes. It catalyses p-nitrophenyl acetate (*p*NPA) hydrolysis with an efficiency only ~100-fold less than that of human carbonic anhydrase (CA)II and at least 550-fold better than comparable synthetic complexes. Similarly, CO2 hydration occurs with an efficiency within ~500-fold of CAII. Although histidine residues in the absence of Zn(II) exhibit pNPA hydrolysis, miniscule apopeptide activity is observed for CO2 hydration. The kinetic and structural analysis of this first de novo designed hydrolytic metalloenzyme reveals necessary design features for future metalloenzymes containing one or more metals.

- Wire-on-Wire Growth of Fluorescent Organic Hetero junctions
  Zheng, J. Y.; Yan, Y.; Wang, X.; Zhao, Y. S.; Huang, J.; Yao, J. *J. Am. Chem. Soc.* **2012**, *134*, 2880–2883.
  Abstract:



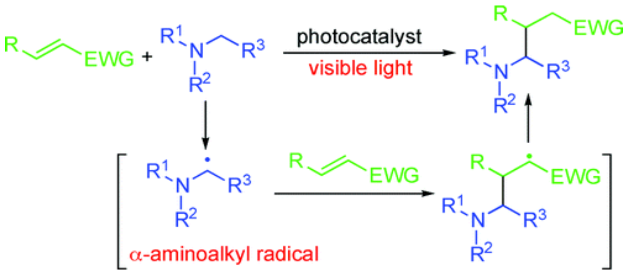
Dendritic organic hetero junctions with aluminum tris(8-hydroxyquinoline) (Alq_3) micro wire trunks and 1,5-diaminoanthraquinone (DAAQ) nano wire branches were prepared by a two-step growth process. The prefabricated Alq_3microwiresact as nucleation centers for site-specific secondary vapor growth of DAAQ nano wires, resulting in the unique dendritichet ero structures. When the trunk was excited with a focused laser beam, emitted light of various colors was simultaneously channeled from the branched nano wires via both wave guiding and energy transfer. The intensity of the out-couple demissions was modulated effectively by changing the polarization of the incident light.

- Selective Stabilization of Self-Assembled Hydrogen-Bonded Molecular Capsules Through π–π Interactions
  Tiefenbacher, K.; Rebek, J. Jr. *J. Am. Chem. Soc.* **2012**, *134*, 2914–2917.
  Abstract:



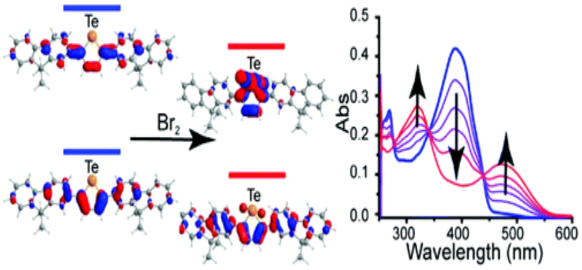
Subtle non covalent forces such as π–π interactions play an import role in the folding of biological macromolecules such as DNA and proteins. We describe here a system where such interactions on the outside of a molecular capsule trigger a selective change of its structure as a self-assembled receptor.

- Visible-Light-Mediated Utilization of α-Aminoalkyl Radicals: Addition to Electron-Deficient Alkenes Using Photoredox Catalysts
  Miyake, Y.; Nakajima, K.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2012**, *134*, 3338-3341.
  Abstract:



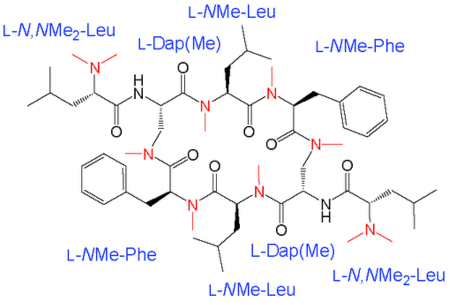
Synthetic use of α-aminoalkyl radicals formed by single electron oxidation of amines is quite limited. Here we demonstrate addition of α-aminoalkyl radicals to electron-deficient alkenes by visible-light-mediated electron transfer using transition metal polypyridyl complexes as photocatalysts, via a sequential redox pathway.

- Tellurophenes with Delocalized π-Systems and Their Extended Valence Adducts
  McCormick, T. M.; Jahnke, A. A.; Lough, A. J.; Seferos, D. S. *J. Am. Chem. Soc.* **2012**, *134*, 3542-3548.
  Abstract:



The π-conjugated 2,5-substituted tellurophene compounds 2,5-bis(2-(9,9-dihexylfluorene))tellurophene (**1**) and 2,5-diphenyltellurophene (**3**) were synthesized through ring closing reactions of 1,4-substituted butadiyne. The oxidative addition of Br_2 to tellurophene compounds **1** and **3** was studied through absorption spectroscopy, NMR, electrochemistry, X-ray crystallography, and density functional theory (DFT) calculations. When Br_2 adds to the tellurium center the absorption spectrum shifts to a lower energy. From electrochemistry and DFT calculations we show that this is caused by lowering the lowest unoccupied orbital. The highest occupied orbital is also lowered, but to a lesser extent. This shift in absorption spectrum and lowering of the oxidation potential can provide a method to modify tellurophene containing materials. The two-electron oxidative addition is promising for catalyzing energy storage reactions.

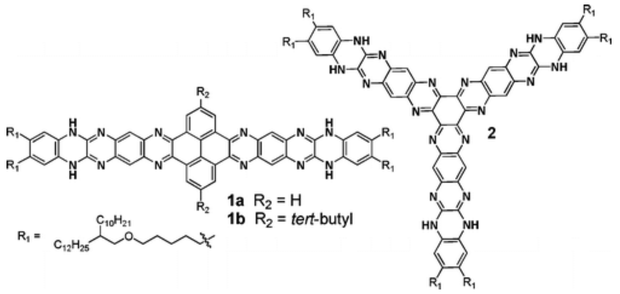
- Solid-Phase Synthesis of *N*Me-IB-01212, a Highly *N*-Methylated Cyclic Peptide
  Marcucci, E.; Tulla-Puche, J.; Albericio, F. *Org. Lett.* **2012**, *14*, 612–615.
  Abstract:



*N*Me-IB-01212, **1**

N-Methylation of peptides is an important synthetic tool in peptide-based medicinal chemistry. Herein, an optimized strategy for solid-phase synthesis of small but highly *N*-methylated cyclic peptides is described. The proposed route addresses several problems associated with the synthesis of peptides containing several sequential *N*-methyl-amino acids, such as in situ *N*-methylation, difficulty of acylation, epimerization, diketopiperazine formation, and stability at the *N*Me sites under trifluoroacetic acid exposure. The resulting *N*Me-IB-01212 exhibits micromolar activity and considerable stability.

- Large-Size Linear and Star-Shaped Dihydropyrazine Fused Pyrazinacenes
  Tong, C.; Zhao, W.; Luo, J.; Mao, H.; Chen, W.; Chan, H. S. O.; Chi, C. *Org. Lett.* **2012**, *14*, 494–497.
  Abstract:



Linear and star-shaped pyrazinacenes **1a**–**b** and **2** were synthesized via condensation between a new building block **11** and pyrene tetraones or cyclohexaone. Compound **2** represents the largest star-shaped dihydropyrazine fused pyrazinacene reported so far. These largely expanded pyrazinacenes show good solubility and have a strong tendency to aggregate in both solution and thin films, indicating their potential applications for organic electronic devices.