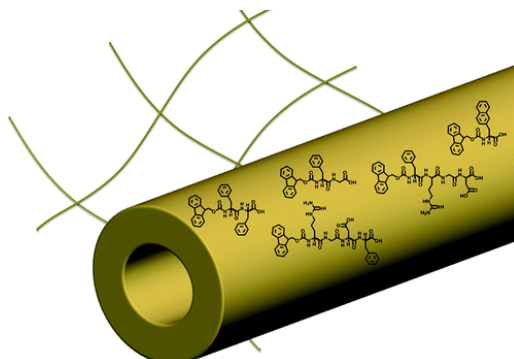


- The Rheological and Structural Properties of Fmoc-Peptide-Based Hydrogels: The Effect of Aromatic Molecular Architecture on Self-Assembly and Physical Characteristics  
Orbach, R.; Mironi-Harpaz, I.; Adler-Abramovich, L.; Mossou, E.; Mitchell, E. P.; Forsyth, V. T.; Gazit, E.; Seliktar, D. *Langmuir* **2012**, 28, 2015-2022.

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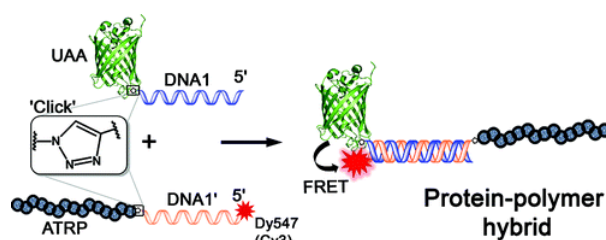
Abstract:



Biocompatible hydrogels are of high interest as a class of biomaterials for tissue engineering, regenerative medicine, and controlled drug delivery. These materials offer three-dimensional scaffolds to support the growth of cells and development of hierarchical tissue structures. Fmoc-peptides were previously demonstrated as attractive building blocks for biocompatible hydrogels. Here, we further investigate the biophysical properties of Fmoc-peptide-based hydrogels for medical applications. We describe the structural and thermal properties of these Fmoc-peptides, as well as their self-assembly process. Additionally, we study the role of interactions between aromatic moieties in the self-assembly process and on the physical and structural properties of the hydrogels.

- A Protein–Polymer Hybrid Mediated By DNA  
Averick, S. E.; Paredes, E.; Grahacharya, D.; Woodman, B. F.; Miyake-Stoner, S. J.; Mehl, R. A.; Matyjaszewski, K.; Das, S. R. *Langmuir* **2012**, 28, 1954-1958.

Abstract:



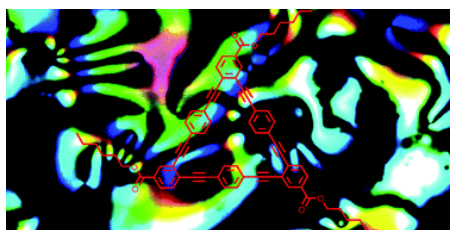
Protein–polymer hybrids (PPHs) represent an important and rapidly expanding class of biomaterials. Typically in these hybrids the linkage between the protein and the polymer is covalent. Here we describe a straightforward approach to a noncovalent PPH that is mediated by DNA. Although noncovalent, the DNA-mediated approach affords the highly specific pairing and assembly properties of DNA. To obtain the protein–DNA conjugate for assembly of the PPH, we report here the first direct copper catalyzed azide–alkyne cycloaddition-based protein–DNA conjugation. This significantly simplifies access to protein–DNA conjugates. The protein–DNA conjugate and partner polymer–DNA conjugate are readily assembled through annealing of the cDNA strands to obtain the PPH, the assembly of which was confirmed via dynamic light scattering and fluorescence spectroscopy.

- Triangular arylene ethynylene macrocycles: syntheses, optical, and thermotropic liquid crystalline properties

Li, T.; Yue, K.; Yan, Q.; Huang, H.; Wu, H.; Zhu, N.; Zhao, D. *Soft Matter* **2012**, 8, 2405-2415.

Abstract:

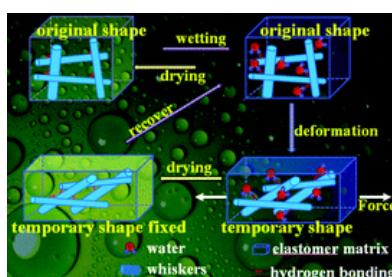
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A series of triangular, shape-persistent arylene-ethynylene macrocycles (AEMs) of related structures were synthesized and studied, with a focus on their mesomorphic behavior in correlation with their chemical structure. Generally, these discotic molecules decorated with flexible side chains demonstrated a propensity to form thermotropic liquid-crystalline (LC) phases. Characterized by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD), four of the eight investigated macrocycles manifested thermodynamically stable mesophases, featuring discotic nematic or columnar structures. Longer alkyl side chains were found more conducive to mesophases, and the alkoxycarbonyl functionality was a more effective side-chain linkage at inducing and stabilizing the LC states than the alkoxy side group. The size and structure of the cyclic aromatic backbone influenced both the occurrence and type of mesophase exhibited.

- Rapidly switchable water-sensitive shape-memory cellulose/elastomer nano-composites  
Zhu, Y.; Hu, J.; Luo, H.; Young, R.-J.; Deng, L.; Zhang, S.; Fan, Y.; Ye, G. *Soft Matter* **2012**, 8, 2509-2517.

Abstract:

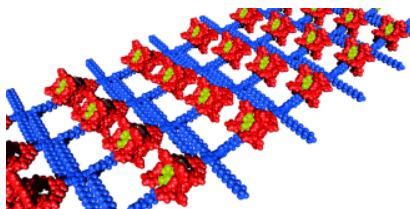


We report a new phenomenon in which the reversible formation and disruption of a cellulose nano-whisker (CNW) percolation network in an elastomeric thermoplastic polyurethane (TPU) matrix leads to an unprecedentedly rapidly switchable shape-memory effect (SME) that may be activated by water. The materials have been fully characterized to investigate the SME phenomenon using a number of different experimental techniques including cyclic tensile deformation, dynamic mechanical analysis, FTIR and polarized Raman spectroscopy. A model is developed in which it is shown that exposure to water allows breakup of the CNW percolation network so that the flexible elastomer matrix can be deformed to the desired shape. The CNW percolation network reforms after drying to provide a fixing force for the temporary shape. The entropy elasticity of the TPU matrix then enables rapid shape recovery when the CNW percolation network is disrupted again during wetting. This completely athermal water-sensitive SME mechanism is totally different from traditional ones, in which the water or other solvents are used as plasticizers to lower the glass transition temperature of shape memory polymers, so as to allow triggering of the shape recovery at room temperature or lower. The reported work provides a novel and effective strategy to achieve rapidly switchable shape recovery in a material by a simple wetting process and fixing through an easily applicable programmed drying process.

- Supramolecular Polymerization Triggered by Molecular Recognition between Bisporphyrin and Trinitrofluorenone

Haino, T.; Watanabe, A.; Hirao, T.; Ikeda, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 1473-1476.

Abstract:

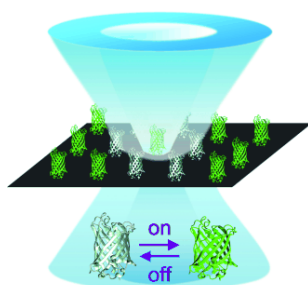


Networking: A bisporphyrin compound possessing an electron-deficient guest moiety assembles in a head-to-tail manner to form polymeric aggregates. Diffusion-ordered NMR spectroscopy and viscosity measurements of the aggregates confirmed the formation of sizable supramolecular polymers. Widely spread nanonetworks (see picture) are formed in solid state.

- A Fatigue-Resistant Photoswitchable Fluorescent Protein for Optical Nanoscopy

Nienhaus, G. U. *Angew. Chem. Int. Ed.* **2012**, *51*, 1312-1314.

Abstract:

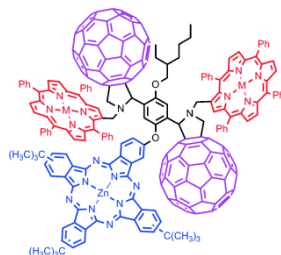


Like the battery bunny: The novel photoswitchable fluorescent protein rsEGFP can be cycled between its fluorescent and nonfluorescent states more than a thousand times and is, therefore, a superb marker for high-resolution RESOLFT imaging (RESOLFT=reversible saturable optical fluorescence transition) and data storage applications.

- Synthesis and Photophysical Properties of Fullerene–Phthalocyanine–Porphyrin Triads and Pentads

Enes, R. F.; Cid, J.-J.; Hausmann, A.; Trukhina, O.; Gouloumis, A.; Vázquez, P.; Cavaleiro, J. A. S.; Tomé, A. C.; Guldi, D. M.; Torres, T. *Chem. Eur. J.* **2012**, *18*, 1727-1736.

Abstract:



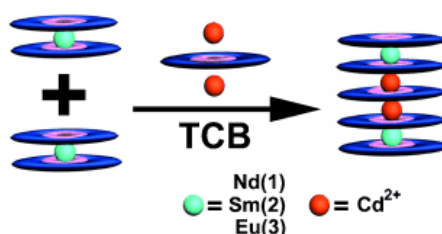
The synthesis and photophysical properties of several fullerene–phthalocyanine–porphyrin triads (1–3) and pentads (4–6) are described. The three photoactive moieties were covalently connected in an one-step synthesis through 1,3-dipolar cyclo addition to C60 of the corresponding azomethineylides generated in situ by condensation reaction of a substituted N-porphyrinylmethylglycine derivative

and an appropriated formylphthalocyanine or a diformylphthalocyanine derivative, respectively. ZnP-C60-ZnP (3), (ZnP)<sub>2</sub>-ZnPc-(C60)<sub>2</sub> (6), and (H2P)<sub>2</sub>-ZnPc-(C60)<sub>2</sub> (5) give rise upon excitation of their ZnP or H2P components to a sequence of energy and charge-transfer reactions with, however, fundamentally different outcomes. With (ZnP)<sub>2</sub>-ZnPc-(C60)<sub>2</sub> (6) the major pathway is an highly exothermic charge transfer to afford (ZnP)(ZnP<sup>+</sup>)-ZnPc-(C60<sup>-</sup>)(C60). The lower singlet excited state energy of H2P (i.e., ca. 0.2 eV) and likewise its more anodic oxidation (i.e., ca. 0.2 V) renders the direct charge transfer in (H2P)<sub>2</sub>-ZnPc-(C60)<sub>2</sub> (5) not competitive. Instead, a transduction of singlet excited state energy prevails to form the ZnPc singlet excited state. This triggers then an intramolecular charge transfer reaction to form exclusively (H2P)<sub>2</sub>-ZnPc<sup>+</sup>-(C60<sup>-</sup>)(C60). A similar sequence is found for ZnP-C60-ZnP (3).

- New Sandwich-Type Phthalocyaninato–Metal Quintuple-Decker Complexes

Wang, H.; Kobayashi, N.; Jiang, J. *Chem. Eur. J.* **2012**, *18*, 1047-1049.

Abstract:

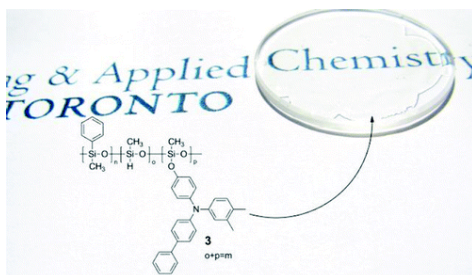


Quintuple-decker sandwich : Homolepticpentakis(2,3,9,10,16,17,23,24 octa (butyloxyphthalocyaninato) lanthanide–cadmium quintuple-decker complexes were isolated and structurally characterized. They represent the first example of sandwich-type stacked tetrapyrrole–metal complexes with five decks (see figure; the tetrapyrrole molecules are represented by the blue/pink discs, TCB=1,2,4-trichlorobenzene).

- The Use of Piers–Rubinsztajn Conditions for the Placement of Triarylamine Pendant to Silicone Polymers

Gretton, M. J.; Kamino, B. A.; Brook, M. A.; Bender, T. P. *Macromolecules* **2012**, *45*, 723–728.

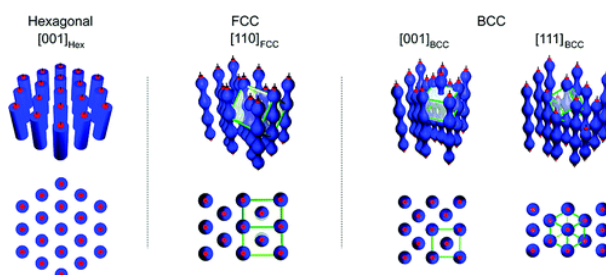
Abstract:



The use of Piers–Rubinsztajn conditions was explored for the synthesis of silicone polymers bearing pendant triarylamine functionality. We have found that up to 60% of the hydride groups of a silicone copolymer can be successfully substituted with a triarylamine moiety, without metathesis or redistribution of the silicone. The resulting polymers are hydrolytically stable. The functionalization procedure is straightforward, conducted under ambient conditions with a simple one-step work-up, and avoids the use of a metal-based catalyst. The resulting phenylated triarylamine–silicone hybrid polymer was characterized by optical absorption and fluorescence spectroscopy, CV, and differential scanning calorimetry. The hybrids maintain the physical appearance of a silicone polymer while adopting the photophysical and electrochemical characteristics of the triarylamine.

- Single-Walled Carbon Nanotube-Induced Lyotropic Phase Behavior of a Polymeric System  
Jang, H.-S.; Do, C.; Kim, T.-H.; Choi, S.-M. *Macromolecules* **2012**, 45, 986–992.

Abstract:



We report for the first time a new single-walled carbon nanotube (SWNT)-induced lyotropic phase behavior of a F108 block copolymer/water system. As the concentration is increased by evaporation, the F108-SWNT/water system exhibits isotropic–hexagonal–FCC–BCC–lamellar transitions. This is in clear contrast with the F108/water system (isotropic–BCC–lamellar transitions), indicating that the hexagonal and the FCC phases are newly induced by the presence of one-dimensional SWNTs. The SWNTs maintain their individuality or very small bundle state in all the phases except the lamellar phase. In the hexagonal phase, the SWNTs are located in the hydrophobic core of F108 cylinders oriented parallel to the [001] direction. The epitaxial transitions between the phases allowed us to identify the possible orientation of SWNTs in each phase: [110] in the FCC and either 100 or 111 in the BCC. In the lamellar phase, the SWNTs exist most likely in the hydrophobic layers forming aggregations among them. This new SWNT-induced lyotropic phase behavior in a block copolymer system may provide a new scalable route to fabricate SWNT superstructures with well-defined architecture and new functionalities.

- Advanced functional materials based on polyhedral oligomeric silsesquioxane (POSS)  
Tanaka, K.; Chujo, Y. *J. Mater. Chem.* **2012**, 22, 1733-1746.

Abstract:

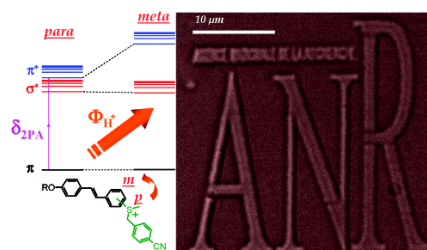


Polysilsesquioxanes are regarded as organic-inorganic hybrid materials at a molecular level. We can readily tune the properties of the materials for realizing the desired ones by changing the contents or types of organic components. In addition, the hierarchical structures have potential for generating further characteristics distinctly different from those of the constituents. From this viewpoint, polyhedral oligomeric silsesquioxane (POSS) is attractive as a cornerstone in highly ordered materials. In this review, we survey recent studies on modified POSS-based functional materials and particularly explain the design concepts for applying the significant characteristics of POSS for the material properties. In the initial sections, we introduce the examples concerning intrinsic properties of POSS such as thermal stability, mechanical property, and structural features. In the latter sections, we describe the application of POSS-based materials for bio-relating functional materials. We describe the validity of POSS for molecular designing of the advanced imaging tools.

- Enhancement of Acid Photogeneration Through a Para-to-Meta Substitution Strategy in a Sulfonium Based Alkoxystilbene Designed for Two-Photon Polymerization.

Xia, R.; Malval, J-P.; Jin, M.; Spangenberg, A.; Wan, D.; Pu, H.; Vergote, T.; Morlet-Savary, F.; Chaumeil, H.; Baldeck, P.; Poizat, O.; Soppera O. *Chem. Mater.* **2012**, *24*, 237-244.

Abstract:

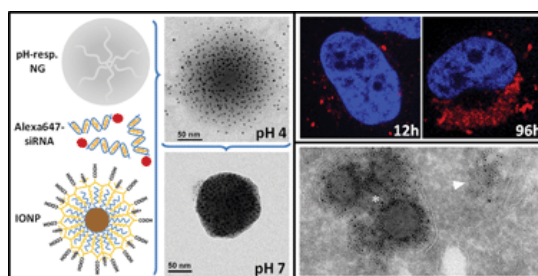


This contribution reports on the synthesis and the photochemical behavior of two new sulfonium-based photoacid generators (PAGs). We demonstrate that a para-to-meta substitution of a methyl (*p*-cyanobenzyl) sulfonium group in a 4-alkoxystilbene core strongly influences the photodissociation efficiency of the PAGs and leads to an increase of the quantum yield for acid generation by a factor 2.4. This substantial effect, which was also corroborated by a reactivity enhancement in cationic photopolymerization, is assigned to the modulation of the electronic interaction between two low lying excited states whose energy gap is strongly influenced by this substitution effect. Moreover, it was found that the position of the sulfonium moiety hardly affects the two-photon absorption properties of these push-pull chromophores. By the two-photon fabrication of microstructures, we finally show the potential use of the meta derivative as cationic two-photon initiator.

- Magnetic pH-responsive nanogels as multifunctional delivery tools for small interfering RNA (siRNA) molecules and iron oxide nanoparticles (IONPs)

Curcio, A.; Marotta, R.; Riedinger, A.; Palumberi, D.; Falqui, A.; Pellegrino, T. *Chem. Commun.* **2012**, *48*, 2400-2402.

Abstract:

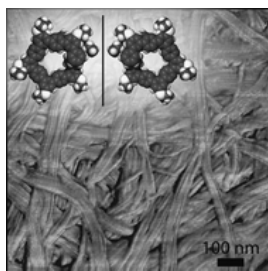


We here exploit pH-responsive nanogels as carriers to deliver functional anti-GFP siRNA and superparamagnetic IONPs to HeLa-GFP cells. The siRNA release *via* pH-mediated endosomal escape is shown. The IONPs act first as magnetofection agents to boost cellular uptake and then as probes to track the release mechanism by electron microscopy.

- Mirror symmetry breaking and chiral amplification in foldamer-based supramolecular helical aggregates

Azeroual, S.; Surprenant, J.; Lazzara, T. D.; Kocun, M.; Tao, Y.; Cuccia, L. A.; Lehn, J.-M. *Chem. Commun.* **2012**, *48*, 2292-2294.

Abstract:

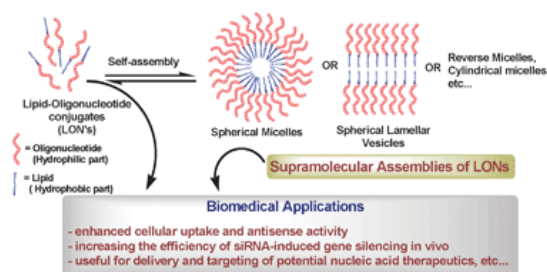


Spontaneous asymmetric generation of supramolecular chiral fibers was observed in the folding induced self-assembly of a lock-washer shaped foldamer. A secondary nucleation growth mechanism is proposed to explain the observed chiral amplification or *deracemization* of these supramolecular fibers.

- Hybrid lipid oligonucleotide conjugates: synthesis, self-assemblies and biomedical applications

Patwa, A.; Gissot, A.; Bestel, I.; Barthélémy, P. *Chem. Soc. Rev.* **2011**, *40*, 5844-5854.

Abstract:



Hybrid lipid oligonucleotide conjugates are finding more and more biotechnological applications. This short *critical review* highlights their synthesis, supramolecular organization as well as their applications in the field of biotechnology (111 references).

- Bioconjugation *via* azide–Staudinger ligation: an overview

Schilling, C. I.; Jung, N.; Biskup, M.; Schepers, U.; Bräse, S. *Chem. Soc. Rev.* **2011**, *40*, 4840-4871.

Abstract:

General ligations with azides

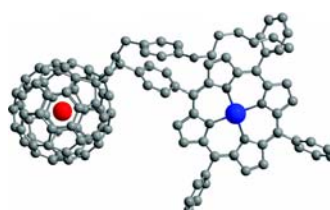


Bioconjugation techniques using organic azides are compared in this *critical review*. A particular focus is on chemical ligation reactions and their application to chemical biology (179 references).

- N@C<sub>60</sub>–Porphyrin: A Dyad of Two Radical Centers

Liu, G.; Khlobystov, A. N.; Charalambidis, G.; Coutsolelos, A. G.; Briggs, G. A. D.; Porfyrakis, K. *J. Am. Chem. Soc.* **2012**, *134*, 1938–1941.

Abstract:

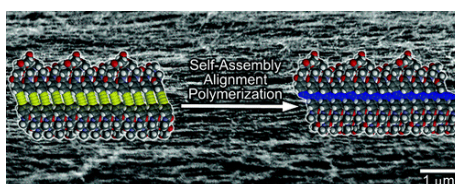


Dyads of endohedral nitrogen fullerene and porphyrin have been synthesized. In the two-radical-center dyad, the copper(II) tetraphenylporphyrin suppressed the electron spin resonance (ESR) signal of  $N@C_{60}$  through intramolecular dipolar coupling with a strength of 27.0 MHz. Demetalation of the metalloporphyrin moiety of the dyad, which effectively turned the two-radical-center dyad into a single-radical-center dyad, recovered 82% of the ESR signal of  $N@C_{60}$ . Such mechanism of switching a spin state on and off could find use in molecular spintronics applications.

- Synthesis and Alignment of Discrete Polydiacetylene-Peptide Nanostructures

Diegelmann, S. R.; Hartman, N.; Markovic, N.; Tovar, J.D. *J. Am. Chem. Soc.* **2012**, *134*, 2028–2031.

Abstract:



Oligopeptides bearing internal diacetylene units are shown to self-assemble in water into one-dimensional nanostructures and aligned macroscopic hydrogels. The diacetylene units can be photo polymerized into poly-diacetylenes that run coincident to the nanostructure and noodle long axis, and the resulting nanostructures show evidence for ambipolar charge transport. This self-assembly, alignment and polymerization technique provides a rapid way to produce globally aligned collections of conjugated polymer chains.

- Stability of Polymer Solar Cells

Jørgensen, M.; Norrman, K.; Gevorgyan, S.-A.; Tromholt, T.; Andreasen, B.; Krebs, F.-C. *Adv. Mater.* **2012**, *24*, 580–612.

Abstract:



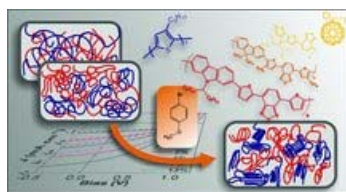
Organic photovoltaics (OPVs) evolve in an exponential manner in the two key areas of efficiency and stability. The power conversion efficiency (PCE) has in the last decade been increased by almost a factor of ten approaching 10%. A main concern has been the stability that was previously measured in minutes, but can now, in favorable circumstances, exceed many thousands of hours. This astonishing achievement is the subject of this article, which reviews the developments in stability/degradation of OPVs in the last five years. This progress has been gained by several developments, such as inverted device structures of the bulk heterojunction geometry device, which allows for more stable metal electrodes, the choice of more photostable active materials, the introduction of interfacial layers, and roll-to-roll fabrication, which promises fast and cheap production methods while creating its own challenges in terms of stability.

- Solvent Additive Control of Morphology and Crystallization in Semiconducting Polymer Blends

Liu, X.; Huettner, S.; Rong, Z.; Sommer, M.; Friend, R.-H. *Adv. Mater.* **2012**, 24, 669 – 674.

Abstract:

9

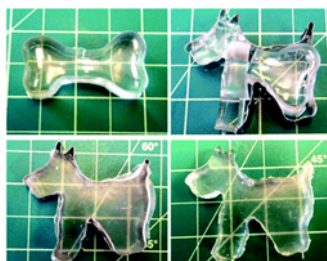


4-bromoanisole is used as a very versatile processing additive to control the phase separation and phase purity of organic photovoltaic devices. Polymer-polymer blends based on P3HT as donor and a wide range of acceptor materials (F8TBT, PCDTBT,...) are investigated. The additive promotes the aggregation of P3HT which improves the morphology for both initially mixed and demixed blends.

- A Surprise from 1954: Siloxane Equilibration Is a Simple, Robust, and Obvious Polymer Self-Healing Mechanism

Zheng, P.; Mc Carthy, T.- J. *J. Am. Chem. Soc.* **2012**, 134, 2024-2027.

Abstract:

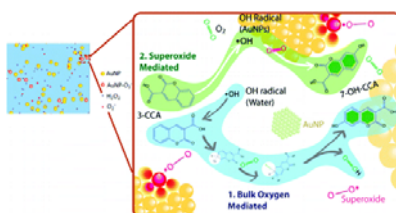


Tetramethylammoniumsilanolate-initiated ring-opening copolymerization of ctamethyl cyclotetrasiloxane ( $D_4$ ) and bis(heptamethylcyclotetrasiloxanyl)ethane (bis- $D_4$ ) renders cross-linked network polymers that contain ethylene bridges and active silanolate end groups. These “living” reactive anionic species are not neutralized by ambient atmosphere exposure (are stable to water, oxygen,  $CO_2$ ) and promote thermally activated equilibration among different network isomers and cyclic oligomers. The cross-link density of these living networks can be controlled by the ratio of  $D_4$ :bis- $D_4$ , and the density of active chain ends is determined from the initiator:monomer ratio. We report that samples prepared with particular ratios of initiator: $D_4$ :bis- $D_4$  can be cut with a sharp knife, even into two pieces, and can heal by siloxane equilibration to restore the original strength of the silicone sample. Fracture toughness measurements were carried out and revealed complete (mechanical) healing. Broken and healed samples generally failed in locations other than the initially cracked region. We call attention to publications and patents from the 1950s that suggest that this self-healing behavior was likely obvious 60 years ago.

- Chemical Enhancement by Nanomaterials under X-ray Irradiation

Cheng, N.-N.; Starkewolf, Z.; Davidson, R.-A.; Sharmah, A.; Lee, C.; Lien, J.; Guo, T. *J. Am. Chem. Soc.* **2012**, 134, 1950-1953.

Abstract:

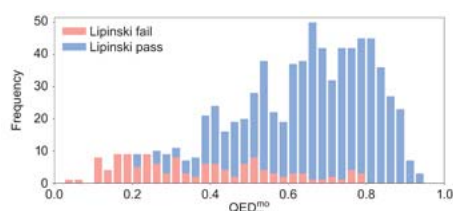


We report here a new phenomenon of dynamic enhancement of chemical reactions by nanomaterials under hard X-ray irradiation. The nanomaterials were gold and platinum nanoparticles, and the chemical reaction employed was the hydroxylation of coumarin carboxylic acid. The reaction yield was enhanced 2000 times over that predicted on the basis of the absorption of X-rays only by the nanoparticles, and the enhancement was found for the first time to depend on the X-ray dose rate. The maximum turnover frequency was measured at  $1 \times 10^{-4} \text{ s}^{-1} \text{ Gy}^{-1}$ . We call this process chemical enhancement, which is defined as the increased yield of a chemical reaction due to the chemical properties of the added materials. The chemical enhancement described here is believed to be ubiquitous and may significantly alter the outcome of chemical reactions under X-ray irradiation with the assistance of nanomaterials.

- Quantifying the chemical beauty of drugs

Bickerton, G. R.; Paolini, G. V.; Besnard, J.; Muresan, S.; Hopkins, A. L. *Nat. Chem.* **2012**, *4*, 90–98.

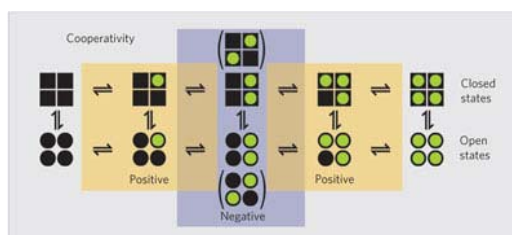
Abstract:



Drug-likeness is a key consideration when selecting compounds during the early stages of drug discovery. However, evaluation of drug-likeness in absolute terms does not reflect adequately the whole spectrum of compound quality. More worryingly, widely used rules may inadvertently foster undesirable molecular property inflation as they permit the encroachment of rule-compliant compounds towards their boundaries. We propose a measure of drug-likeness based on the concept of desirability called the quantitative estimate of drug-likeness (QED). The empirical rationale of QED reflects the underlying distribution of molecular properties. QED is intuitive, transparent, straightforward to implement in many practical settings and allows compounds to be ranked by their relative merit. We extended the utility of QED by applying it to the problem of molecular target druggability assessment by prioritizing a large set of published bioactive compounds. The measure may also capture the abstract notion of aesthetics in medicinal chemistry.

- How subunits cooperate in cAMP-induced activation of homotetrameric HCN2 channels
- Kusch, J.; Thon, S.; Schulz, E.; Biskup, C.; Nache, V.; Zimmer, T.; Seifert, R.; Schwede, F.; Benndorf, K. *Nat. Chem. Biol.* **2012**, *8*, 162–169.

Abstract:

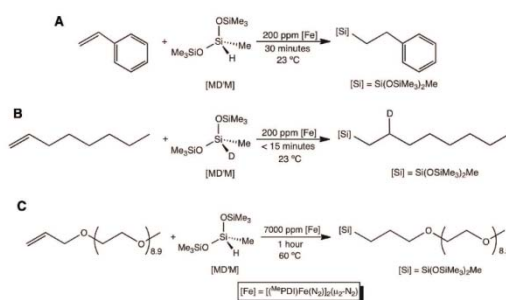


Hyperpolarization-activated cyclic nucleotide-modulated (HCN) channels are tetrameric membrane proteins that generate electrical rhythmicity in specialized neurons and cardiomyocytes. The channels are primarily activated by voltage but are receptors as well, binding the intracellular ligand

cyclic AMP. The molecular mechanism of channel activation is still unknown. Here we analyze the complex activation mechanism of homotetrameric HCN2 channels by confocal patch-clamp fluorometry and kinetically quantify all ligand binding steps and closed-open isomerizations of the intermediate states. For the binding affinity of the second, third and fourth ligand, our results suggest pronounced cooperativity in the sequence positive, negative and positive, respectively. This complex interaction of the subunits leads to a preferential stabilization of states with zero, two or four ligands and suggests a dimeric organization of the activation process: within the dimers the cooperativity is positive, whereas it is negative between the dimers.

- Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes  
Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. *Science* **2012**, 335, 567-570.

Abstract:



Alkene hydrosilylation, the addition of a silicon hydride (Si-H) across a carbon-carbon double bond, is one of the largest-scale industrial applications of homogeneous catalysis and is used in the commercial production of numerous consumer goods. For decades, precious metals, principally compounds of platinum and rhodium, have been used as catalysts for this reaction class. Despite their widespread application, limitations such as high and volatile catalyst costs and competing side reactions have persisted. Here, we report that well-characterized molecular iron coordination compounds promote the selective anti-Markovnikov addition of sterically hindered, tertiary silanes to alkenes under mild conditions. These Earth-abundant base-metal catalysts, coordinated by optimized bis(imino)pyridine ligands, show promise for industrial application.

- Constant-speed vibrational signaling along polyethyleneglycol chain up to 60-Å distance.  
Lin, Z.; Rubtsov, I. V. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, 109, 1413-1418.

Abstract:

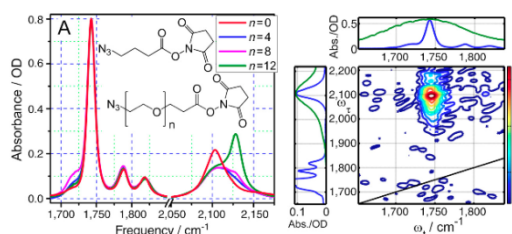


Fig. 2. (A) Linear absorption spectra of the four compounds shown in the inset. (B) 2DIR spectrum of azPEG4 measured at 7 = 60 ps.

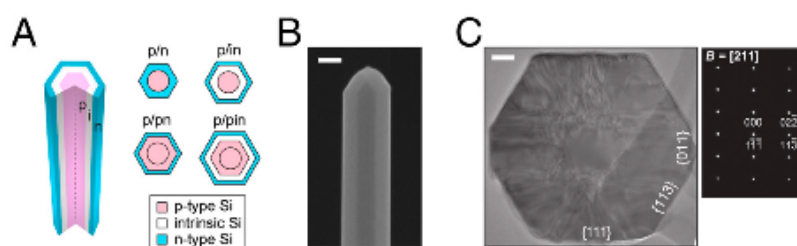
A series of azido-PEG-succinimide ester oligomers with a number of repeating PEG units of 0, 4, 8, and 12 (azPEG0, 4, 8, and 12) was investigated using a relaxation-assisted two-dimensional infrared (RA 2DIR) spectroscopy method. The RA 2DIR method relies on the energy transport in molecules and is capable of correlating the frequencies of vibrational modes separated by large through-bond distances. Excitation of the azido group in the compounds at ca. 2,100 cm<sup>-1</sup> generates an excess

energy which propagates in the molecule as well as dissipates into the solvent. We discovered that a part of the excess energy propagates ballistically via the covalent backbone of the molecules with a constant speed of ca. 550 m/s. The transport is described as a propagation of a vibrational wavepacket having a mean-free-path length of 10–15 Å. The discovery has the potential for developing new efficient signal transduction strategies for molecular electronics and biochemistry. It also permits extending the distances accessible in RA 2DIR structural measurements up to ca. 60 Å.

- Coaxial multishell nanowires with high-quality electronic interfaces and tunable optical cavities for ultrathin photovoltaics.

Kempa, T. J.; Cahoon, J. F.; Kim, S.-K.; Day, R. W.; Bell, D. C.; Park, H.-G.; Lieber, C. M. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 1407-1412.

Abstract:

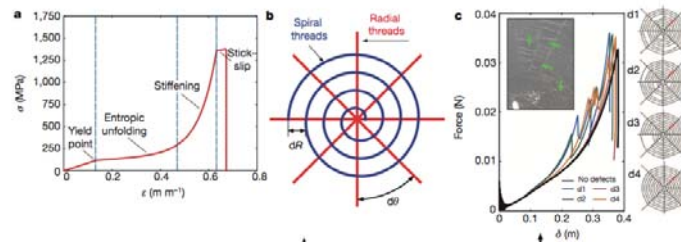


Silicon nanowires (NWs) could enable low-cost and efficient photovoltaics, though their performance has been limited by nonideal electrical characteristics and an inability to tune absorption properties. We overcome these limitations through controlled synthesis of a series of polymorphic core/multishell NWs with highly crystalline, hexagonally-faceted shells, and well-defined coaxial (*p/n*) and *p/intrinsic/n* (*p/i/n*) diode junctions. Designed 200–300 nm diameter *p/i/n* NW diodes exhibit ultralow leakage currents of approximately 1 fA, and open-circuit voltages and fill-factors up to 0.5 V and 73%, respectively, under one-sun illumination. Single-NW wavelength-dependent photocurrent measurements reveal size-tunable optical resonances, external quantum efficiencies greater than unity, and current densities double those for silicon films of comparable thickness. In addition, finite-difference-time-domain simulations for the measured NW structures agree quantitatively with the photocurrent measurements, and demonstrate that the optical resonances are due to Fabry-Perot and whispering-gallery cavity modes supported in the high-quality faceted nanostructures. Synthetically optimized NW devices achieve current densities of 17 mA/cm<sup>2</sup> and power-conversion efficiencies of 6%. Horizontal integration of multiple NWs demonstrates linear scaling of the absolute photocurrent with number of NWs, as well as retention of the high open-circuit voltages and short-circuit current densities measured for single NW devices. Notably, assembly of 2 NW elements into vertical stacks yields short-circuit current densities of 25 mA/cm<sup>2</sup> with a backside reflector, and simulations further show that such stacking represents an attractive approach for further enhancing performance with projected efficiencies of > 15% for 1.2 μm thick 5 NW stacks.

- Nonlinear material behaviour of spider silk yields robust webs.

Cranford, S. W.; Tarakanova, A.; Pugno, N. M.; Buehler, M. J. *Nature* **2012**, *482*, 72-76.

Abstract:



Natural materials are renowned for exquisite designs that optimize function, as illustrated by the elasticity of blood vessels, the toughness of bone and the protection offered by nacre. Particularly intriguing are spider silks, with studies having explored properties ranging from their protein sequence to the geometry of a web. This material system, highly adapted to meet a spider's many needs, has superior mechanical properties. In spite of much research into the molecular design underpinning the outstanding performance of silk fibres, and into the mechanical characteristics of web-like structures, it remains unknown how the mechanical characteristics of spider silk contribute to the integrity and performance of a spider web. Here we report web deformation experiments and simulations that identify the nonlinear response of silk threads to stress—involving softening at a yield point and substantial stiffening at large strain until failure—as being crucial to localize load-induced deformation and resulting in mechanically robust spider webs. Control simulations confirmed that a nonlinear stress response results in superior resistance to structural defects in the web compared to linear elastic or elastic-plastic (softening) material behaviour. We also show that under distributed loads, such as those exerted by wind, the stiff behaviour of silk under small deformation, before the yield point, is essential in maintaining the web's structural integrity. The superior performance of silk in webs is therefore not due merely to its exceptional ultimate strength and strain, but arises from the nonlinear response of silk threads to strain and their geometrical arrangement in a web.