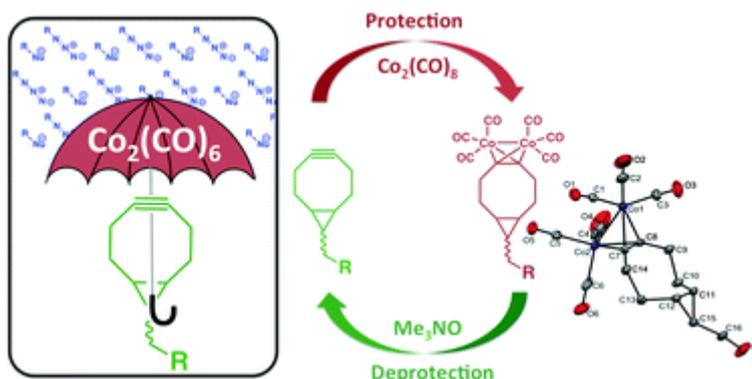


- [Expanding the scope of strained-alkyne chemistry: a protection–deprotection strategy via the formation of a dicobalt–hexacarbonyl complex](#)

Gobbo, P.; Romagnoli, T.; Barbon, S. M.; Price, J. T.; Keir, J.; Gilroy, J. B.; Workentin, M. S. *Chem. Commun.* **2015**, 51, 6647-6650.

Abstract:

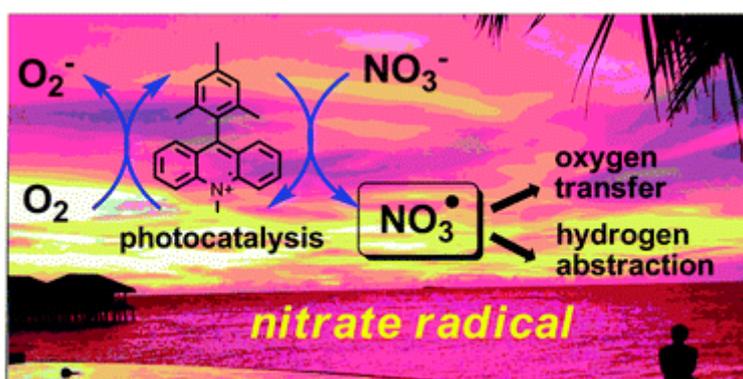


A protection–deprotection strategy for strained alkynes used for bioorthogonal chemistry is reported. A strained alkyne can be protected with dicobalt–octacarbonyl and we demonstrate for the first time that a strained alkyne can be re-formed and isolated under mild reaction conditions for further bioorthogonal reactivity. The protection–deprotection strategy herein reported will expand the versatility of strained alkynes for the preparation of substrates in chemical biology and materials applications.

- [Visible light photooxidation of nitrate: the dawn of a nocturnal radical](#)

Hering, T.; Slanina, T.; Hancock, A.; Wille, U.; König, B. *Chem. Commun.* **2015**, 51, 6568-6571.

Abstract:

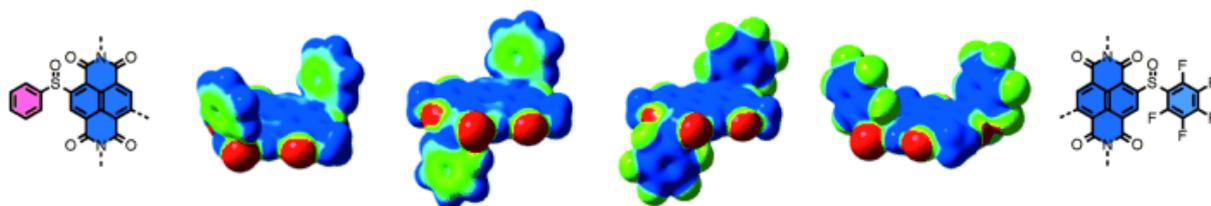


Highly oxidizing nitrate radicals (NO_3^\bullet) are easily accessed from readily available nitrate salts by visible light photoredox catalysis using a purely organic dye as the catalyst and oxygen as the terminal oxidant. The interaction of the excited catalyst and nitrate anions was studied by spectroscopic methods to elucidate the mechanism, and the method was applied to the NO_3^\bullet induced oxidation of alkynes and alcohols.

- [Big, Strong, Neutral, Twisted, and Chiral \$\pi\$ Acids](#)

Zhao, Y.; Huang, G.; Besnard, C.; Mareda, J.; Sakai, N.; Matile, S. *Chem. Eur. J.* **2015**, 21, 6202–6207.

Abstract:

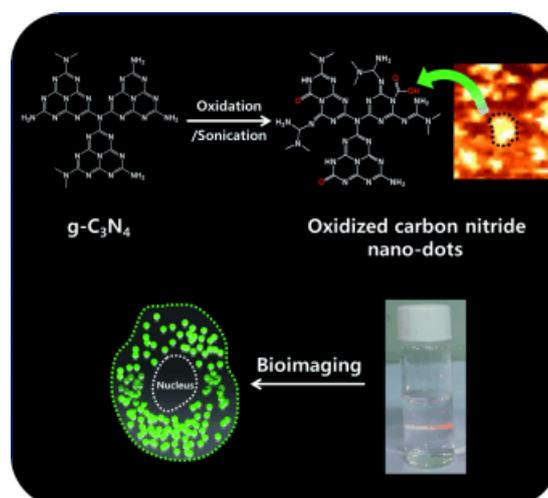


General synthetic access to expanded π -acidic surfaces of variable size, topology, chirality, and π acidity is reported. The availability of π surfaces with these characteristics is essential to develop the functional relevance of anion- π interactions with regard to molecular recognition, translocation, and transformation. The problem is that, with expanded π surfaces, the impact of electron-withdrawing substituents decreases and the high π acidity needed for strong anion- π interactions can be more difficult to obtain. To overcome this problem, it is herein proposed to build large surfaces from smaller fragments and connect these fragments with bridges that are composed only of single atoms. Two central surfaces for powerful anion- π interactions, namely, perfluoroarenes and naphthalenediimides (NDIs), were selected as fragments and coupled with through sulfide bridges. Their oxidation to sulfoxides and sulfones, as well as fluorine substitution in the peripheral rings, provides access to the full chemical space of relevant π acidities. According to cyclic voltammetry, LUMO levels range from -3.96 to -4.72 eV. With sulfoxide bridges, stereogenic centers are introduced to further enrich the intrinsic planar chirality of the expanded surfaces. The stereoisomers were separated by chiral HPLC and characterized by X-ray crystallography. Their topologies range from chairs to π boats, and the latter are reminiscent of the cation- π boxes in operational neuronal receptors. With pentafluorophenyl acceptors, the π acidity of NDIs with two sulfoxide groups in the core reaches -4.45 eV, whereas two sulfone moieties give a value of -4.72 eV, which is as low as with four ethyl sulfone groups, that is, a π superacid near the limit of existence. Beyond anion- π interactions, these conceptually innovative π -acidic surfaces are also of interest as electron transporters in conductive materials.

- [Oxidized Carbon Nitrides: Water-Dispersible, Atomically Thin Carbon Nitride-Based Nanodots and Their Performances as Bioimaging Probes](#)

Oh, J.; Yoo, R. J.; Kim, S. Y.; Lee, Y. J.; Kim, D. W.; Park, S. *Chem. Eur. J.* **2015**, *21*, 6241–6246.

Abstract:



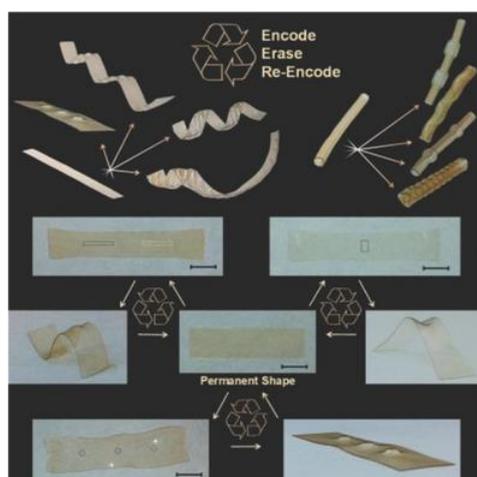
Three-dimensional (3D) carbon nitride (C_3N_4)-based materials show excellent performance in a wide range of applications because of their suitable band structures. To realize the great promise of two-dimensional (2D) allotropes of various 3D materials, it is highly important to develop routes for the

production of 2D C_3N_4 materials, which are one-atom thick, in order to understand their intrinsic properties and identify their possible applications. In this work, water-dispersible, atomically thin, and small carbon nitride nanodots were produced using the chemical oxidation of graphitic C_3N_4 . Various analyses, including X-ray diffraction, X-ray photoelectron, Fourier-transform infrared spectroscopy, and combustion-based elemental analysis, and thermogravimetric analysis, confirmed the production of 3D oxidized C_3N_4 materials. The 2D C_3N_4 nanodots were successfully exfoliated as individual single layers; their lateral dimension was several tens of nanometers. They showed strong photoluminescence in the visible region as well as excellent performances as cell-imaging probes in an in vitro study using confocal fluorescence microscopy.

- [Shape-Reprogrammable Polymers: Encoding, Erasing, and Re-Encoding](#)

Kohlmeyer, R. R.; Buskohl, P. R.; Deneault, J. R.; Durstock, M. F.; Vaia, R. A.; Chen, J. *Adv. Mater.* **2014**, *26*, 8114–8119.

Abstract:

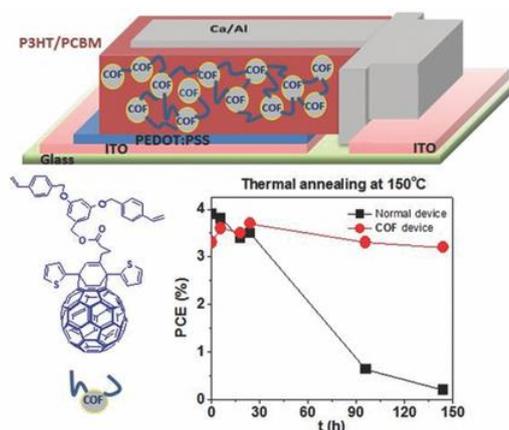


Shape-reprogramming in a polymer is demonstrated, where prescribed 3D geometric information can be encoded, decoded, erased, and re-encoded. In essence, the shape-reprogrammable polymer (SRP) acts as computer hardware that can be reformatted and reprogrammed repeatedly. Such SRPs have the potential to be repurposed directly without going through material disposal and recycling.

- [Highly Thermal Stable and Efficient Organic Photovoltaic Cells with Crosslinked Networks Appending Open-Cage Fullerenes as Additives](#)

Chen, C.-P.; Huang, C.-Y.; Chuang, S.-C. *Adv. Funct. Mater.* **2015**, *25*, 207–213.

Abstract:

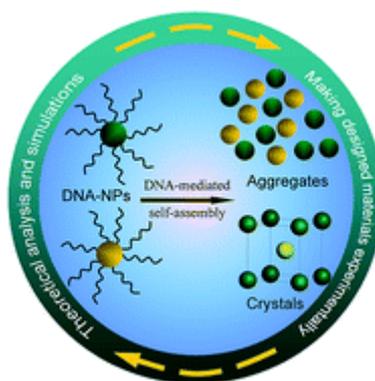


Highly thermal stable organic bulk heterojunction (OBHJ) photovoltaic cells are demonstrated with crosslinkable open-cage fullerenes (COF) as additives in the active layer. Partial incorporation of COF, $\approx 10\text{--}15\text{ wt}\%$ with weight ratio of P3HT:PC61BM = 1:0.9, builds up three-dimensional local borders upon heating treatment at $150\text{ }^\circ\text{C}$ for 10 min. This process induces crosslinking chemical reaction through activating the styryl moiety in COF and reduces phase aggregation rates of fullerenes materials. Supported by statistics of devices degradation data analysis and optical microscopy study, the devices with COF show longer lifetime with keeping their efficiency ($t = 144\text{ h}$) under accelerated heating test at $150\text{ }^\circ\text{C}$, while PCE of normal devices without COF drop dramatically. These results demonstrate that the thermally crosslinkable COF is an excellent additive for highly thermal stable and durable OPVs applications.

- [Programming macro-materials from DNA-directed self-assembly](#)

Zhang, X.; Wang, R.; Xue, G. *Soft Matter* **2015**, *11*, 1862-1870.

Abstract:

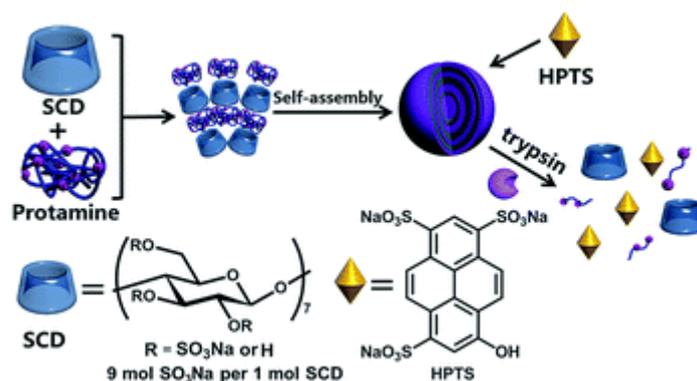


DNA is a powerful tool that can be attached to nano- and micro-objects and direct the self-assembly through base pairing. Since the strategy of DNA programmable nanoparticle self-assembly was first introduced in 1996, it has remained challenging to use DNA to make powerful diagnostic tools and to make designed materials with novel properties and highly ordered crystal structures. In this review, we summarize recent experimental and theoretical developments of DNA-programmable self-assembly into three-dimensional (3D) materials. Various types of aggregates and 3D crystal structures obtained from an experimental DNA-driven assembly are introduced. Furthermore, theoretical calculations and simulations for DNA-mediated assembly systems are described and we highlight some typical theoretical models for Monte Carlo and Molecular Dynamics simulations.

- [Enzyme-responsive protein/polysaccharide supramolecular nanoparticles](#)

Hou, X.-F.; Chen, Y.; Liu, Y. *Soft Matter* **2015**, *11*, 2488-2493.

Abstract:

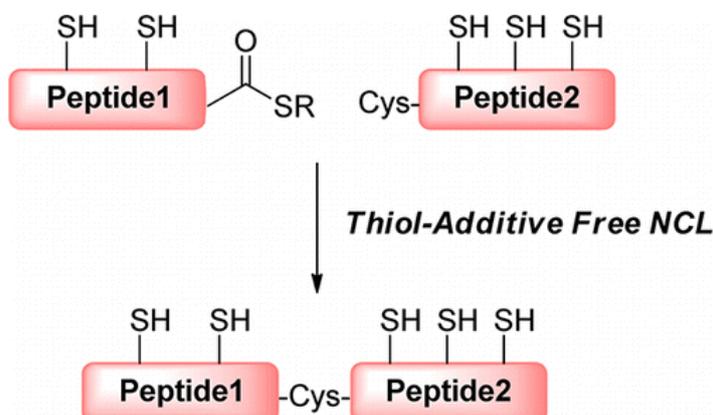


Biocompatible and enzyme-responsive supramolecular assemblies have attracted more and more interest in biomaterial fields, and find many feasible applications especially in the controlled drug release at specific sites where the target enzyme is located. In this work, novel supramolecular nanoparticles were successfully constructed from two biocompatible materials, i.e. a cyclic polysaccharide named sulfato-β-cyclodextrin (SCD) and a protein named protamine, through non-covalent association, and fully characterized by means of atomic force microscopy (AFM) and high-resolution transmission electron microscopy (TEM). Significantly, the disassembly of the resulting nanoparticles can respond especially to trypsin over other enzymes. Owing to their trypsin-triggered disassembly behaviors, these nanoparticles can efficiently release the encapsulated model substrate in a controlled manner. That is, the model substrate can be encapsulated inside the nanoparticles with a high stability and released when treated with trypsin.

- [Synthesis of Cysteine-Rich Peptides by Native Chemical Ligation without Use of Exogenous Thiols](#)

Tsuda, S.; Yoshiya, T.; Mochizuki, M.; Nishiuchi, Y. *Org. Lett.* **2015**, *17*, 1806–1809.

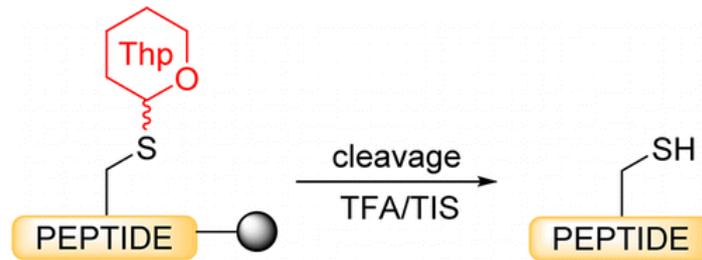
Abstract:



Native chemical ligation (NCL) performed without resorting to the use of thiol additives was demonstrated to be an efficient and effective procedure for synthesizing Cys-rich peptides. This method using tris(2-carboxyethyl)phosphine (TCEP) as a reducing agent facilitates the ligation reaction even at the Thr-Cys or Ile-Cys site and enables one-pot synthesis of Cys-rich peptides throughout NCL and oxidative folding

- [Tetrahydropyranyl, a Nonaromatic Acid-Labile Cys Protecting Group for Fmoc Peptide Chemistry](#)

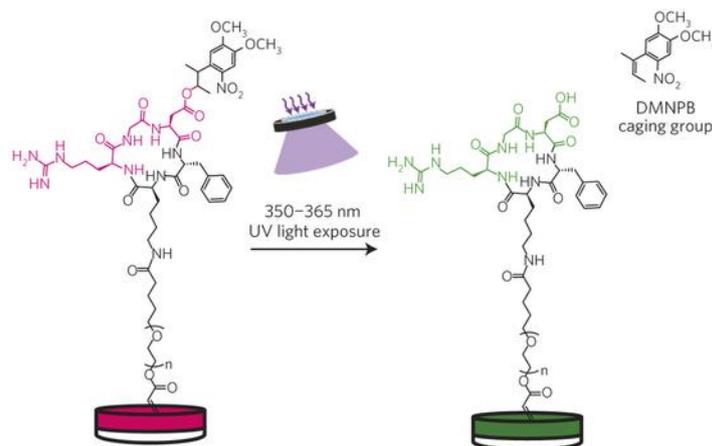
Ramos-Tomillero, I.; Rodríguez, H.; Albericio, F. *Org. Lett.* **2015**, *17*, 1680–1683.

Abstract:

Tetrahydropyranyl (Thp), which exploits the concept of being an S,O-acetal nonaromatic protecting group for cysteine, has been shown to be superior to Trt, Dpm, Acn, and StBu in solid-phase peptide synthesis using the Fmoc/tBu strategy. Thus, Cys racemization and C-terminal 3-(1-piperidinyl)alanine formation were minimized when the Cys was protected with Thp. This nonaromatic protecting group also improved the solubility of Cys-containing protected peptides.

- [Light-triggered in vivo activation of adhesive peptides regulates cell adhesion, inflammation and vascularization of biomaterials](#)

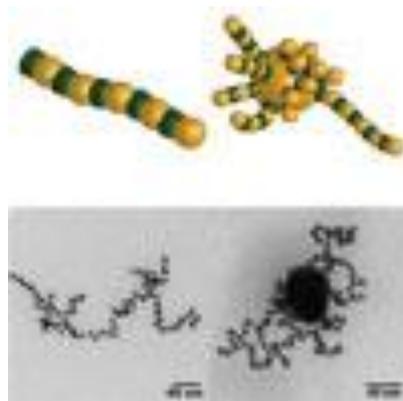
Lee, T. T.; García, J. R.; Paez, J. I.; Singh, A.; Phelps, E. A.; Weis, S.; Shafiq, Z.; Shekaran, A.; del Campo, A.; García, A. J. *Nature Mater.* **2015**, *14*, 352-360.

Abstract:

Materials engineered to elicit targeted cellular responses in regenerative medicine must display bioligands with precise spatial and temporal control. Although materials with temporally regulated presentation of bioadhesive ligands using external triggers, such as light and electric fields, have recently been realized for cells in culture, the impact of in vivo temporal ligand presentation on cell-material responses is unknown. Here, we present a general strategy to temporally and spatially control the in vivo presentation of bioligands using cell-adhesive peptides with a protecting group that can be easily removed via transdermal light exposure to render the peptide fully active. We demonstrate that non-invasive, transdermal time-regulated activation of cell-adhesive RGD peptide on implanted biomaterials regulates in vivo cell adhesion, inflammation, fibrous encapsulation, and vascularization of the material. This work shows that triggered in vivo presentation of bioligands can be harnessed to direct tissue reparative responses associated with implanted biomaterials.

- [Molecular protein adaptor with genetically encoded interaction sites guiding the hierarchical assembly of plasmonically active nanoparticle architectures](#)

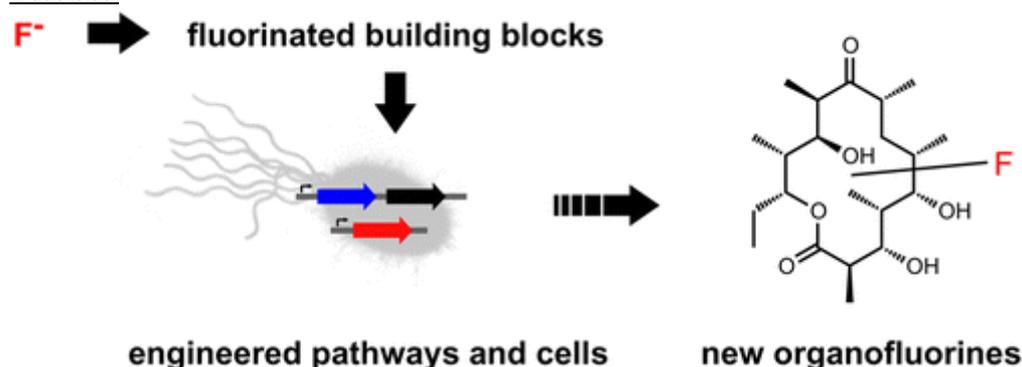
Schreiber, A.; Huber, M. C.; Cölfen, H.; Schiller, S. M. *Nature Comm.* **2015**, *6*, 6705.

Abstract:

The control over the defined assembly of nano-objects with nm-precision is important to create systems and materials with enhanced properties, for example, metamaterials. In nature, the precise assembly of inorganic nano-objects with unique features, for example, magnetosomes, is accomplished by efficient and reliable recognition schemes involving protein effectors. Here we present a molecular approach using protein-based ‘adaptors/connectors’ with genetically encoded interaction sites to guide the assembly and functionality of different plasmonically active gold nanoparticle architectures (AuNP). The interaction of the defined geometrically shaped protein adaptors with the AuNP induces the self-assembly of nanoarchitectures ranging from AuNP encapsulation to one-dimensional chain-like structures, complex networks and stars. Synthetic biology and bionanotechnology are applied to co-translationally encode unnatural amino acids as additional site-specific modification sites to generate functionalized biohybrid nanoarchitectures. This protein adaptor-based nano-object assembly approach might be expanded to other inorganic nano-objects creating biohybrid materials with unique electronic, photonic, plasmonic and magnetic properties.

- [Synthetic Biology Approaches to Fluorinated Polyketides](#)

Thuronyi, B. W.; Chang, M. C. Y. *Acc. Chem. Res.* **2015**, *48*, 584–592.

Abstract:

The catalytic diversity of living systems offers a broad range of opportunities for developing new methods to produce small molecule targets such as fuels, materials, and pharmaceuticals. In addition to providing cost-effective and renewable methods for large-scale commercial processes, the exploration of the unusual chemical phenotypes found in living organisms can also enable the expansion of chemical space for discovery of novel function by combining orthogonal attributes from both synthetic and biological chemistry. In this context, we have focused on the development of new fluorine chemistry using synthetic biology approaches. While fluorine has become an important

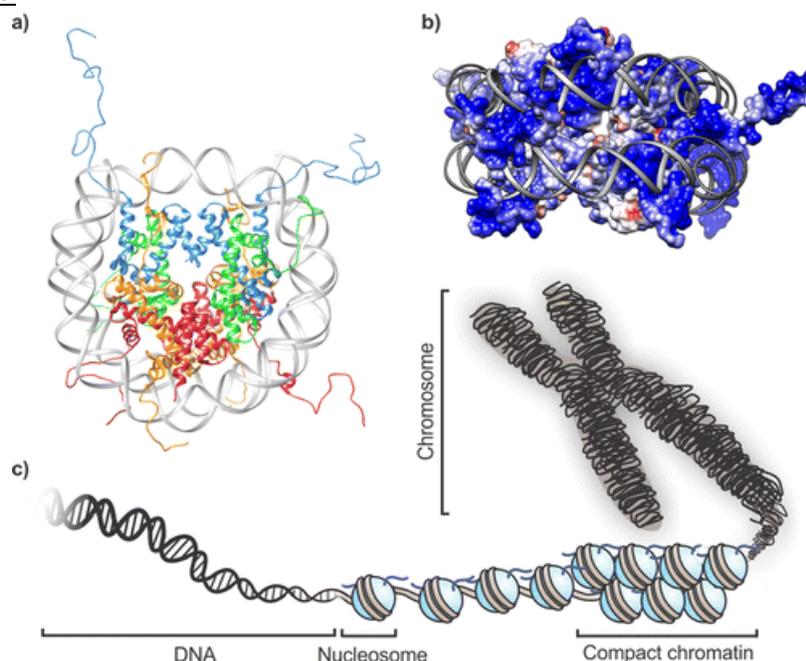
feature in compounds of synthetic origin, the scope of biological fluorine chemistry in living systems is limited, with fewer than 20 organofluorine natural products identified to date.

In order to expand the diversity of biosynthetically accessible organofluorines, we have begun to develop methods for the site-selective introduction of fluorine into complex natural products by engineering biosynthetic machinery to incorporate fluorinated building blocks. To gain insight into how both enzyme active sites and metabolic pathways can be evolved to manage and select for fluorinated compounds, we have studied one of the only characterized natural hosts for organofluorine biosynthesis, the soil microbe *Streptomyces cattleya*. This information provides a template for designing engineered organofluorine enzymes, pathways, and hosts and has allowed us to initiate construction of enzymatic and cellular pathways for the production of fluorinated polyketides. The development of anticancer vaccines requires the identification of unique epitope markers, preferably expressed exclusively on the surface of cancer cells.

- [Histones: At the Crossroads of Peptide and Protein Chemistry](#)

Muler, M. M.; Muir, T.W. *Chem. Rev.* **2015**, *115*, 2296-2349.

Abstract:

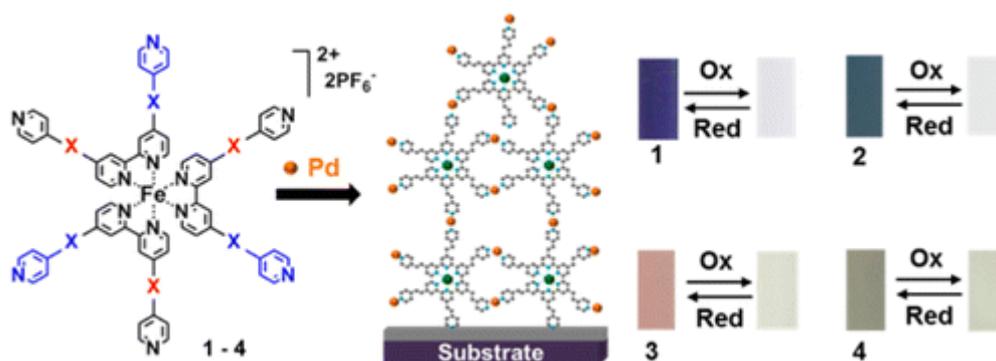


Great review about the chemistry of histones.

- [Coordination-Based Molecular Assemblies as Electrochromic Materials: Ultra-High Switching Stability and Coloration Efficiencies](#)

Shankar, S.; Lahav, M.; van der Boom, M. E. *J. Am. Chem. Soc.* **2015**, *137*, 4050-4053.

Abstract:

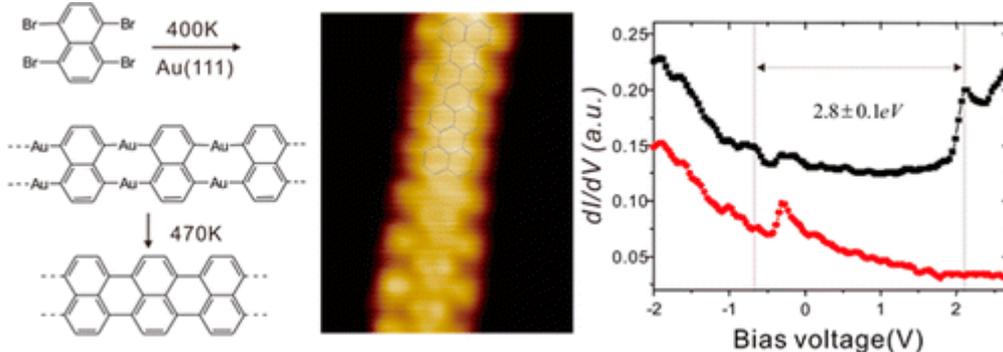


We demonstrate high-performance electrochromic assemblies that exhibit a practical combination of low-voltage operation and efficient electrochromic switching as well as long-term thermal and redox stability (1.12×10^5 cycles). Our molecular assemblies can be integrated into a solid-state configuration. Furthermore, we also show how the molecular structure of the chromophores correlates with the materials' growth and function. The coloration efficiencies of our assemblies are higher than those of inorganic materials and many conducting polymers, in addition to offering an alternative fabrication approach.

- [On-Surface Synthesis of Rylene-Type Graphene Nanoribbons](#)

Zhang, H.; Lin, H.; Sun, K.; Chen, L.; Zagranyski, Y.; Aghdassi, N.; Duhr, S.; Li, Q.; Zhong, D.; Li, Y.; Müllen, K.; Fuchs, Chi, L. *J. Am. Chem. Soc.* **2015**, *137*, 4022–4025.

Abstract:

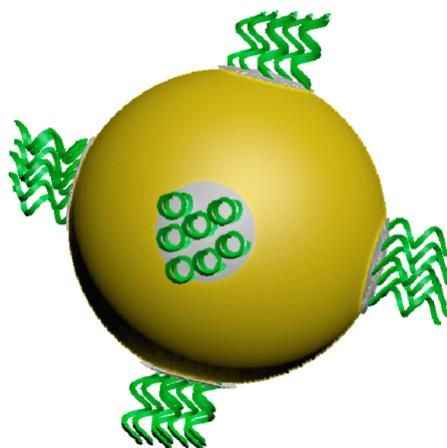


The narrowest armchair graphene nanoribbon (AGNR) with five carbons across the width of the GNR (5-AGNR) was synthesized on Au(111) surfaces via sequential dehalogenation processes in a mild condition by using 1,4,5,8-tetrabromonaphthalene as the molecular precursor. Gold-organic hybrids were observed by using high-resolution scanning tunneling microscopy and considered as intermediate states upon AGNR formation. Scanning tunneling spectroscopy reveals an unexpectedly large band gap of $\Delta = 2.8 \pm 0.1$ eV on Au(111) surface which can be interpreted by the hybridization of the surface states and the molecular states of the 5-AGNR.

- [Self-Assembly of Molecule-like Nanoparticle Clusters Directed by DNA Nanocages](#)

Li, Y. L.; Liu, Z. Y.; Yu, G. M.; Jiang, W.; Mao, C. D. *J. Am. Chem. Soc.* **2015**, *137*, 4320-4323.

Abstract:

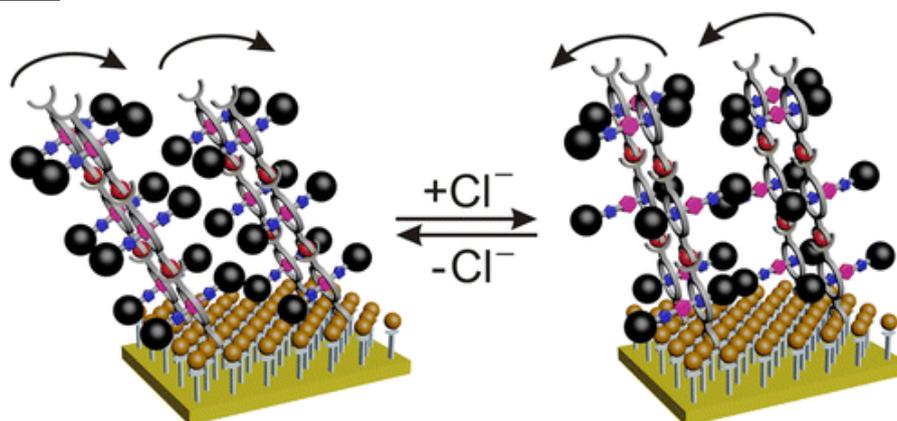


Analogous to the atom–molecule relationship, nanoparticle (NP) clusters (or NP-molecules) with defined compositions and directional bonds could potentially integrate the properties of the component individual NPs, leading to emergent properties. Despite extensive efforts in this direction, no general approach is available for assembly of such NP-molecules. Here we report a general method for building this type of structures by encapsulating NPs into self-assembled DNA polyhedral wireframe nanocages, which serve as guiding agents for further assembly. As a demonstration, a series of NP-molecules have been assembled and validated. Such NP-molecules will, we believe, pave a way to explore new nanomaterials with emergent functions/properties that are related to, but do not belong to the individual component nanoparticles.

- [Coupled Molecular Switching Processes in Ordered Mono- and Multilayers of Stimulus-Responsive Rotaxanes on Gold Surfaces](#)

Thomas, H.; Christoph, H.H.T.; Markus, H.; Sebastian, R.; Valentin, K.; Sarah, K. K.; Sven, O. K.; Jurriaan, H.; Wolfgang, E. S. U.; Christoph, A. S. *J. Am. Chem. Soc.* **2015**, *137*, 4382-4390.

Abstract:



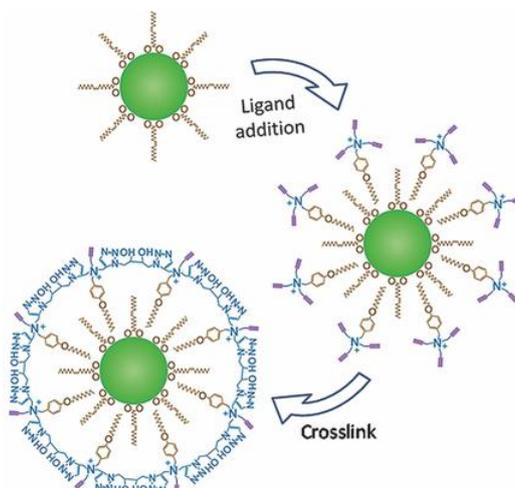
Interfaces provide the structural basis for function as, for example, encountered in nature in the membrane-embedded photosystem or in technology in solar cells. Synthetic functional multilayers of molecules cooperating in a coupled manner can be fabricated on surfaces through layer-by-layer self-assembly. Ordered arrays of stimulus-responsive rotaxanes undergoing well-controlled axle shuttling are excellent candidates for coupled mechanical motion. Such stimulus-responsive surfaces may help integrate synthetic molecular machines in larger systems exhibiting even macroscopic effects or generating mechanical work from chemical energy through cooperative action. The present work demonstrates the successful deposition of ordered mono- and multilayers of

chemically switchable rotaxanes on gold surfaces. Rotaxane mono- and multilayers are shown to reversibly switch in a coupled manner between two ordered states as revealed by linear dichroism effects in angle-resolved NEXAFS spectra. Such a concerted switching process is observed only when the surfaces are well packed, while less densely packed surfaces lacking lateral order do not exhibit such effects.

- [A versatile 'click chemistry' route to size-restricted, robust, and functionalizable hydrophilic nanocrystals](#)

Bian, T.; Wang, C.; Lu, Z.; Xie, R.; Yang, Q.-Z.; Wu, L.-Z.; Tung, C.-H.; Liu, Z.; Yin, Y.; Zhang, T. *Small* **2015**, *11*, 1644–1648.

Abstract:

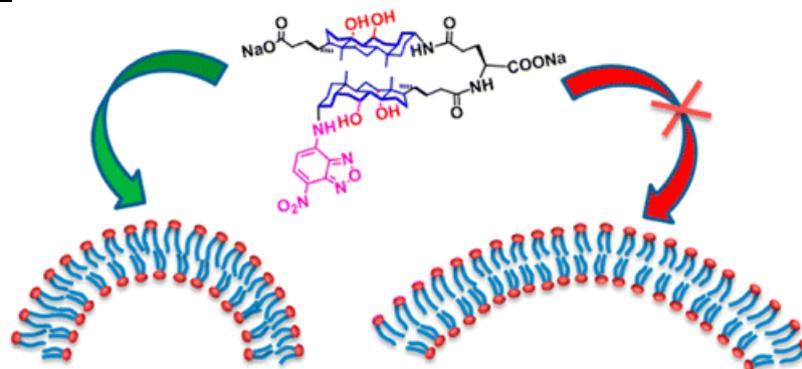


A versatile addition-crosslinking route is developed to transfer various hydrophobic nanocrystals into water. By assembling amphiphilic ligands and then crosslinking through 'click chemistry', a monolayer of polymer forms on the nanocrystal surface, leading to excellent stability and limited increase in hydrodynamic diameter. These nanocrystals can also be further functionalized easily for various applications such as catalysis, bioimaging, and medical therapy.

- [Conformationally Switchable Water-Soluble Fluorescent Bischoleate Foldamers as Membrane-Curvature Sensors](#)

Gunasekara, R. W.; Zhao, Y. *Langmuir* **2015**, *31*, 3919–3925.

Abstract:



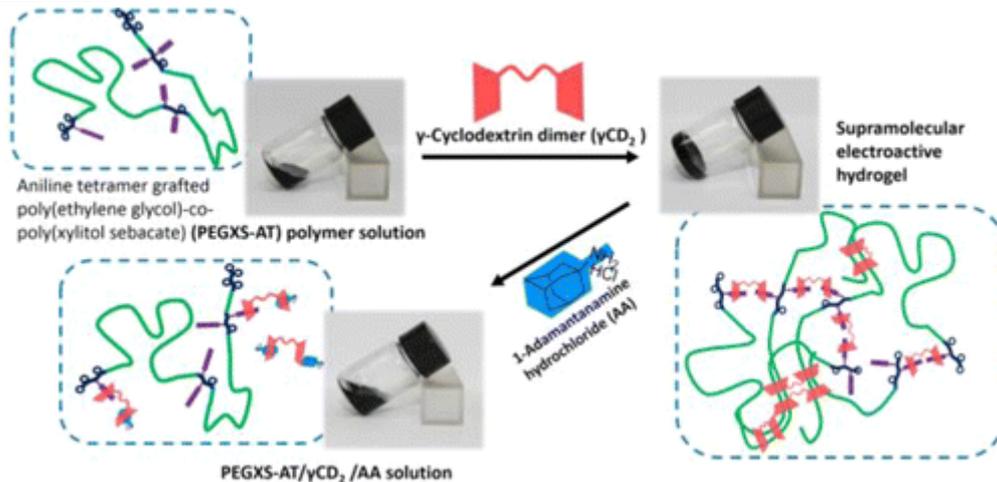
Membrane curvature is an important parameter in biological processes such as cellular movement, division, and vesicle fusion and budding. Traditionally, only proteins and protein-derived peptides have been used as sensors for membrane curvature. Three water-soluble bischoleate foldamers were synthesized, all labeled with an environmentally sensitive fluorophore to report their binding with

lipid membranes. The orientation and ionic nature of the fluorescent label were found to be particularly important in their performance as membrane-curvature sensors. The bischolate with an NBD group in the hydrophilic α -face of the cholate outperformed the other two analogues as a membrane-curvature sensor and responded additionally to the lipid composition including the amounts of cholesterol and anionic lipids in the membranes.

- [Injectable Electroactive Hydrogels Formed via Host–Guest Interactions](#)

Wu, Y.; Guo, B.; Ma, P. X. *ACS Macro. Lett.* **2014**, *3*, 1145–1150.

Abstract:

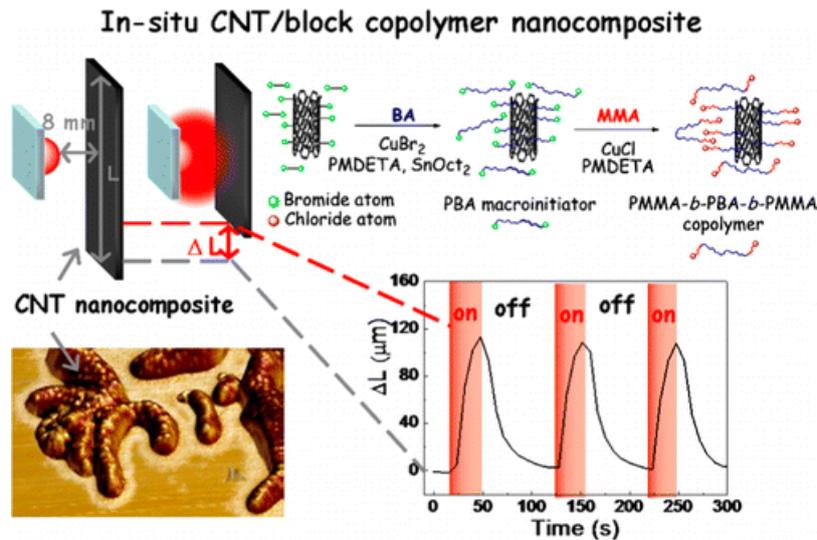


Injectable conducting hydrogels (ICHs) are promising conductive materials in biomedicine and bioengineering fields. However, the synthesis of ICHs in previous work involved chemical cross-linking, and this may result in biocompatibility problems of the hydrogels. We present the successful synthesis of ICHs via non-covalent host–guest interactions, avoiding the side effect of covalent chemical cross-linking. The ICHs are based on the γ -cyclodextrin dimer as the host molecule and tetraaniline and poly(ethylene glycol) as the guests in a synthetic well-defined hydrophilic copolymer. The sol–gel transition mechanism of the in situ hydrogel is thoroughly investigated. This novel synthesis approach of ICHs via supramolecular chemistry will lead to various new biomedical applications for conducting polymers.

- [Synthesis of Photoactuating Acrylic Thermoplastic Elastomers Containing Diblock Copolymer-Grafted Carbon Nanotubes](#)

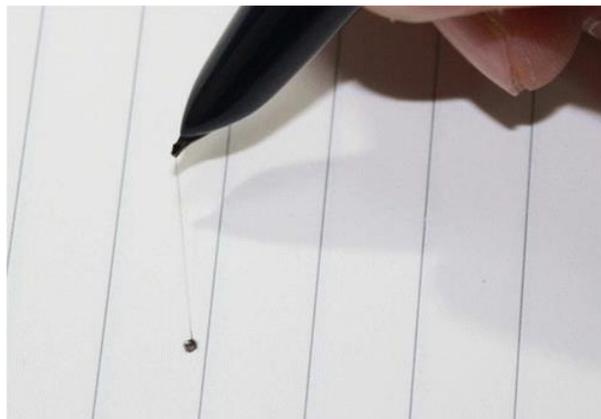
Ilčíkova, M.; Mrlík, M.; Sedláček, T.; Šlouf, M.; Zhigunov, A.; Koynov, K.; Mosnáček, J. *ACS Macro. Lett.* **2014**, *3*, 999–1003.

Abstract:



A photoactuating nanocomposite was prepared by the in situ grafting of carbon nanotubes with PBA-*b*-PMMA diblock copolymer during the synthesis of the linear triblock copolymer poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate) (PMMA-*b*-PBA-*b*-PMMA). Control over the molecular characteristics of the block copolymers was achieved by applying atom transfer radical polymerization. This synthetic approach allowed for the excellent dispersion and distribution of carbon nanotubes within the polymer matrix. The final nanocomposite containing 1 wt % grafted carbon nanotubes exhibited improved elasticity compared to that of the pure triblock copolymer, as demonstrated by dynamic mechanical analysis and rotational rheology measurements. The photoactuating behavior of the nanocomposite was demonstrated by thermomechanical analysis.

- [Direct Writing of Half-Meter Long CNT Based Fiber for Flexible Electronics](#)
Huang, S.; Zhao, C.; Pan, W.; Cui, Y.; Wu, H. *Nano Lett.* **2015**, *15*, 1609–1614.
Abstract:



Rapid construction of flexible circuits has attracted increasing attention according to its important applications in future smart electronic devices. Herein, we introduce a convenient and efficient “writing” approach to fabricate and assemble ultralong functional fibers as fundamental building blocks for flexible electronic devices. We demonstrated that, by a simple hand-writing process, carbon nanotubes (CNTs) can be aligned inside a continuous and uniform polymer fiber with length of more than 50 cm and diameters ranging from 300 nm to several micrometers. The as-prepared continuous fibers exhibit high electrical conductivity as well as superior mechanical flexibility (no

obvious conductance increase after 1000 bending cycles to 4 mm diameter). Such functional fibers can be easily configured into designed patterns with high precision according to the easy “writing” process. The easy construction and assembly of functional fiber shown here holds potential for convenient and scalable fabrication of flexible circuits in future smart devices like wearable electronics and three-dimensional (3D) electronic devices.

- [Switchable Catalytic DNA Catenanes](#)

Hu, L.; Lu, C.-H.; Willner, I. *Nano Lett.* **2015**, *13*, 2099–2103.

Abstract:

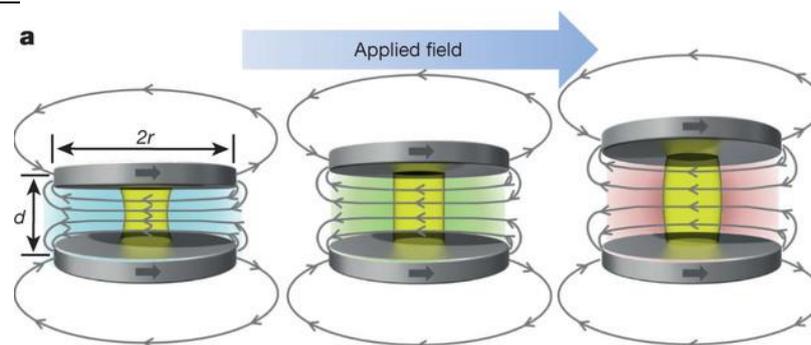


Two-ring interlocked DNA catenanes are synthesized and characterized. The supramolecular catenanes show switchable cyclic catalytic properties. In one system, the catenane structure is switched between a hemin/G-quadruplex catalytic structure and a catalytically inactive state. In the second catenane structure the catenane is switched between a catalytically active Mg²⁺-dependent DNAzyme-containing catenane and an inactive catenane state. In the third system, the interlocked catenane structure is switched between two distinct catalytic structures that include the Mg²⁺- and the Zn²⁺-dependent DNAzymes.

- [Shape-changing magnetic assemblies as high-sensitivity NMR-readable nanoprob](#)

Zabow, G.; Dodd, S. J.; Koretsky, A. P. *Nature* **2015**, *520*, 73–77.

Abstract:



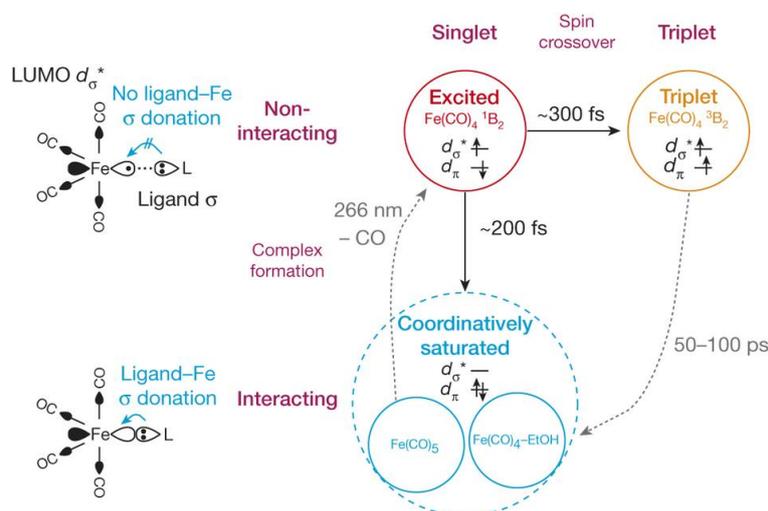
Fluorescent and plasmonic labels and sensors have revolutionized molecular biology, helping visualize cellular and biomolecular processes. Increasingly, such probes are now being designed to respond to wavelengths in the near-infrared region, where reduced tissue autofluorescence and photon attenuation enable subsurface in vivo sensing. But even in the near-infrared region, optical resolution and sensitivity decrease rapidly with increasing depth. Here we present a sensor design that obviates the need for optical addressability by operating in the nuclear magnetic resonance (NMR) radio-frequency spectrum, where signal attenuation and distortion by tissue and biological media are negligible, where background interferences vanish, and where sensors can be spatially located using standard magnetic resonance imaging (MRI) equipment. The radio-frequency-

addressable sensor assemblies presented here comprise pairs of magnetic disks spaced by swellable hydrogel material; they reversibly reconfigure in rapid response to chosen stimuli, to give geometry-dependent, dynamic NMR spectral signatures. The sensors can be made from biocompatible materials, are themselves detectable down to low concentrations, and offer potential responsive NMR spectral shifts that are close to a million times greater than those of traditional magnetic resonance spectroscopies. Inherent adaptability should allow such shape-changing systems to measure numerous different environmental and physiological indicators, thus providing broadly generalizable, MRI-compatible, radio-frequency analogues to optically based probes for use in basic chemical, biological, medical and engineering research.

- [Orbital-specific mapping of the ligand exchange dynamics of Fe\(CO\)₅ in solution](#)

Wernet, Ph.; Kunnus, K.; Josefsson, I.; Rajkovic, I.; Quevedo, W.; Beye, M.; Schreck, S.; Grübel, S.; Scholz, M.; Nordlund, D.; Zhang, W.; Hartsock, R. W.; Schlotter, W. F.; Turner, J. J.; Kennedy, B.; Hennies, F.; de Groot, F. M. F.; Gaffney, K. J.; Techert, S.; Odelius, M.; Föhlisch, A. *Nature* **2015**, *520*, 78–81.

Abstract:



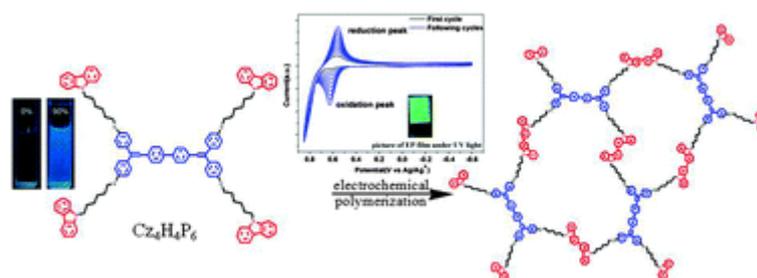
Transition-metal complexes have long attracted interest for fundamental chemical reactivity studies and possible use in solar energy conversion. Electronic excitation, ligand loss from the metal centre, or a combination of both, creates changes in charge and spin density at the metal site that need to be controlled to optimize complexes for photocatalytic hydrogen production and selective carbon-hydrogen bond activation. An understanding at the molecular level of how transition-metal complexes catalyse reactions, and in particular of the role of the short-lived and reactive intermediate states involved, will be critical for such optimization. However, suitable methods for detailed characterization of electronic excited states have been lacking. Here we show, with the use of X-ray laser-based femtosecond-resolution spectroscopy and advanced quantum chemical theory to probe the reaction dynamics of the benchmark transition-metal complex Fe(CO)₅ in solution, that the photo-induced removal of CO generates the 16-electron Fe(CO)₄ species, a homogeneous catalyst with an electron deficiency at the Fe centre, in a hitherto unreported excited singlet state that either converts to the triplet ground state or combines with a CO or solvent molecule to regenerate a penta-coordinated Fe species on a sub-picosecond timescale. This finding, which resolves the debate about the relative importance of different spin channels in the photochemistry of Fe(CO)₅ was made possible by the ability of femtosecond X-ray spectroscopy to probe frontier-

orbital interactions with atom specificity. We expect the method to be broadly applicable in the chemical sciences, and to complement approaches that probe structural dynamics in ultrafast processes.

- [Luminescent network film deposited electrochemically from a carbazole functionalized AIE molecule and its application for OLEDs](#)

Liu, C.; Luo, H.; Shi, G.; Yang, J.; Chi, Z.; Ma, Y. *J. Mater. Chem. C* **2015**, *3*, 3752-3759.

Abstract:

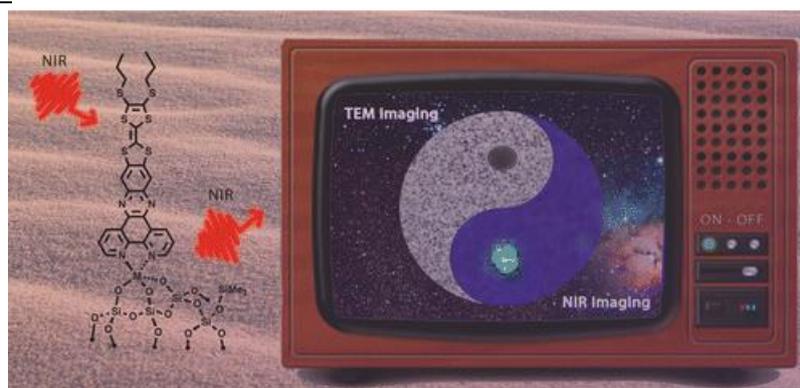


A carbazole functionalized AIE molecule was constructed and applied as a precursor to prepare the luminescent network films for organic light-emitting devices (OLEDs) by electrochemical polymerization. The resultant cross-linked electrochemically polymerized films have smooth surface and exhibit high thermal stability. OLEDs with these films as light emitting layer have a maximum luminance of 489 cd m⁻², a maximum luminance efficiency of 0.38 cd A⁻¹, and a turn-on voltage of 3.4 V. These results indicate that electrochemical synthesis can be a new facile route for constructing the cross-linked polymer luminescent films with AIE molecules, which show potential applications in OLEDs.

- [One-Photon Near-Infrared Sensitization of Well-Defined Yb\(III\) Surface Complexes for NIR-to-NIR Single Nanoparticle Imaging](#)

Lapadula, G.; Trummer, D.; Conley, M. P.; Steinmann, M.; Ran, Y.-F.; Brasselet, S.; Guyot, Y.; Maury, O.; Decurtins, S.; Liu, S.-X.; Copéret, C. *Chem. Mater.* **2015**, *27*, 2033-2039.

Abstract:



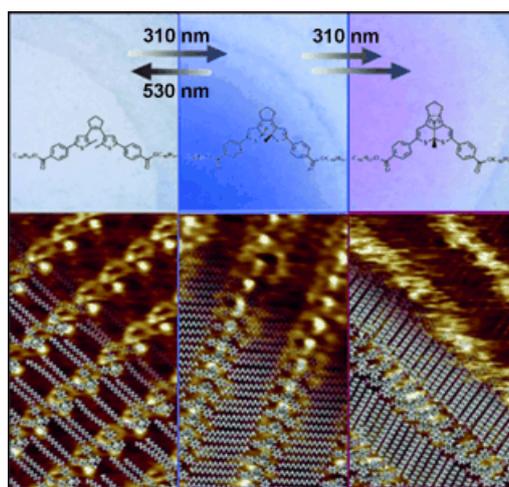
Silica nanoparticles of 12 nm diameter were surface-doped with ca. 350 (TTF-dppz)Yb(III) surface species, containing bis(propylthio)tetrathiafulvenyl[dipyrido-3,2-a:2',3-c]phenazine (TTF-dppz) as an antenna ligand through a surface organometallic chemistry approach. These nanoparticles absorb and emit in the NIR ($\lambda_{\text{abs}} = 750$ nm, $\lambda_{\text{em}} = 983$ and 1050 nm) with a lifetime (τ_1) of 2.8 μs , similarly to the corresponding Yb(III) molecular complex ($\lambda_{\text{abs}} = 750$ nm, $\lambda_{\text{em}} = 975, 986, 1009,$ and 1020 nm with $\tau_1 = 6.93$ μs). The silica materials were fully characterized using combined spectroscopic techniques

(IR, NMR, UV–vis, luminescence and lifetime), molecular models and isostructural diamagnetic yttrium-containing materials for easier characterization by NMR spectroscopy. Having established the surface structures and photophysical properties of these nanoparticles, we transposed this methodology to larger silica particles with a diameter of ca. 100 nm. These larger nanoparticles have similar photophysical properties and contain ca. 30 000 chromophores, making possible one-photon NIR-to-NIR emission optical microscopy imaging of single nanoparticles.

- [Surface-Induced Selection During In Situ Photoswitching at the Solid/Liquid Interface](#)

Bonacchi, S.; Garah, M.; Ciesielski, A.; Herder, M.; Conti, S.; Cecchini, M.; Hecht, S.; Samori, P. *Angew. Chem. Int. Ed.* **2015**, *54*, 4865–4869.

Abstract:

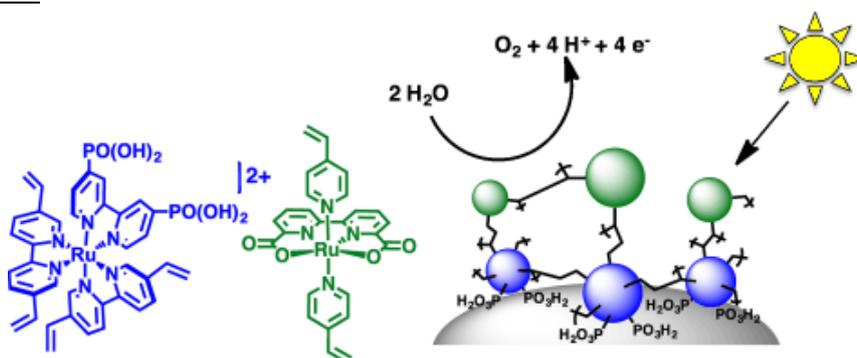


Here we report for the first time a submolecularly resolved scanning tunneling microscopy (STM) study at the solid/liquid interface of the in situ reversible interconversion between two isomers of a diarylethene photoswitch, that is, open and closed form, self-assembled on a graphite surface. Prolonged irradiation with UV light led to the in situ irreversible formation of another isomer as by-product of the reaction, which due to its preferential physisorption accumulates at the surface. By making use of a simple yet powerful thermodynamic model we provide a quantitative description for the observed surface-induced selection of one isomeric form.

- [Electro-assembly of a Chromophore–Catalyst Bilayer for Water Oxidation and Photocatalytic Water Splitting](#)

Ashford, D. L.; Sherman, B. D.; Binstead, R. A.; Templeton, J. L.; Meyer, T. J. *Angew. Chem. Int. Ed.* **2015**, *54*, 4778–4781.

Abstract:

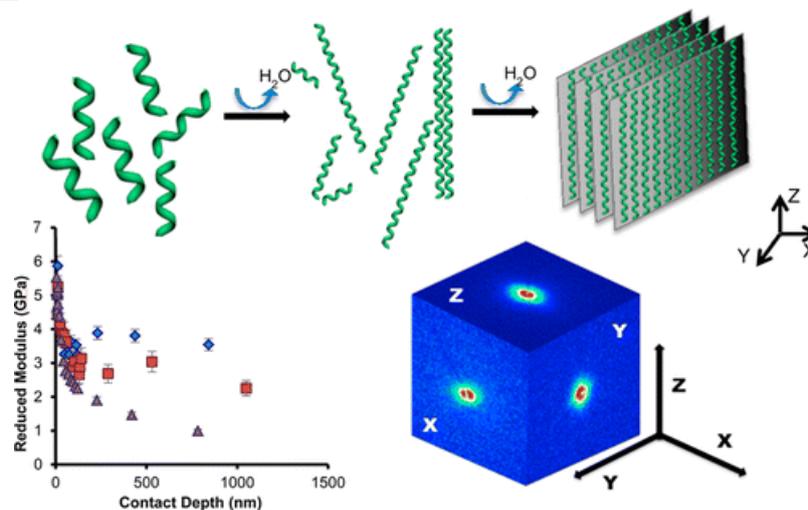


The use of electropolymerization to prepare electrocatalytically and photocatalytically active electrodes for water oxidation is described. Electropolymerization of the catalyst $\text{Ru}^{\text{II}}(\text{bda})(4\text{-vinylpyridine})_2$ (bda=2,2'-bipyridine-6,6'-dicarboxylate) on planar electrodes results in films containing semirigid polymer networks. In these films there is a change in the water oxidation mechanism compared to the solution analogue from bimolecular to single-site. Electro-assembly construction of a chromophore–catalyst structure on mesoporous, nanoparticle TiO_2 films provides the basis for a dye-sensitized photoelectrosynthesis cell (DSPEC) for sustained water splitting in a pH 7 phosphate buffer solution. Photogenerated oxygen was measured in real-time by use of a two-electrode cell design.

- [Repeat-Proteins Films Exhibit Hierarchical Anisotropic Mechanical Properties](#)

Carter, A. N.; Grove, Z. T. *Biomacromolecules* **2015**, *16*, 706–714.

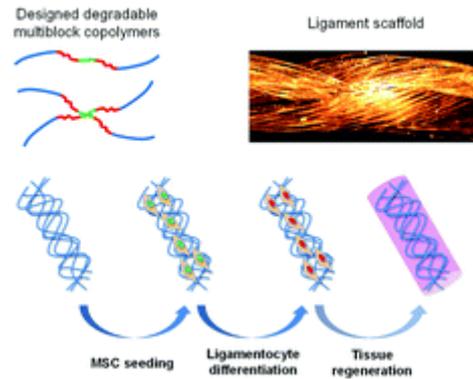
Abstract:



Complex hierarchical structures provide beneficial structure–property relationships that can be exploited for a variety of applications in engineering and biomedical fields. Here we report on molecular organization and resulting mechanical properties of self-assembled designed repeat-protein films. Wide-angle X-ray diffraction indicates the designed 18-repeat consensus tetratricopeptide repeat protein (CTPR18) orients normal to the casting surface, while small-angle measurements and electron microscopy show a through-plane transversely aligned laminar sheet-like morphology. Self-assembly is driven by the combination of CTPRs head-to-tail stacking and weak dipole–dipole interactions. We highlight the effect that this hierarchical structure has on the material’s mechanical properties. We use nanoindentation and dynamic mechanical analysis to test the mechanical properties over multiple length scales, from the molecular level to the bulk. We find that morphology predictably affects the film’s mechanics from the nano- to the macroscale, with the axial modulus values ranging from 2 to 5 GPa. The predictable nature of the structure–property relationship of CTPR proteins and their assemblies proves them a promising platform for material engineering.

- [PLA-poloxamer/poloxamine copolymers for ligament tissue engineering: sound macromolecular design for degradable scaffolds and MSC differentiation](#)

Leroy, A.; Nottelet, B.; Bony, C.; Pinese, C.; Charlot, B.; Garric, X.; Noël, D.; Coudane, J. *Biomater. Sci.* **2015**, *3*, 617-626.

Abstract:

The treatment of anterior cruciate ligament (ACL) failures remains a current clinical challenge. The present study aims at providing suitable degradable scaffolds for ligament tissue engineering. First, we focus on the design and the evaluation of poly(lactide)/poloxamer or poly(lactide)/poloxamine multiblock copolymers selected and developed to have suitable degradation and mechanical properties to match ACL repair. In the second part, it is shown that the copolymers can be processed in the form of microfibers and scaffolds consisting of a combination of twisted/braided fibers to further modulate the mechanical properties and prepare scaffold prototypes suitable for ligament application. Finally, after assessment of their cytocompatibility, the polymer scaffolds are associated with mesenchymal stem cells (MSCs). MSC differentiation toward a ligament fibroblast phenotype is promoted by a dual stimulation including an inductive culture medium and cyclic mechanical loads. RT-qPCR analyses confirm the potential of our scaffolds and MSCs for ACL regeneration with upregulation of some differentiation markers including Scleraxis, Tenascin-C and Tenomodulin.