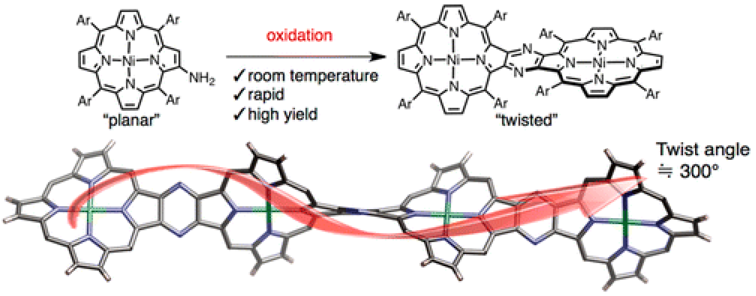
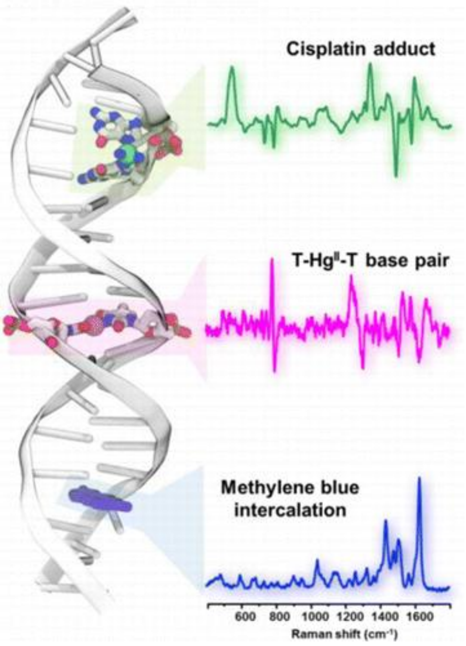
- Synthesis of Highly Twisted and Fully π-Conjugated Porphyrinic Oligomers
  Ito, S.; Hiroto, S.; Lee, S.; Son, M.; Hisaki, I.; Yoshida, T.; Kim, D.; Kobayashi, N.; Shinokubo, H. *J. Am. Chem. Soc.* **2015**, *137*, 142-145.
  Abstract:



Highly twisted π-conjugated molecules have been attractive but challenging targets. We report here an efficient synthesis of highly twisted diporphyrins with 126° and 136° twist angles that involves an oxidative fusion reaction of planar aminoporphyrin precursors at room temperature. Repeated amination–oxidative fusion sequences provide a unidirectionally twisted tetramer. The twisting angle of the tetramer is 298°.

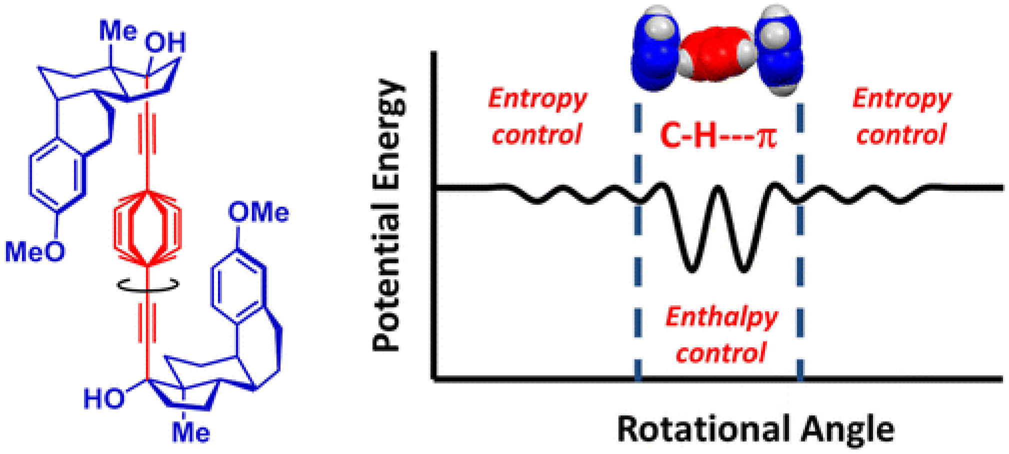
- Revealing DNA Interactions with Exogenous Agents by Surface-Enhanced Raman Scattering
  Masetti, M.; Xie, H.; Krpetić, Ž.; Recanatini, M.; Alvarez-Puebla, R. A.; Guerrini, L. *J. Am. Chem. Soc.* **2015**, *137*, 469-476.
  Abstract:



The standard protocols for DNA analysis largely involve polymerase chain reaction (PCR). However, DNA structures bound to chemical agents cannot be PCR-amplified, and therefore any sequence changes induced by external agents may be neglected. Thus, the development of analytical tools capable of characterizing the biochemical mechanisms associated with chemically induced DNA damage is demanded for the rational design of more effective chemotherapy drugs, understanding the mode of actions of carcinogenic chemicals, and monitoring the genotypic toxicology of environments. Here we report a fast, high-throughput, low-cost method for the characterization and quantitative recognition of DNA interactions with exogenous agents based on surface-enhanced

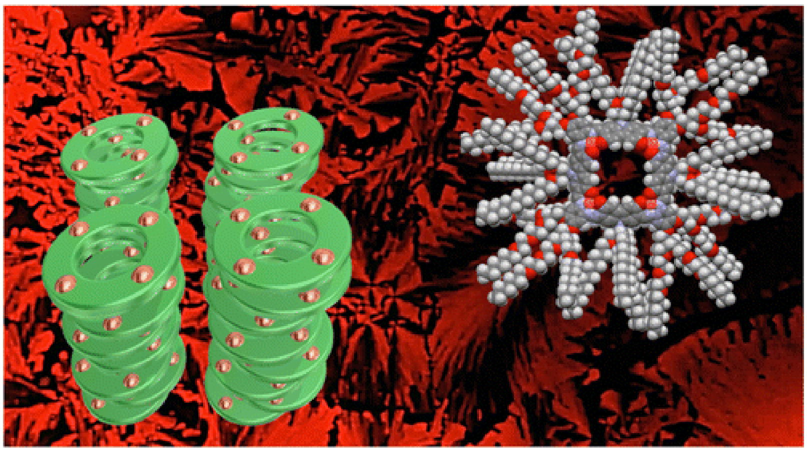
Raman scattering spectroscopy. As representative chemical agents, we selected a chemotherapeutic drug (cisplatin) which forms covalent adducts with DNA, a duplex intercalating agent (methylene blue), and a cytotoxic metal ion (HgII) which inserts into T:T mismatches. Rich structural information on the DNA complex architecture and properties is provided by the unique changes of their SERS spectra, which also offer an efficient analytical tool to quantify the extent of such binding.

- Thermodynamic Evaluation of Aromatic CH/π Interactions and Rotational Entropy in a Molecular Rotor
  Pérez-Estrada, S.; Rodríguez-Molina, B.; Xiao, L.; Santillan, R.; Jiménez-Osés, G.; Houk, K. N.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2015**, *137*, 2175-2178.
  Abstract:



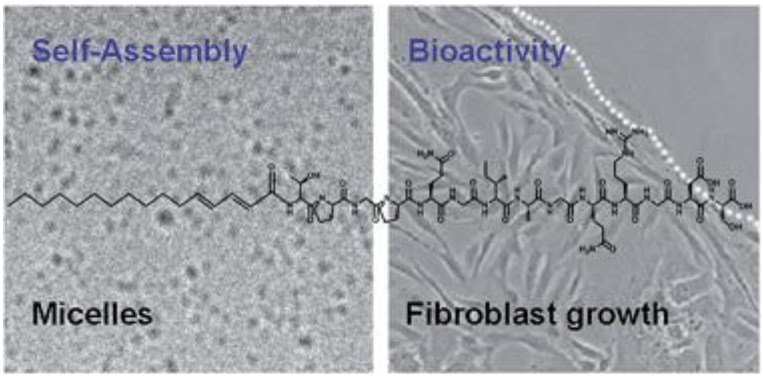
A molecular rotor built with a stator formed by two rigid 9β-mestranol units having a 90° bent angle linked to a central phenylene rotator has an ideal structure to examine aromatic CH/π interactions. Energies and populations of the multiple solution conformations from quantum-mechanical calculations and molecular dynamics simulations were combined with variable-temperature (VT) ^{1}H NMR data to establish the enthalpy of this interaction and the entropy associated with rotation about a single bond. Rotational dynamics in the solid state were determined via VT cross-polarization magic-angle spinning ^{13}C NMR spectroscopy.

- Columnar Liquid-Crystalline Metallomacrocycles
  Kawano, S.-I.; Ishida, Y.; Tanaka, K. *J. Am. Chem. Soc.* **2015**, *137*, 2295–2302.
  Abstract:



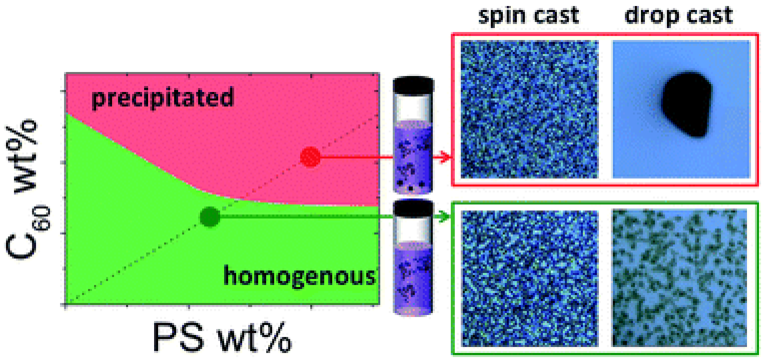
We report synthesis of novel macrocyclic molecules and their metal complexes as well as their thermotropic columnar liquid-crystalline behavior. The macrocyclic ligands were prepared size-selectively based on dynamic covalent chemistry. X-ray study of a model macrocycle with short alkyl chains revealed that they were discrete and highly symmetric, with an inner vacant cavity of 9 Å diameter enclosed by a 56π planar ring composed of four bis(salicylidene)-*o*-phenylenediamine (salphen) moieties alternating with four carbazoles. Ni^{2+} and Cu^{2+} ions were incorporated into the four salphen ligands and formed square-planar metal complexes inside the macrocycles. From the structural and thermal analyses via X-ray diffraction measurements, differential scanning calorimetry, and polarized optical-microscopic observations, it was revealed that the macrocyclic ligand and its metal complexes self-assembled into columnar liquid-crystalline phases depending on the temperature and displayed a highly fluid character over a wide range of temperatures. The peripheral alkyl chains were influential in controlling the temperature range and flowability of the liquid-crystalline phases, and the range of the liquid-crystalline temperature of the metallo-macrocycles was significantly higher than those of the metal-free macrocycles. To the best of our knowledge, these are the first examples of thermotropic columnar liquid crystals of macrocyclic metal complexes with a large hollow area.

- Self-assembly of a dual functional bioactive peptide amphiphile incorporating both matrix metalloprotease substrate and cell adhesion motifs
  Dehsorkhi, A.; Gouveia, R. M.; Smith, A. M.; Hamley, I. W.; Castelleto, V.; Connon, C. J.; Reza, M.; Ruokolainen, J. *Soft Matter* **2015**, *11,* 3115-3124.
  Abstract:



We describe a bioactive lipopeptide that combines the capacity to promote the adhesion and subsequent self-detachment of live cells, using template-cell-environment feedback interactions. This self-assembling peptide amphiphile comprises a diene-containing hexadecyl lipid chain (C_{16}e) linked to a matrix metalloprotease-cleavable sequence, Thr-Pro-Gly-Pro-Gln-Gly-Ile-Ala-Gly-Gln, and contiguous with a cell-attachment and signalling motif, Arg-Gly-Asp-Ser. Biophysical characterisation revealed that the PA self-assembles into 3 nm diameter spherical micelles above a critical aggregation concentration (cac). In addition, when used in solution at 5–150 nM (well below the cac), the PA is capable of forming film coatings that provide a stable surface for human corneal fibroblasts to attach and grow. Furthermore, these coatings were demonstrated to be sensitive to metalloproteases expressed endogenously by the attached cells, and consequently to elicit the controlled detachment of cells without compromising their viability. As such, this material constitutes a novel class of multi-functional coating for both fundamental and clinical applications in tissue engineering.

- Polymer fullerene solution phase behaviour and film formation pathways
  Dattani, R.; Cabral, J. T. *Soft Matter* **2015**, *11,* 3125-3131.
  Abstract:

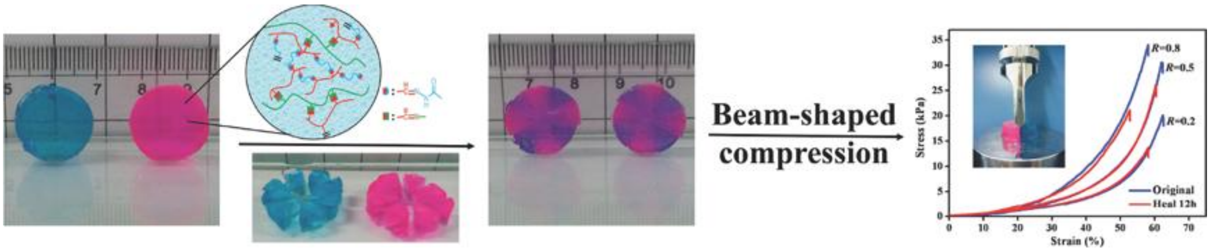


We report the phase behaviour of polymer/fullerene/solvent ternary mixtures and its consequence for the morphology of the resulting composite thin films. We focus particularly on solutions of polystyrene (PS), C_{60} fullerene and toluene, which are examined by static and dynamic light scattering, and films obtained from various solution ages and thermal annealing conditions, using atomic force and light microscopy. Unexpectedly, the solution phase behaviour below the polymer overlap concentration, c*, is found to be described by a simple excluded volume argument (occupied by the polymer chains) and the neat C_{60}/solvent miscibility. Scaling consistent with full exclusion is found when the miscibility of the fullerene in the solvent is much lower than that of the polymer, giving way to partial exclusion with more soluble fullerenes (phenyl-C61-butyric acid methyl ester, PCBM) and a less asymmetric solvent (chlorobenzene), employed in photovoltaic devices. Spun cast and drop cast films were prepared from PS/C_{60}/toluene solutions across the phase diagram to yield an identicalPS/C_{60} composition and film thickness, resulting in qualitatively different morphologies in agreement with our measured solution phase boundaries. Our findings are relevant to the solution processing of polymer/fullerene composites (including organic photovoltaic devices), which generally require effective solubilisation of fullerene derivatives and polymer pairs in this concentration range, and the design of well-defined thin film morphologies.

- Self-Beating Artificial Cells: Design of Cross-Linked Polymersomes Showing Self-Oscillating Motion
  Tamate, R.; Ueki, T.; Yoshida, R. *Adv. Mater.* **2015**, *27*, 837–842.
  Abstract:

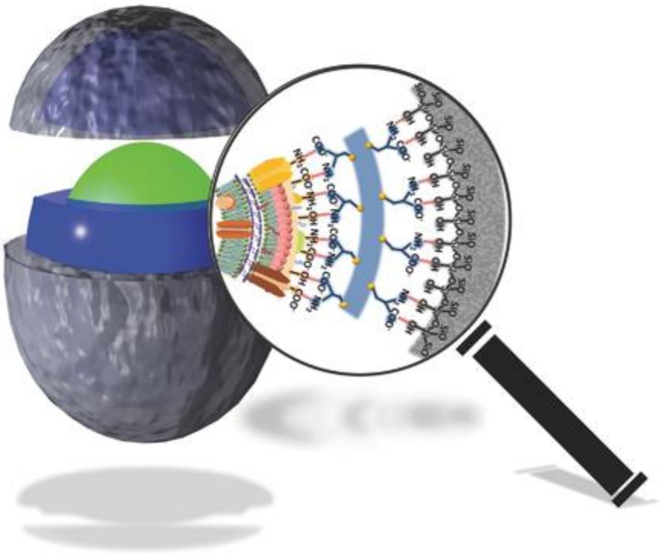
Biomimetic cross-linked polymersomes that exhibit a self-beating motion without any on–off switching are developed. The polymersomes are made from a well-defined synthetic thermoresponsive diblock copolymer, and the thermoresponsive segment includes ruthenium catalysts for the oscillatory chemical reaction and vinylidene groups to cross-link the polymersomes. Autonomous volume and shape oscillations of the cross-linked polymersomes are realized following redox changes of the catalysts.

- Novel Biocompatible Polysaccharide-Based Self-Healing Hydrogel
  Wei, Z.; Yang, J. H.; Liu, Z. Q.; Xu, F.; Zhou, J. X.; Zrínyi, M.; Osada, Y.; Chen, Y. M. *Adv. Funct. Mater.* **2015**, *25*, 1352–1359.
  Abstract:



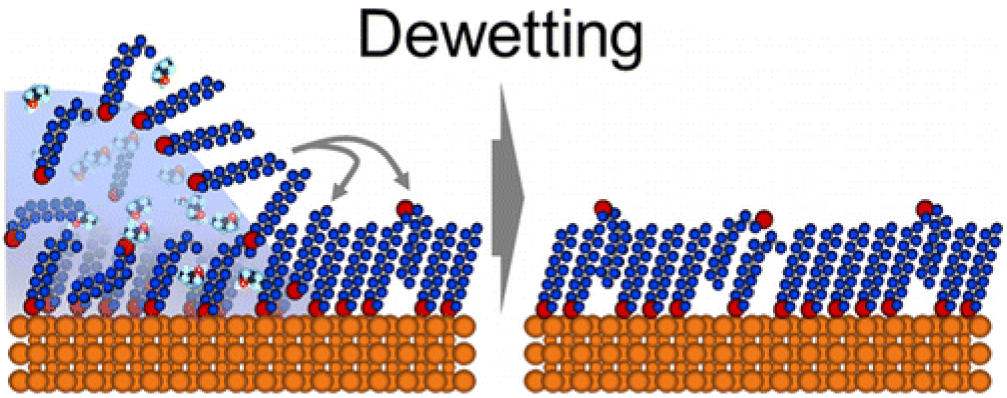
A novel biocompatible polysaccharide-based self-healing hydrogel, CEC-l-OSA-l-ADH hydrogel ("l" means "linked-by"), is developed by exploiting the dynamic reaction of *N*-carboxyethyl chitosan (CEC) and adipic acid dihydrazide (ADH) with oxidized sodium alginate (OSA). The self-healing ability, as demonstrated by rheological recovery, macroscopic observation, and beam-shaped strain compression measurement, is attributed to the coexistence of dynamic imine and acylhydrazone bonds in the hydrogel networks. The CEC-l-OSA-l-ADH hydrogel shows excellent self-healing ability under physiological conditions with a high healing efficiency (up to 95%) without need for any external stimuli. In addition, the CEC-l-OSA-l-ADH hydrogel exhibits good cytocompatibility and cell release as demonstrated by three-dimensional cell encapsulation. With these superior properties, the developed hydrogel holds great potential for applications in various biomedical fields, e.g., as cell or drug delivery carriers.

- A Stable, Reusable, and Highly Active Photosynthetic Bioreactor by Bio-Interfacing an Individual Cyanobacterium with a Mesoporous Bilayer Nanoshell
  Jiang, N.; Yang, X.-Y.; Deng, Z.; Wang, L.; Hu, Z.-Y.; Tian, G.; Ying, G.-L.; Shen, L.; Zhang, M.-X.; Su, B.-L. *Small* **2015**, *11*, 2003-2010.
  Abstract:



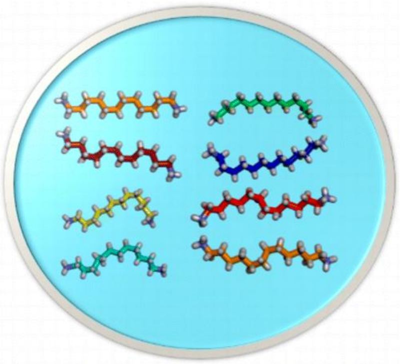
An individual cyanobacterium cell is interfaced with a nanoporous biohybrid layer within a mesoporous silica layer. The bio-interface acts as an egg membrane for cell protection and growth of outer shell. The resulting bilayer shell provides efficient functions to create a single cell photosynthetic bioreactor with high stability, reusability, and activity.

- Self-Assembled Monolayers Get Their Final Finish via a QuasiLangmuir–Blodgett Transfer
  Meltzer, C.; Dietrich, H.; Zahn, D.; Peukert, W.; Braunschweig, B. *Langmuir* **2015**, *31*, 4678-4685.
  Abstract:



The growth of self-assembled monolayers (SAMs) of octadecylphosphonic acid (ODPA) molecules on α-Al_2O_3(0001) and subsequent dewetting of the SAMs were studied with a combination of in situ sum-frequency generation (SFG) and molecular dynamics (MD) simulations. Although SAM growth after deposition times >8 h reduces to nearly negligible values, the resultant ODPA SAMs in solution are still not in a well-ordered state with the alkyl chains in all-trans configurations. In fact, in situ SFG spectroscopy revealed a comparatively high concentration of gauche defects of the SAM in the ODPA 2-propanol solution even after a growth time of 16 h. Here, results of the MD simulations strongly suggest that defects can be caused by ODPA molecules which are not attached to the substrate but are incorporated into the SAM layer with the polar headgroup oriented into the 2-propanol solvent. This inverted adsorption geometry of additional ODPA molecules blocks adsorption sites and thus stabilizes the SAM without improving ordering to an extent that all molecules are in the all-trans configuration. While persistent in solution, the observed defects can be healed out when the SAMs are transferred from the solvent to a gas phase. During this process, a quasi-Langmuir–Blodgett transfer of molecules takes place which drives the SAM into a higher conformational state and significantly improves its quality.

- New “Pyrene Box” Cages for Adaptive Guest Conformations
  Dumitrescu, D.; Dumitru, F.; Legrand, Y.-M.; Petit, E.; van der Lee, A.; Barboiu, M. *Org. Lett.* **2015**, *17*, 2178–2181.
  Abstract:

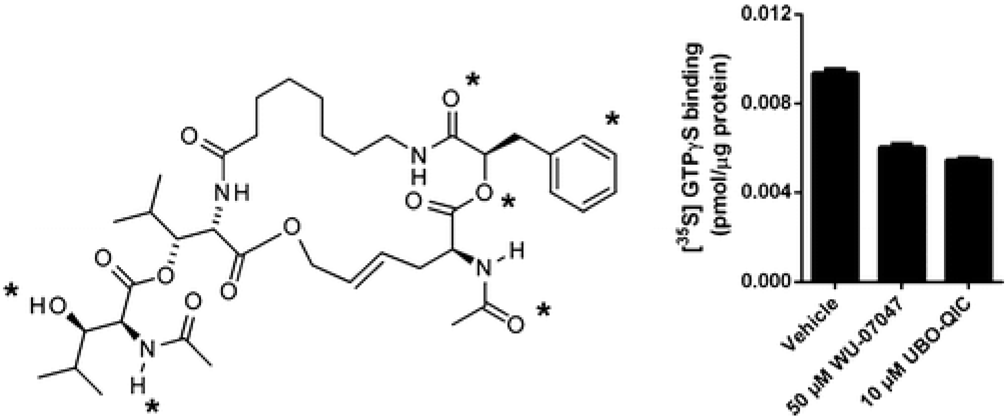


The possibility of controlling the compression extent and the coiling shape of the 1,12-diammoniumdodecane guest is shown by changing the dimensions of the internal space of the host guanidinium 1,3,5,8 pyrene-tetrasulfonate **PTS**$^{4-}$ crystalline capsules by using guanidinium (**G**$^{+}$), amino-guanidinium (**AG**$^{+}$), and diaminoguanidinium (**A$_2$G**$^{+}$) cations.

- Toward the Selective Inhibition of G Proteins: Total Synthesis of a Simplified YM-254890 Analog

  Rensing, D. T.; Uppal, S.; Blumer, K. J.; Moeller; K. D. *Org. Lett.* **2015**, *17*, 1918–1921.

  Abstract:

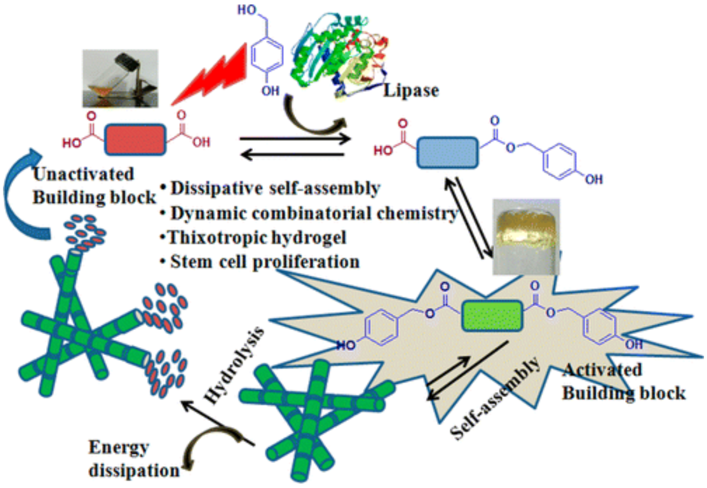


A simplified analog (WU-07047) of the selective Gαq/11 inhibitor YM-254890 has been synthesized, and an initial probe of its activity conducted. In the analog, the two peptide-based linkers in the cyclic YM-254890 have been replaced with hydrocarbon chains. This enables a convergent approach to the synthesis of the analog. Biochemical assays showed that while the simplified analog is not as potent as YM-254890, it does still inhibit Gq.

- Lipase-Catalyzed Dissipative Self-Assembly of a Thixotropic Peptide Bolaamphiphile Hydrogel for Human Umbilical Cord Stem-Cell Proliferation

  Das, K. A.; Maity, I.; Parmar, S. H.; McDonald, O. T.; Konda, M. *Biomacromolecules* **2015**, *16*, 1157–1168.

  Abstract:



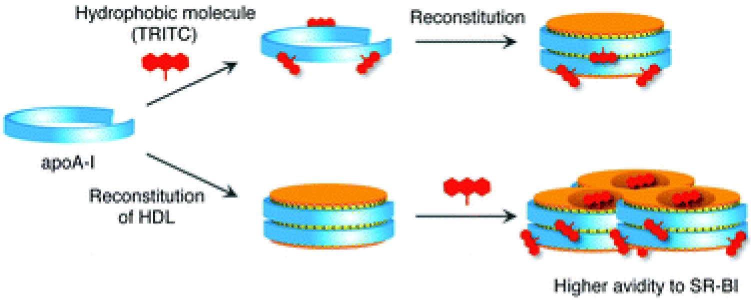
We report lipase-catalyzed inclusion of p-hydroxy benzylalcohol to peptide bolaamphiphiles. The lipase-catalyzed reactions of peptide bolaamphiphiles with p-hydroxy benzylalcohol generate dynamic combinatorial libraries (DCL) in aqueous medium that mimic the natural dissipative system.

The peptide bolaamphiphile 1 (HO-WY-Suc-YW–OH) reacts with p-hydroxy benzylalcohol in the presence of lipase forming an activated diester building block. The activated diester building block self-assembles to produce nanofibrillar thixotropic hydrogel. The subsequent hydrolysis results in the dissipation of energy to form nonassembling bolaamphiphile 1 with collapsed nanofibers. The thixotropic DCL hydrogel matrix is used for 3D cell culture experiments for different periods of time, significantly supporting the cell survival and proliferation of human umbilical cord mesenchymal stem cells.

- Structural and functional changes in high-density lipoprotein induced by chemical modification

  Murakami, T.; Okamotoa, H.; Kima, H. *Biomater. Sci.* **2015**, *3*, 712-715.

  Abstract:

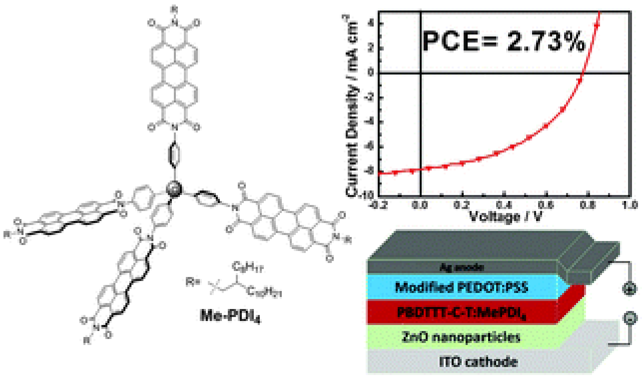


Reconstituted high-density lipoprotein (rHDL), a natural nanoparticle consisting of apolipoprotein A-I and phospholipids, was modified with a hydrophobic fluorescent dye before (pre-rHDL) and after (post-rHDL) reconstitution. Pre-rHDL particles had a similar size to unmodified rHDL, but post-rHDL particles were significantly larger and their avidity for a HDL receptor was 2.6 times of that shown by pre-rHDL.

- A perylene diimide (PDI)-based small molecule with tetrahedral configuration as a non-fullerene acceptor for organic solar cells

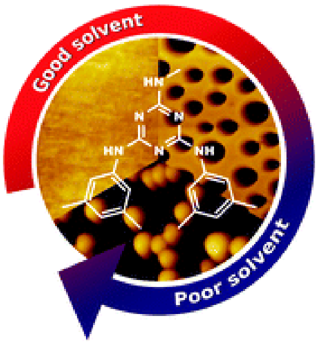
  Chen, W.; Yang, X.; Long, G.; Wan, X.; Chen, Y.; Zhang, Q. *J. Mater. Chem. C* **2015**, *3*, 4698-4705.

  Abstract:



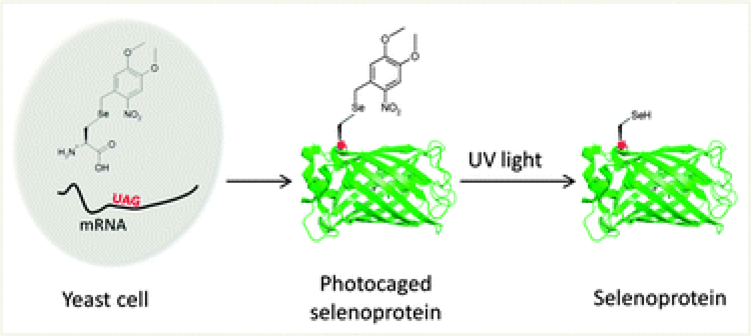
In this paper, a new perylene diimide (PDI)-based acceptor **Me-PDI$_4$** with tetrahedral configuration (or 3D) has been synthesized and characterized. Solution-processed organic solar cells (OSCs) based on **Me-PDI$_4$** have been investigated and our results show that the device performance can reach as high as 2.73%. Our new design with tetrahedral configuration (or 3D) could be an efficient approach to increase the PCE of OSCs with non-fullerene acceptors.

- Water-triggered spontaneous surface patterning in thin films of mexylaminotriazine molecular glasses
  Melito, E.; Laventure, A.; Aldea-Nunzi, G.; Pellerin, C.; Buncel, E.; Lebel, O.; Nunzi, J.-M., *J. Mater. Chem. C* **2015**, *3*, 4729-4736.
  Abstract:



Surface patterning that occurs spontaneously during the formation of a thin film is a powerful tool for controlling film morphology at the nanoscale level because it avoids the need for further processing. However, one must first learn under which conditions these patterning phenomena occur or not, and how to achieve control over the surface morphologies that are generated. Mexylaminotriazine-based molecular glasses are small molecules that can readily form amorphous thin films. It was discovered that this class of materials can either form smooth films, or films exhibiting either dome or pore patterns. Depending on the conditions, these patterns can be selectively obtained during film deposition by spin-coating. It was determined that this behavior is controlled by the presence of water or, more generally, of a solvent in which the compounds are insoluble, and that the relative amount and volatility of this poor solvent determines which type of surface relief is obtained. Moreover, AFM and FT-IR spectroscopy have revealed that the thin films are amorphous independently of surface morphology, and no difference was observed at the molecular or supramolecular level. These findings make this class of materials and this patterning approach in general extremely appealing for the control of surface morphology with organic nanostructures.

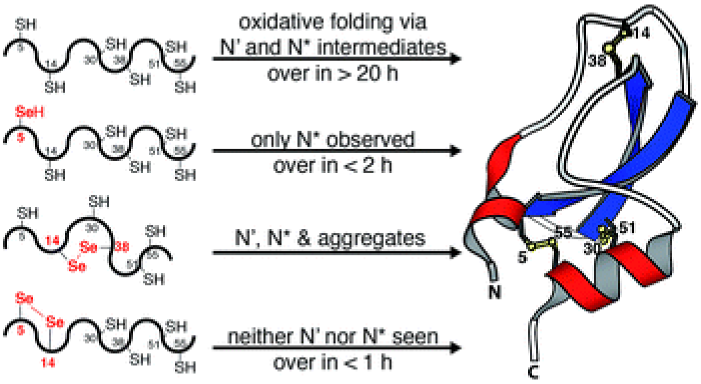
- Biosynthetic selenoproteins with genetically-encoded photocaged selenocysteines
  Rakauskaitė, R.; Urbanavičiūtė, G.; Rukšėnaitė, A.; Liutkevičiūtė, Z.; Juškėnas, R.; Masevičiusab, V.; Klimašauskas, S. *Chem. Commun.* **2015**, *51*, 8245-8248.
  Abstract:



Selenocysteine is a valuable component of both natural selenoproteins and designer biocatalysts; however the availability of such proteins is hampered by technical limitations. Here we report the

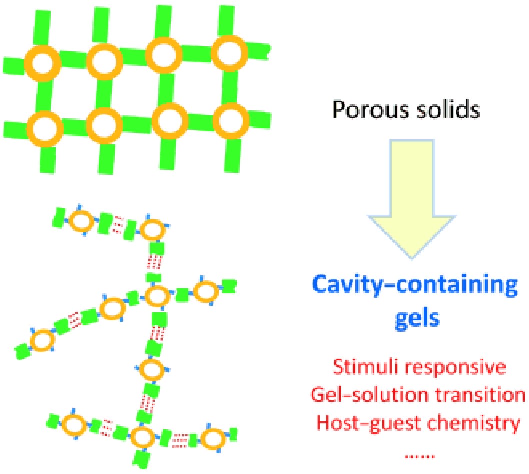
first general strategy for the production of selenoproteins via genetically-encoded incorporation of a synthetic photocaged selenocysteine residue in yeast cells, and provide examples of light-controlled protein dimerization and targeted covalent labeling *in vitro*.

- Harnessing selenocysteine reactivity for oxidative protein folding
  Metanis, N.; Hilvert, D. *Chem. Sci.* **2015**, *6*, 322-325.
  Abstract:



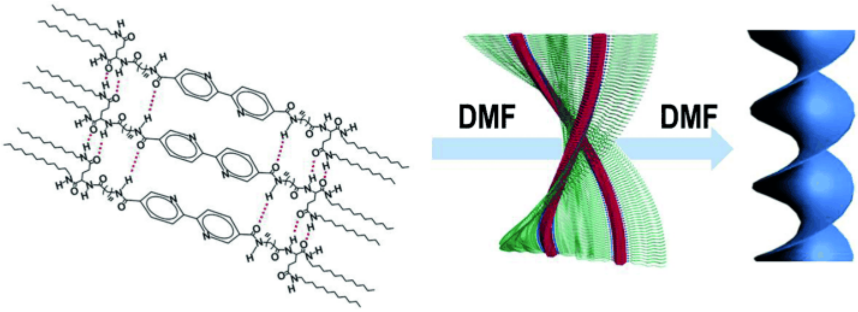
Although oxidative folding of disulfide-rich proteins is often sluggish, this process can be significantly enhanced by targeted replacement of cysteines with selenocysteines. In this study, we examined the effects of a selenosulfide and native versus nonnative diselenides on the folding rates and mechanism of bovine pancreatic trypsin inhibitor. Our results show that such sulfur-to-selenium substitutions alter the distribution of key folding intermediates and enhance their rates of interconversion in a context-dependent manner.

- Creating Coordination-Based Cavities in a Multiresponsive Supramolecular Gel
  Wei, S.-C.; Pan, M.; Fan, Y.-Z.; Liu, H.; Zhang, J.; Su, C.-Y. *Chem. Eur. J.* **2015**, *21*, 7418–7427.
  Abstract:



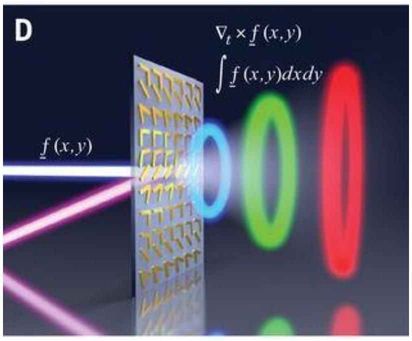
Creating cavities in varying levels, from molecular containers to macroscopic materials of porosity, have long been motivated for biomimetic or practical applications. Herein, we report an assembly approach to multiresponsive supramolecular gels by integrating photochromic metal–organic cages as predefined building units into the supramolecular gel skeleton, providing a new approach to create cavities in gels. Formation of discrete O-Pd_2L_4 cages is driven by coordination between Pd^{2+} and a photochromic dithienylethene bispyridine ligand (O-PyFDTE). In the presence of suitable solvents (DMSO or MeCN/DMSO), the O-Pd_2L_4 cage molecules aggregate to form nanoparticles, which are further interconnected through supramolecular interactions to form a three-dimensional (3D) gel matrix to trap a large amount of solvent molecules. Light-induced phase and structural transformations readily occur owing to the reversible photochromic open-ring/closed-ring isomeric conversion of the cage units upon UV/visible light radiation. Furthermore, such Pd_2L_4 cage-based gels show multiple reversible gel–solution transitions when thermal-, photo-, or mechanical stimuli are applied. Such supramolecular gels consisting of porous molecules may be developed as a new type of porous materials with different features from porous solids.

- Multiple-Stimulus-Responsive Supramolecular Gels and Regulation of Chiral Twists: The Effect of Spacer Length
  Miao, W.; Yang, D.; Liu, M. *Chem. Eur. J.* **2015**, *21*, 7562–7570.
  Abstract:



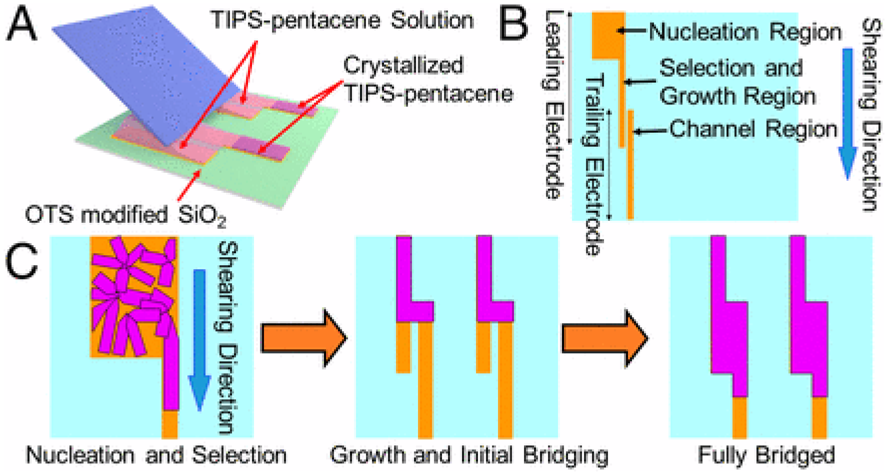
A new class of homologous gelators, LG_{12}-$(CH_2)_n$-BSA, composed of bipyridinyl groups, L-glutamic moieties having double dodecyl chains, and linked alkyl spacers with different lengths were synthesized. It was found that these gelators could immobilize medium-polarity solvents readily and the behaviors of these gels showed a dependence on the spacer length. Of all the gels, the LG_{12}-$(CH_2)_{11}$-BSA gels exhibited self-healing property and multiple-stimulus responsibility, such as heating, shaking, and sonication. The investigation of CD spectra indicated that the supramolecular chirality, which was attributed to the chiral transfer from the chiral center to the assemblies, was also closely related to the length of methylene spacers. The longer the alkyl spacers, the weaker the transmitted supramolecular chirality. Only LG_{12}-$(CH_2)_1$-BSA gelators, which had the shortest spacers, formed right-handed nanoscale chiral twists owing to crowded hydrogen bonding interactions. Moreover, the high-polarity solvent DMF was found to be able to regulate the chiral twist as well as its pitch length readily.

- Nanophotonics: Shrinking light-based technology
  Koenderink, A. F.; Alù, A.; Polman, A. *Science* **2015**, *348*, 516-521.
  Abstract:



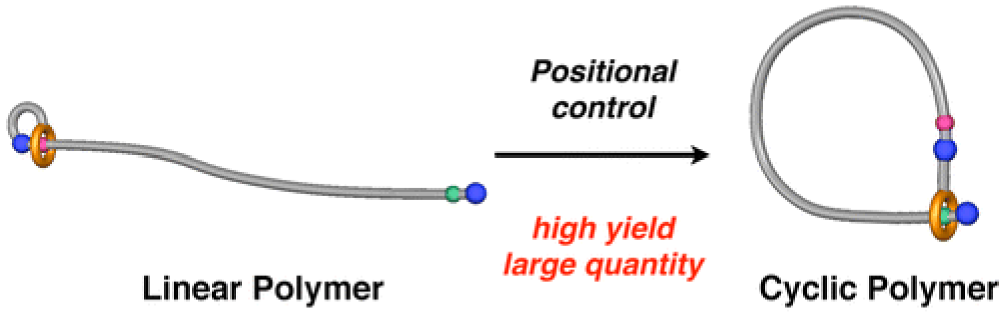
The study of light at the nanoscale has become a vibrant field of research, as researchers now master the flow of light at length scales far below the optical wavelength, largely surpassing the classical limits imposed by diffraction. Using metallic and dielectric nanostructures precisely sculpted into two-dimensional (2D) and 3D nanoarchitectures, light can be scattered, refracted, confined, filtered, and processed in fascinating new ways that are impossible to achieve with natural materials and in conventional geometries. This control over light at the nanoscale has not only unveiled a plethora of new phenomena but has also led to a variety of relevant applications, including new venues for integrated circuitry, optical computing, solar, and medical technologies, setting high expectations for many novel discoveries in the years to come.

- Large-area formation of self-aligned crystalline domains of organic semiconductors on transistor channels using CONNECT
  Park, S.; Giri, G.; Shaw, L.; Pitner, G.; Ha, J.; Koo, J. H.; Gu, X.; Park, J.; Lee, T. H.; Nam, J. H.; Hong, Y.; Bao, Z. *Proc. Nat. Acad. Sci. USA* **2015**, *112*, 5561-5566.
  Abstract:



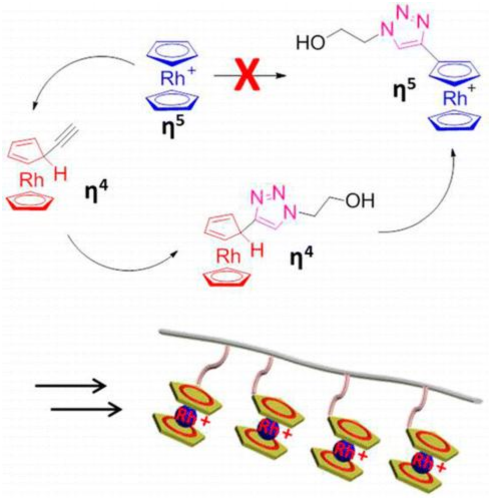
The electronic properties of solution-processable small-molecule organic semiconductors (OSCs) have rapidly improved in recent years, rendering them highly promising for various low-cost large-area electronic applications. However, practical applications of organic electronics require patterned and precisely registered OSC films within the transistor channel region with uniform electrical properties over a large area, a task that remains a significantchallenge. Here, we present a technique termed “controlled OSC nucleation and extension for circuits” (CONNECT), which uses differential surface energy and solution shearing to simultaneously generate patterned and precisely registered OSC thin films within the channel region and with aligned crystalline domains, resulting in low device-to-device variability. We have fabricated transistor density as high as 840 dpi, with a yield of 99%. We have successfully built various logic gates and a 2-bit half-adder circuit, demonstrating the practical applicability of our technique for large-scale circuit fabrication.

- Effective Approach to Cyclic Polymer from Linear Polymer: Synthesis and Transformation of Macromolecular [1]Rotaxane
  Ogawa, T.; Nakazono, K.; Aoki, D.; Uchida, S.; Takata, T. *ACS Macro Lett.* **2015**, *4*, 343-347.
  Abstract:



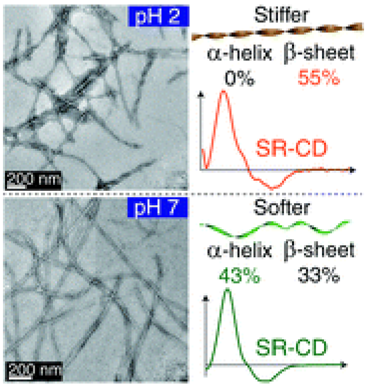
We report a convenient and scalable synthesis of cyclic poly(ε-caprolactone) (PCL) from its linear counterpart based on the rotaxane protocol. Cyclic PCL was prepared by ring-opening polymerization of ε-caprolactone (ε-CL) initiated by a pseudo[2]rotaxane initiator in the presence of diphenylphosphate (DPP) as a catalyst, followed by capping of the propagation end by using a bulky isocyanate to afford macromolecular [2]rotaxane. The successive intramolecular cyclization to macromolecular [1]rotaxane at the polymer terminus proceeded with good yield. The attractive interaction of the terminal ammonium/crown ether moiety was removed via N-acetylation. This enabled movement of the crown ether wheel along the axle PCL chain to the urethane region of the other terminus in solution state. Size-exclusion chromatography and 2D diffusion-ordered spectroscopy (DOSY) results demonstrated the formation of cyclic PCL from linear PCL, which is further supported by thermal property or crystallinity change before and after transformation.

- Syntheses of Monosubstituted Rhodocenium Derivatives, Monomers, and Polymers
  Yan, Y.; Deaton, T. M.; Zhang, J.; He, H.; Hayat, J.; Pageni, P.; Matyjaszewski, K.; Tang, C. *Macromolecules* **2015**, *48*, 1644–1650.
  Abstract:



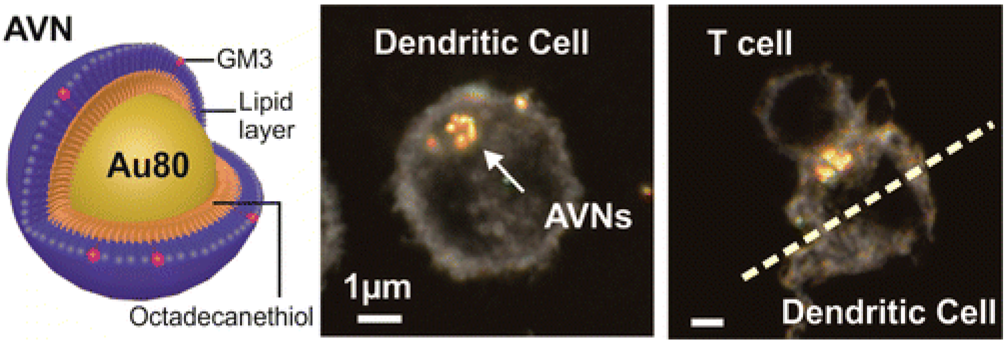
We report the first chemoselective, high yield synthesis of monosubstituted rhodocenium through a "$\eta^5 \rightarrow \eta^4 \rightarrow \eta^5$" strategy detailing sequential nucleophilic addition and endohydride abstraction. Monosubstituted rhodocenium derivatives are then used as versatile synthons for the preparation of the first-ever vinyl monomers that allow controlled polymerizations including ROMP and RAFT, leading to rhodocenium-containing metallopolymers. Exploratory ion-exchange and self-assembly of this new class of polyelectrolytes cultivates the potential of side-chain rhodocenium-containing polymers.

- Mechanical properties of amyloid-like fibrils defined by secondary structures
  Bortolini, C.; Jones, N. C.; Hoffmann, S. V.; Wang, C.; Besenbacher, F.; Dong, M. *Nanoscale* **2015**, *7*, 7745 – 7752.
  Abstract:



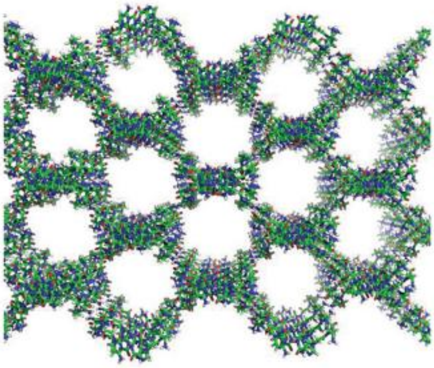
Amyloid and amyloid-like fibrils represent a generic class of highly ordered nanostructures that are implicated in some of the most fatal neurodegenerative diseases. On the other hand, amyloids, by possessing outstanding mechanical robustness, have also been successfully employed as functional biomaterials. For these reasons, physical and chemical factors driving fibril self-assembly and morphology are extensively studied – among these parameters, the secondary structures and the pH have been revealed to be crucial, since a variation in pH changes the fibril morphology and net chirality during protein aggregation. It is important to quantify the mechanical properties of these fibrils in order to help the design of effective strategies for treating diseases related to the presence of amyloid fibrils. In this work, we show that by changing pH the mechanical properties of amyloid-like fibrils vary as well. In particular, we reveal that these mechanical properties are strongly related to the content of secondary structures. We analysed and estimated the Young's modulus (E) by comparing the persistence length (Lp) – measured from the observation of TEM images by using statistical mechanics arguments – with the mechanical information provided by peak force quantitative nanomechanical property mapping (PF-QNM). The secondary structure content and the chirality are investigated by means of synchrotron radiation circular dichroism (SR-CD). Results arising from this study could be fruitfully used as a protocol to investigate other medical or engineering relevant peptide fibrils.

- Dressing up Nanoparticles: A Membrane Wrap to Induce Formation of the Virological Synapse
  Yu, X.; Xu, F.; Ramirez, N.-G. P.; Kijewski, S. D. G.; Akiyama, H.; Gummuluru, S.; Reinhard, B. M. *ACS Nano* **2015**, *9*, 4182 – 4192.
  Abstract:



Next-generation nanoparticle-based drug delivery systems require the ability to target specific organelles or subcellular regions in selected target cells. Human immunodeficiency virus type I (HIV-1) particles are evolutionarily optimized nanocarriers that have evolved to avoid intracellular degradation and achieve enrichment at the synapse between mature dendritic cells (mDCs) and T cells by subverting cellular trafficking mechanisms. This study demonstrates that integration of the glycosphingolipid, GM3, in a membrane around a solid nanoparticle (NP) core is sufficient to recapitulate key aspects of the virus particle trafficking in mDCs. GM3-presenting artificial virus NPs (GM3-AVNs) accumulate in $CD169^+$ and $CD81^+$ nonlysosomal compartments in an actin-dependent process that mimics the sequestration of HIV-1. Live-cell optical tracking studies reveal a preferential recruitment and arrest of surface scanning $CD4^+$ T cells in direct vicinity to the AVN-enriched compartments. The formed mDC–T cell conjugates exhibit strong morphological similarities between the GM3-AVN-containing mDC–T cell synapse and the HIV-1 virological synapse, indicating that GM3–CD169 interactions alone are sufficient for establishing the mDC–T cell virological synapse. These results emphasize the potential of the GM3-AVN approach for providing therapeutic access to a key step of the host immune response—formation of the synaptic junction between an antigen-presenting cell (mDC) and T cells—for modulating and controlling immune responses.

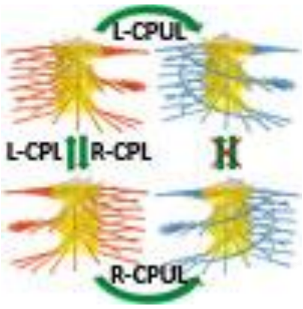
- Light-emitting self-assembled peptide nucleic acids exhibit both stacking interactions and Watson–Crick base pairing
  Berger, O.; Adler-Abramovich, L.; Levy-Sakin, M.; Grunwald, A.; Liebes-Peer, Y.; Bachar, M.; Buzhansky, L.; Mossou, E.; Forsyth, V. T.; Schwartz, T.; Ebenstein, Y.; Frolow, F.; Shimon, L. J. W.; Patolsky, F.; Gazit, E. *Nature Nanotech.* **2015**, *10*, 353-360.
  Abstract:



The two main branches of bionanotechnology involve the self-assembly of either peptides or DNA. Peptide scaffolds offer chemical versatility, architectural flexibility and structural complexity, but they lack the precise base pairing and molecular recognition available with nucleic acid assemblies. Here, inspired by the ability of aromatic dipeptides to form ordered nanostructures with unique physical properties, we explore the assembly of peptide nucleic acids (PNAs), which are short DNA mimics that have an amide backbone. All 16 combinations of the very short di-PNA building blocks were synthesized and assayed for their ability to self-associate. Only three guanine-containing di-PNAs—CG, GC and GG—could form ordered assemblies, as observed by electron microscopy, and these di-PNAs efficiently assembled into discrete architectures within a few minutes. The X-ray crystal structure of the GC di-PNA showed the occurrence of both stacking interactions and Watson–Crick base pairing. The assemblies were also found to exhibit optical properties including voltage-

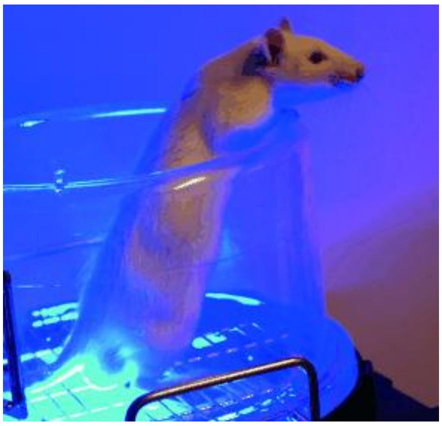
dependent electroluminescence and wide-range excitation-dependent fluorescence in the visible region.

- Induction and control of supramolecular chirality by light in self-assembled helical nanostructures
  Kim, J.; Lee, J.; Kim, W. Y.; Kim, H.;S.; Lee, H. C.; Lee, Y. S.; Seo, M.; Kim, S. Y. *Nature Comm.* **2015**, *6*, 6959.
  Abstract:



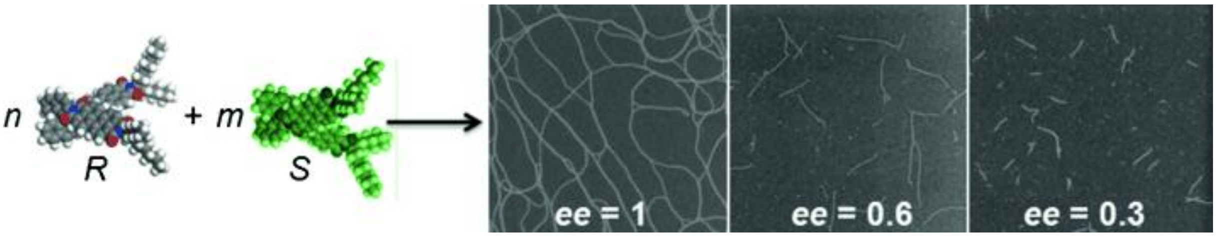
Evolution of supramolecular chirality from self-assembly of achiral compounds and control over its handedness is closely related to the evolution of life and development of supramolecular materials with desired handedness. Here we report a system where the entire process of induction, control and locking of supramolecular chirality can be manipulated by light. Combination of triphenylamine and diacetylene moieties in the molecular structure allows photoinduced self-assembly of the molecule into helical aggregates in a chlorinated solvent by visible light and covalent fixation of the aggregate via photopolymerization by ultraviolet light, respectively. By using visible circularly polarized light, the supramolecular chirality of the resulting aggregates is selectively and reversibly controlled by its rotational direction, and the desired supramolecular chirality can be arrested by irradiation with ultraviolet circularly polarized light. This methodology opens a route to ward the formation of supramolecular chiral conducting nanostructures from the self-assembly of achiral molecules.

- A Synthetic Erectile Optogenetic Stimulator Enabling Blue-Light-Inducible Penile Erection
  Kim, T.; Folcher, M.; Baba, M. D.-E.; Fussenegger, M. *Angew.Chem. Int. Ed.* **2015**, 54, 5933 – 5938.
  Abstract:



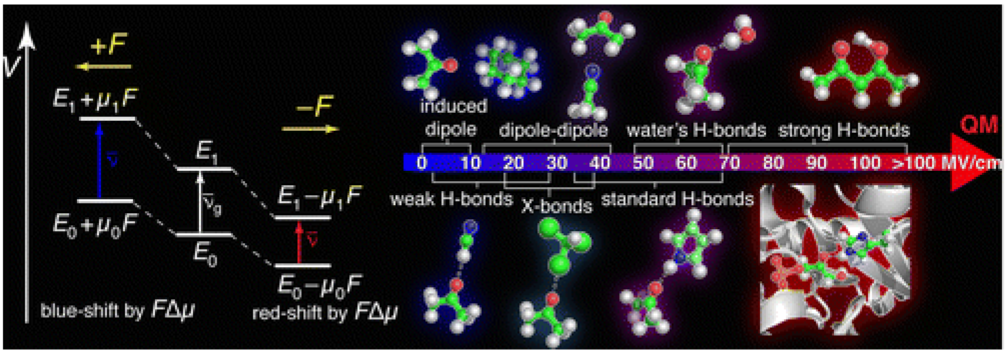
Precise spatiotemporal control of physiological processes by optogenetic devices inspired by synthetic biology may provide novel treatment opportunities for gene- and cell-based therapies. An erectile optogenetic stimulator (EROS), a synthetic designer guanylate cyclase producing a blue-light-inducible surge of the second messenger cyclic guanosine monophosphate (cGMP) in mammalian cells, enabled blue-light-dependent penile erection associated with occasional ejaculation after illumination of EROS-transfected corpus cavernosum in male rats. Photostimulated short-circuiting of complex psychological, neural, vascular, and endocrine factors to stimulate penile erection in the absence of sexual arousal may foster novel advances in the treatment of erectile dysfunction.

- Self-Discriminating Termination of Chiral Supramolecular Polymerization: Tuning the Length of Nanofibers
  Kumar, J.; Tsumatori, H.; Yuasa, J.; Kawai, T.; Nakashima, T. *Angew.Chem.Int. Ed*. **2015**, 54, 5943 –5947.
  Abstract:



Directing the supramolecular polymerization towards a preferred type of organization is extremely important in the design of functional soft materials. Proposed herein is a simple methodology to tune the length and optical chirality of supramolecular polymers formed from a chiral bichromophoric binaphthalene by the control of enantiomeric excess (*ee*). The enantiopure compound gave thin fibers longer than a few microns, while the racemic mixture favored the formation of nanoparticles. The thermodynamic study unveils that the heterochiral assembly gets preference over the homochiral assembly. The stronger heterochiral binding over homochiral one terminated the elongation of fibrous assembly, thus leading to a control over the length of fibers in the nonracemic mixtures. The supramolecular polymerization driven by π–π interactions highlights the effect of the geometry of a twisted π-core on this self-sorting assembly.

- Measuring Electric Fields and Noncovalent Interactions Using the Vibrational Stark Effect
  Fried, S. D.; Boxer, S. G. *Acc. Chem. Res.* **2015**, *48*, 998-1006.
  Abstract:

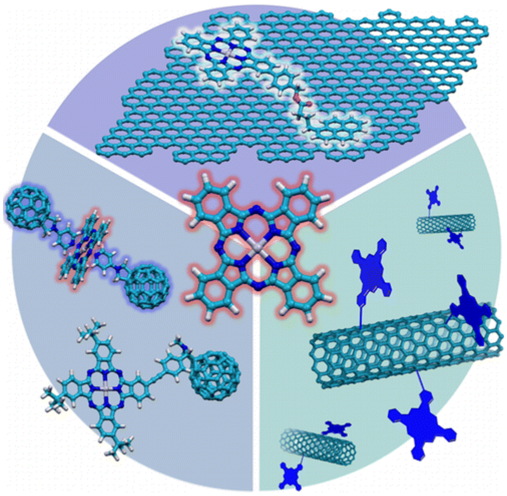


Over the past decade, we have developed a spectroscopic approach to measure electric fields inside matter with high spatial (<1 Å) and field (<1 MV/cm) resolution. The approach hinges on exploiting a physical phenomenon known as the vibrational Stark effect (VSE), which ultimately provides a direct mapping between observed vibrational frequencies and electric fields. Therefore, the frequency of a vibrational probe encodes information about the local electric field in the vicinity around the probe. The VSE method has enabled us to understand in great detail the underlying physical nature of several important biomolecular phenomena, such as drug–receptor selectivity in tyrosine kinases, catalysis by the enzyme ketosteroid isomerase, and unidirectional electron transfer in the photosynthetic reaction center. Beyond these specific examples, the VSE has provided a conceptual foundation for how to model *intermolecular* (noncovalent) interactions in a quantitative, consistent, and general manner.

The starting point for research in this area is to choose (or design) a vibrational probe to interrogate the particular system of interest. Vibrational probes are sometimes intrinsic to the system in question, but we have also devised ways to build them into the system (extrinsic probes), often with minimal perturbation. With modern instruments, vibrational frequencies can increasingly be recorded with very high spatial, temporal, and frequency resolution, affording electric field maps correspondingly resolved in space, time, and field magnitude.

In this Account, we set out to explain the VSE in broad strokes to make its relevance accessible to chemists of all specialties. Our intention is not to provide an encyclopedic review of published work but rather to motivate the underlying framework of the methodology and to describe how we make and interpret the measurements. Using certain vibrational probes, benchmarked against computer models, it is possible to use the VSE to measure *absolute* electric fields in arbitrary environments. The VSE approach provides an organizing framework for thinking generally about intermolecular interactions in a quantitative way and may serve as a useful conceptual tool for molecular design.

- Phthalocyanine–Nanocarbon Ensembles: From Discrete Molecular and Supramolecular Systems to Hybrid Nanomaterials
  Bottari, G.; de la Torre, G.; Torres, T. *Acc. Chem. Res.* **2015**, *48*, 900-910.
  Abstract:



Phthalocyanines (Pcs) are macrocyclic and aromatic compounds that present unique electronic features such as high molar absorption coefficients, rich redox chemistry, and photoinduced energy/electron transfer abilities that can be modulated as a function of the electronic character of their counterparts in donor–acceptor (D–A) ensembles. In this context, carbon nanostructures such as fullerenes, carbon nanotubes (CNTs), and, more recently, graphene are among the most suitable Pc “companions”. Pc–C_{60} ensembles have been for a long time the main actors in this field, due to the commercial availability of C_{60} and the well-established synthetic methods for its functionalization. As a result, many Pc–C_{60} architectures have been prepared, featuring different connectivities (covalent or supramolecular), intermolecular interactions (self-organized or molecularly dispersed species), and Pc HOMO/LUMO levels. All these elements provide a versatile toolbox for tuning the photophysical properties in terms of the type of process (photoinduced energy/electron transfer), the nature of the interactions between the electroactive units (through bond or space), and the kinetics of the formation/decay of the photogenerated species. Some recent trends in this field include the preparation of stimuli-responsive multicomponent systems with tunable photophysical properties and highly ordered nanoarchitectures and surface-supported systems showing high charge mobilities. A breakthrough in the Pc–nanocarbon field was the appearance of CNTs and graphene, which opened a new avenue for the preparation of intriguing photoresponsive hybrid ensembles showing light-stimulated charge separation. The scarce solubility of these 1-D and 2-D nanocarbons, together with their lower reactivity with respect to C_{60} stemming from their less strained sp^2 carbon networks, has not meant an unsurmountable limitation for the preparation of variety of Pc-based hybrids. These systems, which show improved solubility and dispersibility features, bring together the unique electronic transport properties of CNTs and graphene with the excellent light-harvesting and tunable redox properties of Pcs. A singular and distinctive feature of these Pc–CNT/graphene (single- or few-layers) hybrid materials is the control of the direction of the photoinduced charge transfer as a result of the band-like electronic structure of these carbon nanoforms and the adjustable electronic levels of Pcs. Moreover, these conjugates present intensified light-harvesting capabilities resulting from the grafting of several chromophores on the same nanocarbon platform.

In this Account, recent progress in the construction of covalent and supramolecular Pc–nanocarbon ensembles is summarized, with a particular emphasis on their photoinduced behavior. We believe that the high degree of control achieved in the preparation of Pc–carbon nanostructures, together with the increasing knowledge of the factors governing their photophysics, will allow for the design of next-generation light-fueled electroactive systems. Possible implementation of these Pc–nanocarbons in high performance devices is envisioned, finally turning into reality much of the expectations generated by these materials.