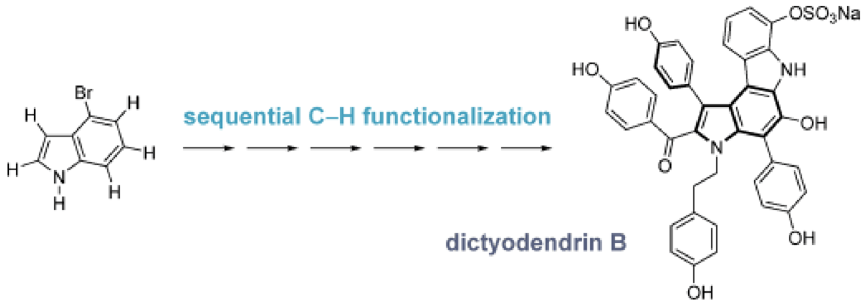
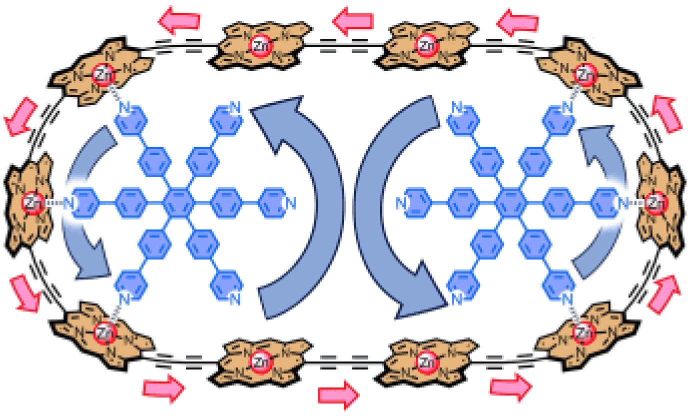
- A Concise and Scalable Strategy for the Total Synthesis of Dictyodendrin B Based on Sequential C-H Functionalization
  Pitts, A. K.; O'Hara, F.; Snell, R. H.; Gaunt, M. J. *Angew.Chem. Int. Ed.* **2015**, *54*, 5451 –5455.
  Abstract:



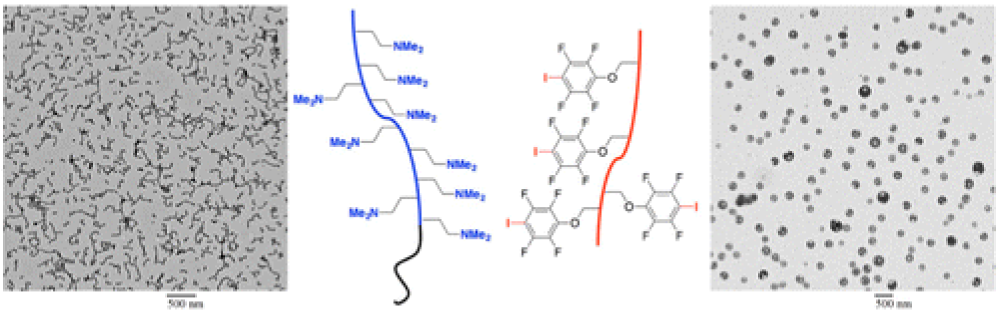
One by one: A sequential C[BOND]H functionalization strategy for the synthesis of the marine alkaloid dictyodendrin B is reported. The synthetic route begins from commercially available 4-bromoindole and involves six direct functionalizations around the heteroarene core as part of a gram-scale strategy towards the natural product.

- Caterpillar Track Complexes in Template-Directed Synthesis and Correlated Molecular Motion
  Liu, S.; Kondratuk, D. V.; Rousseaux, S. A. L.; Gil-Ramírez, G.; O'Sullivan, M. C.; Cremers, J.; Claridge, T. D. W.; Anderson, H. L. *Angew.Chem.Int. Ed*. **2015**, *54*, 5355 –5359.
  Abstract:



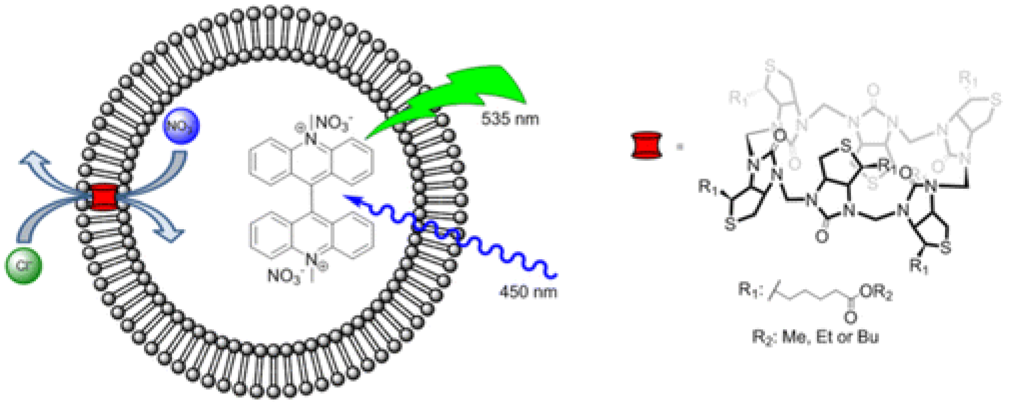
Turning in unison: Two wheel-like templates work together to direct the synthesis of a nanoring. Their rotation is synchronized in the resulting 2:1 caterpillar track complex.

- Solution-Phase Self-Assembly of Complementary Halogen Bonding Polymers
  Vanderkooy, A.; Taylor, M. S. *J. Am. Chem. Soc.* **2015**, *137*, 5080–5086.
  Abstract:



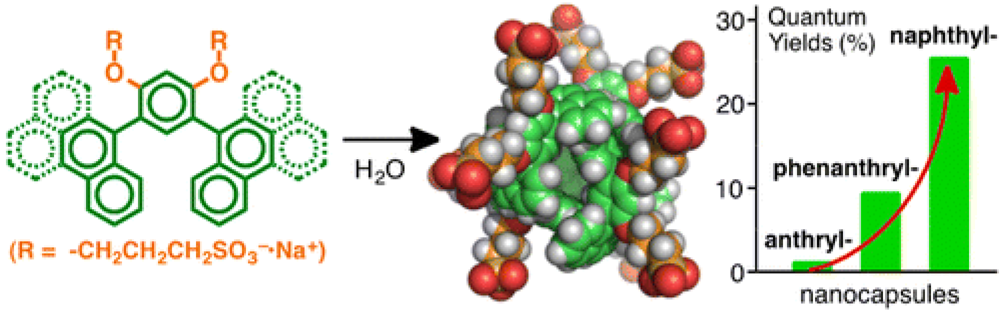
Noncovalent halogen bonding interactions are explored as a driving force for solution phase macromolecular self-assembly. Conditions for controlled radical polymerization of an iodoperfluoroarene-bearing methacrylate halogen bond donor were identified. An increase in association constant relative to monomeric species was observed for the interaction between halogen bond donor and acceptor polymers in solution. When the polymeric donor was combined with a block copolymer bearing halogen bond-accepting amine groups, higher-order structures were obtained in both organic solvent and in water. Transmission electron microscopy, dynamic light scattering and nuclear magnetic resonance spectroscopic data are consistent with structures having cores composed of the interacting halogen bond donor and acceptor segments.

- Biotin[6]uril Esters: Chloride-Selective Transmembrane Anion Carriers Employing C—H•••Anion Interactions
  Lisbjerg, M.; Valkenier, H.; Jessen, B. M.; Al-Kerdi, H.; Davis, A. P.; Pittelkow, M. *J. Am. Chem. Soc.* **2015**, *137*, 4948–4951.
  Abstract:



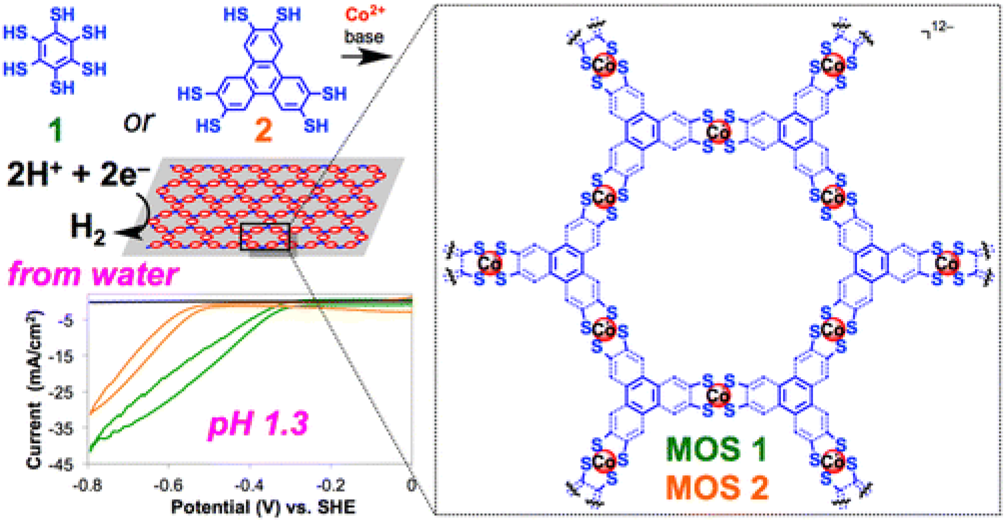
Biotin[6]uril hexaesters represent a new class of anionophores which operate solely through C—H···anion interactions. The use of soft H-bond donors favors the transport of less hydrophilic anions (e.g., Cl$^-$, NO$_3^-$) over hard, stongly hydrated anions (e.g., HCO$_3^-$ and SO$_4^{2-}$). Especially relevant is the selectivity between chloride and bicarbonate, the major inorganic anions in biological systems.

- Polyaromatic Nanocapsules Displaying Aggregation-Induced Enhanced Emissions in Water
  Okazawa, Y.; Kondo, K.; Akita, M.; Yoshizawa, M. *J. Am. Chem. Soc.* **2015**, *137*, 98-101.
  Abstract:



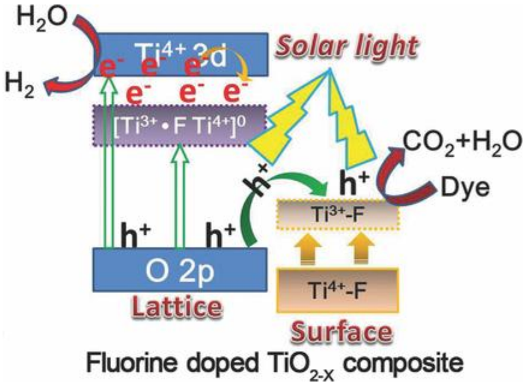
V-shaped polyaromatic amphiphiles with phenanthrene or naphthalene rings spontaneously and quantitatively formed micelle-like nanocapsules in water at room temperature. In contrast to usual polyaromatic aggregates with weak fluorescent properties, the new capsules providing spherical polyaromatic shells with diameters of ~2 nm show strong fluorescent emissions due to an aggregation-induced enhanced emission (AIEE) effect and moreover encapsulate a fluorescent coumarin dye to generate highly emissive host–guest composites.

- [Two-Dimensional Metal-Organic Surfaces for Efficient Hydrogen Evolution from Water]
  Clough, A. J.; Yoo, J. W.; Mecklenburg, M. H.; Marinescu, S. C. *J. Am. Chem. Soc.* **2015**, *137*, 118-121.
  Abstract:



Hydrogen production through the reduction of water has emerged as an important strategy for the storage of renewable energy in chemical bonds. One attractive scenario for the construction of efficient devices for electrochemical splitting of water requires the attachment of stable and active hydrogen evolving catalysts to electrode surfaces, which remains a significant challenge. We demonstrate here the successful integration of cobalt dithiolene catalysts into a metal–organic surface to generate very active electrocatalytic cathode materials for hydrogen generation from water. These surfaces display high catalyst loadings and remarkable stability even under very acidic aqueous solutions.

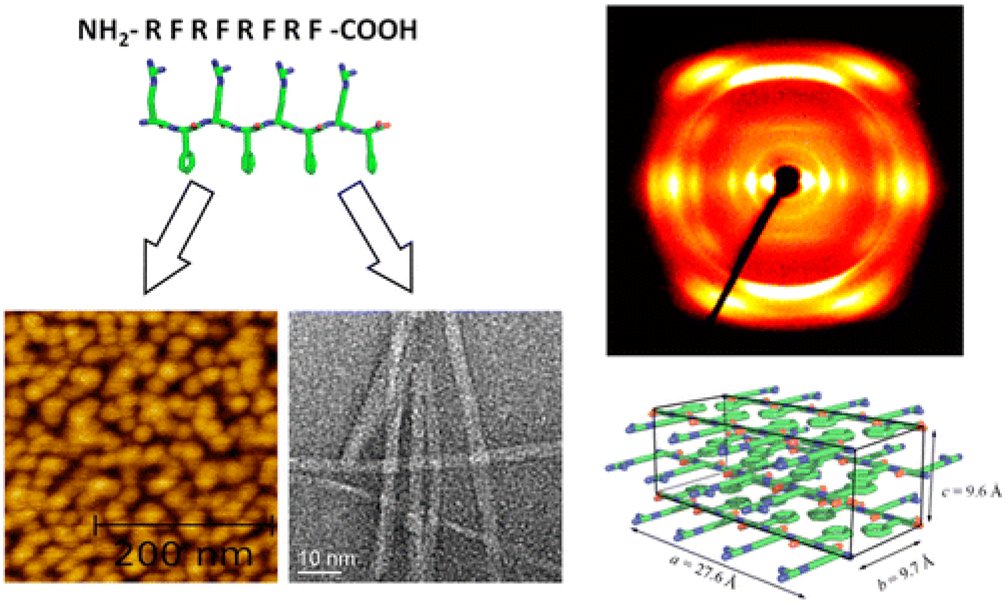
- [A Brown Mesoporous TiO_{2-x}/MCF Composite with an Extremely High Quantum Yield of Solar Energy Photocatalysis for H_2 Evolution]
  Xing, M.; Zhang, J.; Qiu, B.; Tian, B.; Anpo, M.; Che, M. *Small* **2015**, *11*, 1920-1929.
  Abstract:



A brown mesoporous TiO_{2-x}/MCF composite with a high fluorine dopant concentration (8.01 at%) is synthesized by a vacuum activation method. It exhibits an excellent solar absorption and a record-breaking quantum yield (Φ = 46%) and a high photon–hydrogen energy conversion efficiency (η =

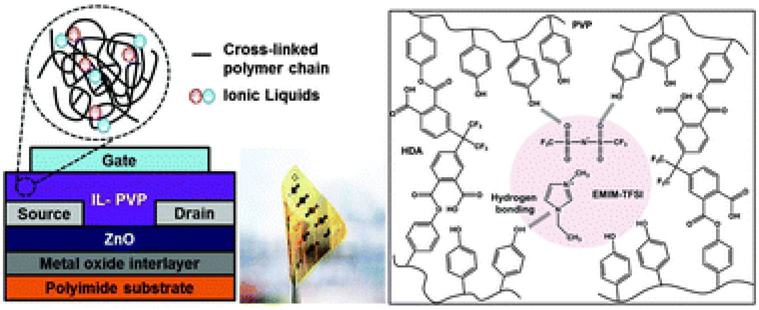
34%,) for solar photocatalytic H_2 production, which are all higher than that of the black hydrogen-doped TiO_2 (Φ = 35%, η = 24%). The MCFs serve to improve the adsorption of F atoms onto the TiO_2/MCF composite surface, which after the formation of oxygen vacancies by vacuum activation, facilitate the abundant substitution of these vacancies with F atoms. The decrease of recombination sites induced by high-concentration F doping and the synergistic effect between lattice Ti^{3+}–F and surface Ti^{3+}–F are responsible for the enhanced lifetime of electrons, the observed excellent absorption of solar light, and the photocatalytic production of H_2 for these catalysts. The as-prepared F-doped composite is an ideal solar light-driven photocatalyst with great potential for applications ranging from the remediation of environmental pollution to the harnessing of solar energy for H_2 production.

- Self-Assembly of a Designed Alternating Arginine/Phenylalanine Oligopeptide
  Decandio, C. C.; Silva, E. R.; Hamley, I. W.; Castelletto, V.; Liberato, M. S.; Oliveira, Jr., V. X.; Oliveira, C. L. P.; Alves, W. A. *Langmuir* **2015**, *31*, 4513–4523.
  Abstract:



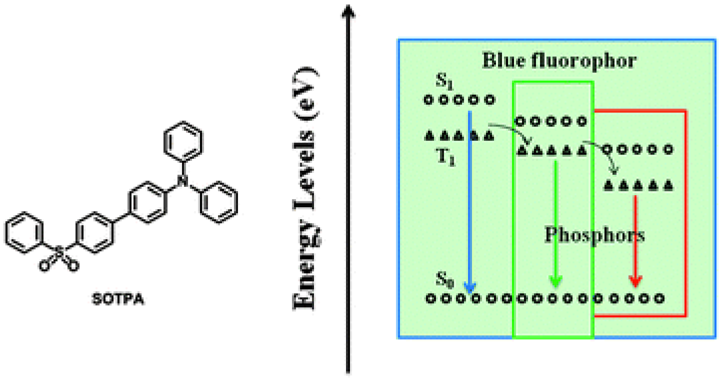
A model octapeptide peptide consisting of an alternating sequence of arginine (Arg) and phenylalanine (Phe) residues, namely, $[Arg\text{-}Phe]_4$, was prepared, and its self-assembly in solution studied. The simple alternating $[Arg\text{-}Phe]_4$ peptide sequence allows for unique insights into the aggregation process and the structure of the self-assembled motifs. Fluorescence and UV–vis assays were used to determine critical aggregation concentrations, corresponding to the formation of oligomeric species and β-sheet rich structures organized into both spheroidal aggregates and highly ordered fibrils. Electron and atomic force microscopy images show globular aggregates and long unbranched fibers with diameters ranging from ∼4 nm up to ∼40 nm. Infrared and circular dichroism spectroscopy show the formation of β-sheet structures. X-ray diffraction on oriented stalks show that the peptide fibers have an internal lamellar structure, with an orthorhombic unit cell with parameters $a \sim 27.6$ Å, $b \sim 9.7$ Å, and $c \sim 9.6$ Å. In situ small-angle X-ray scattering (SAXS) shows the presence of low molecular weight oligomers in equilibrium with mature fibers which are likely made up from 5 or 6 intertwined protofilaments. Finally, weak gel solutions are probed under gentle shear, suggesting the ability of these arginine-rich fibers to form networks.

- A robust ionic liquid-polymer gate insulator for high-performance flexible thin film transistors
  Ko, J.; Lee, S. J.; Kim, K.; Lee, E.; Lim, K.-H.; Myoung, J.-M.; Yoo, J.; Kim, Y. S. *J. Mater. Chem. C* **2015**, *3*, 4239-4243.
  Abstract:



Herein, we propose an ionic liquid–polymer dielectric layer for flexible electronics reinforced by a chemical interaction between the polymer matrix (PVP) and the ionic liquid. Due to the robust structures of the cross-linked PVP matrix and hydrogen bonding between the ionic liquid and PVP, the ionic liquid–PVP (IL–PVP) layer exhibited a good mechanical strength when bending up to 1000 times and a stable thermal behaviour up to 300 °C. Furthermore, the IL–PVP dielectric layer showed a high capacitance value of ∼2 μF cm^{-2} and was operated well as a gate insulator for flexible ZnO thin film transistors with a linear field-effect mobility of ∼3.3 cm^{2} V^{-1} s^{-1} at a gate bias of 3 V.

- A high-efficiency hybrid white organic light-emitting diode enabled by a new blue fluorophor
  Chen, Z.; Liu, X.-K.; Zheng, C.-J.; Ye, J.; Li, X.-Y.; Li, F.; Ou, X.-M.; Zhang, X.-H. *J. Mater. Chem. C* **2015**, *3*, 4283-4289.
  Abstract:

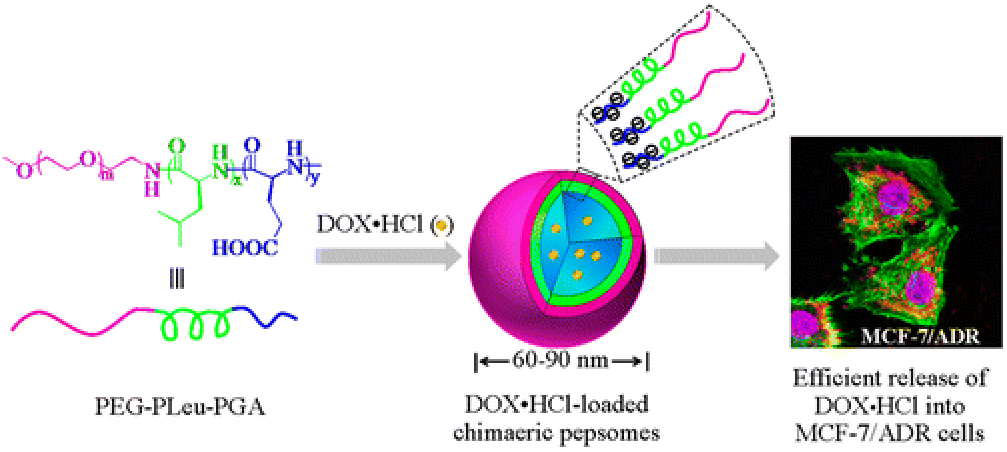


A new efficient blue fluorophor 4-(4-diphenylaminophenyl)diphenylsulfone (SOTPA), with high triplet energy and balanced charge-transporting properties, has been designed and synthesized, and showed impressive performance both as blue emitter and as a host for phosphors. A green phosphorescent device containing SOTPA as host showed a maximum external quantum efficiency (EQE) as high as 19.2%, suggesting almost complete triplet harvesting from the blue fluorophor by the green phosphor. Single-emitting layer (EML) F–P hybrid white organic light-emitting devices (WOLEDs) based on SOTPA also gave outstanding electroluminescence performance, with a low turn-on voltage of 2.7 V and maximum EQE and power efficiency (PE) of 15.4% and 40.2 lm W^{-1}, respectively. Even at a practical brightness of 1000 cd m^{-2} the PE still remained as high as 24.1 lm W^{-1}. This excellent performance represents the highest efficiency yet reported among single-EML F–P hybrid WOLEDs.

- pH-Responsive Chimaeric Pepsomes Based on Asymmetric Poly(ethylene glycol)-b-Poly(l-leucine)-b-Poly(l-glutamic acid) Triblock Copolymer for Efficient Loading and Active Intracellular Delivery of Doxorubicin Hydrochloride

  Chen, P.; Qiu, M.; Deng, C.; Meng, F.; Zhang, J.; Cheng, R.; Zhong, Z. *Biomacromolecules* **2015**, *16*, 1322–1130.

  Abstract:

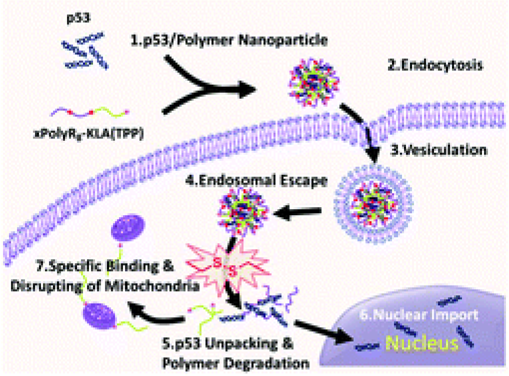


pH-Responsive chimaeric polypeptide-based polymersomes (refer to as pepsomes) were designed and developed from asymmetric poly(ethylene glycol)-*b*-poly(l-leucine)-*b*-poly(l-glutamic acid) (PEG-PLeu-PGA, PEG is longer than PGA) triblock copolymers for efficient encapsulation and triggered intracellular delivery of doxorubicin hydrochloride (DOX·HCl). PEG-PLeu-PGA was conveniently prepared by sequential ring-opening polymerization of l-leucine *N*-carboxyanhydride and γ-benzyl-l-glutamate *N*-carboxyanhydride using PEG-NH_2 as an initiator followed by deprotection. Pepsomes formed from PEG-PLeu-PGA had unimodal distribution and small sizes of 64–71 nm depending on PLeu block lengths. Interestingly, these chimaeric pepsomes while stable at pH 7.4 were quickly disrupted at pH 5.0, likely due to alternation of ionization state of the carboxylic groups in PGA that shifts PGA blocks from hydrophilic and random coil structure into hydrophobic and α-helical structure. DOX·HCl could be actively loaded into the watery core of pepsomes with a high loading efficiency. Remarkably, the in vitro release studies revealed that release of DOX·HCl was highly dependent on pH, in which about 24.0% and 75.7% of drug was released at pH 7.4 and 5.0, respectively, at 37 °C in 24 h. MTT assays demonstrated that DOX·HCl-loaded pepsomes exhibited high antitumor activity, similar to free DOX·HCl in RAW 264.7 cells. Moreover, they were also potent toward drug-resistant MCF-7 cancer cells (MCF-7/ADR). Confocal microscopy studies showed that DOX·HCl-loaded pepsomes delivered and released drug into the cell nuclei of MCF-7/ADR cells in 4 h, while little DOX·HCl fluorescence was observed in MCF-7/ADR cells treated with free drug under otherwise the same conditions. These chimaeric pepsomes with facile synthesis, efficient drug loading, and pH-triggered drug release behavior are an attractive alternative to liposomes for targeted cancer chemotherapy.

- Co-delivery of proapoptotic peptide and p53 DNA by reduction-sensitive polypeptides for cancer therapy

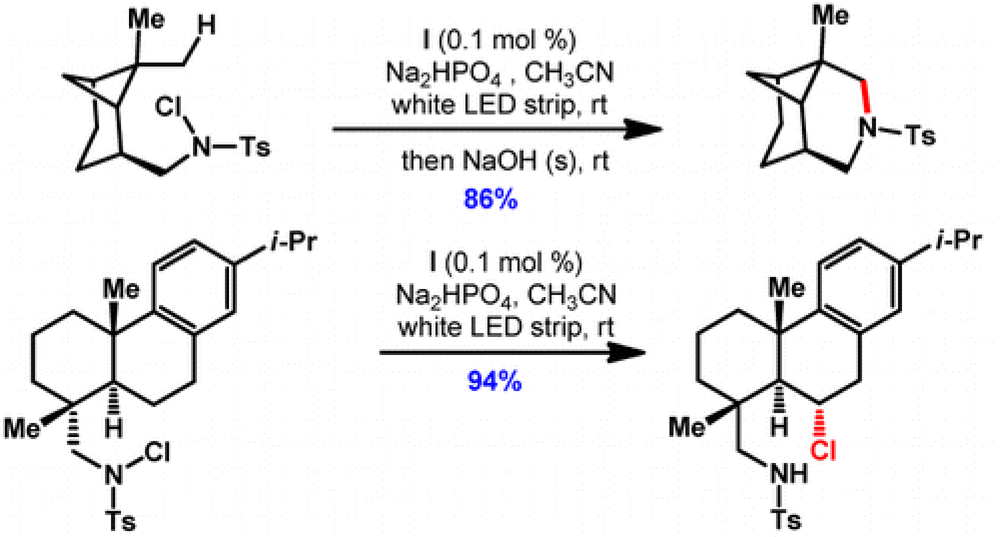
  Chen, S.; Rong, L.; Jia, Z.H.; Qin, Y.S.; Zeng, X.; Zhuo, X.R.; Zhang, Z.X. *Biomater. Sci.* **2015**, *3*, 753-763.

  Abstract:



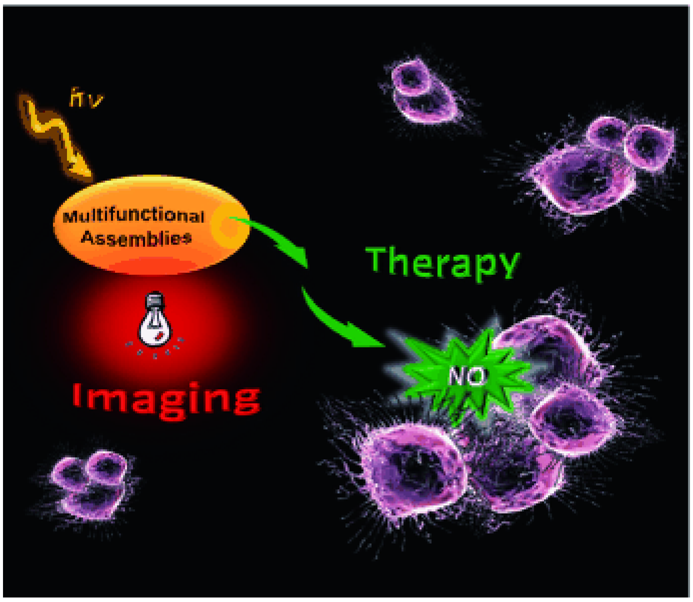
In order to produce a more efficient cancer cell death, a dual-functional polypeptide, xPolyR$_8$–KLA(TPP), was synthesized by disulfide cross-linking CR$_8$C and C-KLA(TPP). The obtained xPolyR$_8$–KLA(TPP) could not only initiate tumor cell apoptosis by C-KLA(TPP) with improved cell penetrating ability, but was also capable of loading and delivering the tumor cell suppressing p53 gene. It was found that, after internalization by cancer cells, the xPolyR$_8$–KLA(TPP)/p53 complex released the C-KLA(TPP) moiety and the p53 gene in the cytoplasm due to its reducible disulfide bonds. By regulating both the intrinsic and extrinsic apoptotic pathways, the xPolyR$_8$–KLA(TPP)/p53 complex performed as a synergetic system and lead to a more efficient cancer cell death.

- Visible-Light-Promoted Remote C(sp^3)–H Amidation and Chlorination
  Qin, Q.; Yu, S. *Org. Lett.* **2015**, *17*, 1894–1897.
  Abstract:



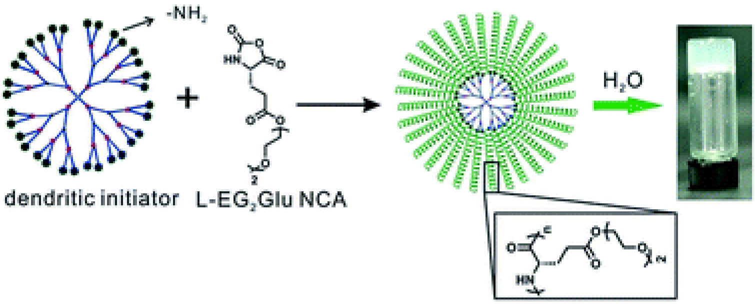
A visible-light-promoted C(sp^3)–H amidation and chlorination of *N*-chlorosulfonamides (NCSs) is reported. This remote C(sp^3)–H functionalization can be achieved in weak basic solution at room temperature with as little as 0.1 mol % of a photocatalyst. A variety of nitrogen-containing heterocycles (up to 94% yield) and chlorides (up to 93% yield) are prepared from NCSs. Late-stage C(sp^3)–H functionalization of complex and biologically important (−)-*cis*-myrtanylamine and (+)-dehydroabietylamine derivatives can also be achieved with excellent yields and regioselectivity.

- Photoactivable Platforms for Nitric Oxide Delivery with Fluorescence Imaging
  Fraix, A.; Sortino, S. *Chem. Asian J.* **2015**, *10*, 1116–1125.
  Abstract:



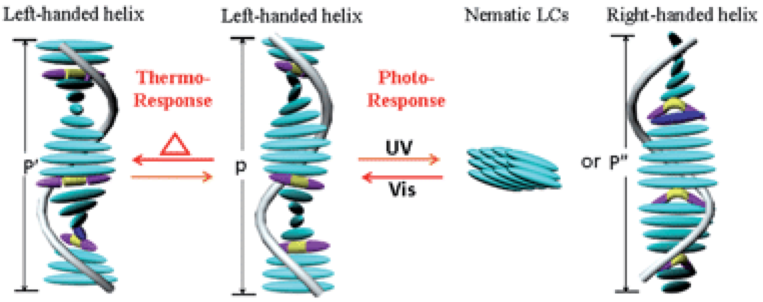
The multifaceted role nitric oxide (NO) plays in human physiology and pathophysiology has stimulated a massive interest on NO-releasing compounds for therapeutic purposes. A main issue associated with use of NO donors is the precise spatiotemporal control of the NO release, as its effects are strictly site- and dose-dependent. NO photochemical precursors permit surmounting this difficulty since triggering with light offers an exquisite control of location and timing of NO delivery. On the other hand, the combination of NO photodonors with fluorescent components remains an urgent need for image-guided phototherapeutic treatments based on the use of NO. Fluorescence techniques permit not only an easy tracking of the photoprecursor in a biological environment but also the real-time quantification of the NO photoreleased therein in a non-invasive fashion. In this Focus Review we seek to provide an overview of recent advances in photoactivable platforms developed in our and other laboratories which combine the photoregulated release of NO with fluorescent functionalities. We shall focus attention on NO photoreleasing systems exhibiting 1) persistent fluorescence and 2) photoactivable fluorescence signals, highlighting their logical design and potential developments for phototheranostics.

- Hydrogels assembled from star-shaped polypeptides with a dendrimer as the core
  Shen, Y.; Zhang, S.; Wan, Y.; Fu, W.; Li, Z. *Soft Matter* **2015**, *11*, 2945-2951.
  Abstract:



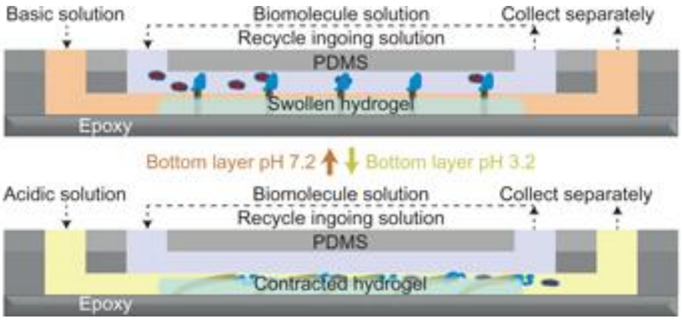
A second or fourth generation dendrimer with primary amine as the peripheral terminal group was first synthesized via Michael addition and thiol–yne addition. A series of star-shaped polypeptides was synthesized by ring opening polymerization (ROP) of γ-(2-(2-methoxyethoxy)ethyl) L-glutamate (L-EG$_2$Glu) N-carboxyanhydride (NCA) using the amine group terminated dendrimer as the initiator. Taking advantage of the well-defined dendrimer and ROP, the arm number and arm length can be easily controlled. These star-shaped poly(L-EG$_2$Glu) can spontaneously form hydrogels instead of micelles in water at low concentration. The critical gelation concentration (CGC) and hydrogel strength displayed a stronger dependence on arm numbers than the arm length under similar conditions. These properties can be easily modulated by varying the poly(L-EG$_2$Glu) arm length and arm number. The hydrogels showed shear thinning and rapid recovery properties. TEM and AFM characterization revealed that the hydrogel networks were constituted by entangled and branched fibrils.

- Effects of terminal chain length in hydrogen-bonded chiral switches on phototunable behavior of chiral nematic liquid crystals: helicity inversion and phase transition
  Fu, D.; Li, J.; Wei, J.; Guo, J. *Soft Matter* **2015**, *11*, 3034-3045.
  Abstract:



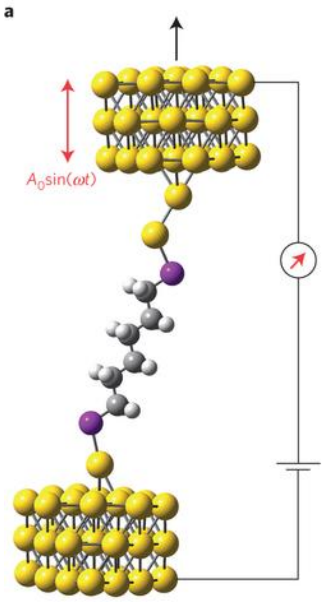
A novel series of photoresponsive chiral switches are fabricated by a facile hydrogen-bonded (H-bonded) assembly method, in which the binaphthyl azobenzene molecule is used as the proton acceptor, and binaphthyl acids with opposite chiral configuration are proton donors. We find that the helical twisted power of H-bonded chiral switches and the helical handedness of induced chiral nematic liquid crystals (N*-LCs) are mainly determined by the terminal flexible chain length in proton donors of binaphthyl acids. Controlling the lengths of the terminal flexible chain leads to different photoswitching behaviors by light irradiation, such as a helical inversion in the N*-LCs and a phase transition from N*-LCs to nematic LCs. This is mainly because of chiral counteraction and intensity attenuation of opposite chiral configurations between the proton acceptor and proton donor during UV-vis irradiation. Additionally, the thermal switching behavior of N*-LCs doped with H-bonded chiral switches is also demonstrated, and the related tuning mechanism may be attributed to the H-bonded effect and the changes in a dihedral angle of the binaphthyl rings. This facile assembly approach provides a new way for the fabrication of functional chiral switches for photonic applications.

- An aptamer-functionalized chemomechanically modulated biomolecule catch-and-release system
  Shastri, A.; McGregor, L. M.; Liu, Y.; Harris, V.; Nan, H.; Mujica, M.; Vasquez, Y.; Bhattacharya, A.; Ma, Y.; Aizenberg, M.; Kuksenok, O.; Balazs, A. C.; Aizenberg, J.; He, X. *Nature Chem.* **2015**, *7*, 447-454.
  Abstract:



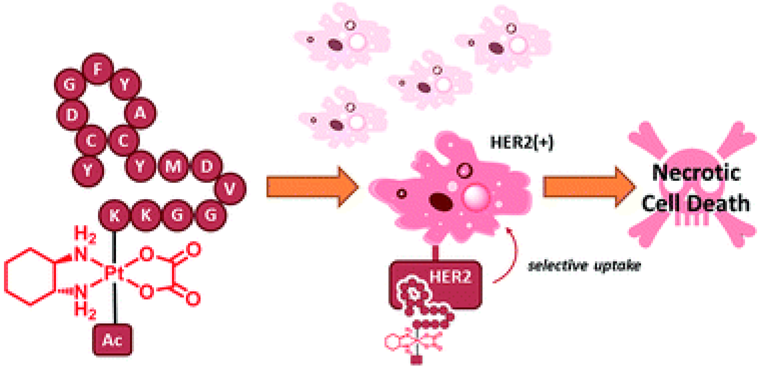
The efficient extraction of (bio)molecules from fluid mixtures is vital for applications ranging from target characterization in (bio)chemistry to environmental analysis and biomedical diagnostics. Inspired by biological processes that seamlessly synchronize the capture, transport and release of biomolecules, we designed a robust chemomechanical sorting system capable of the concerted catch and release of target biomolecules from a solution mixture. The hybrid system is composed of target-specific, reversible binding sites attached to microscopic fins embedded in a responsive hydrogel that moves the cargo between two chemically distinct environments. To demonstrate the utility of the system, we focus on the effective separation of thrombin by synchronizing the pH-dependent binding strength of a thrombin-specific aptamer with volume changes of the pH-responsive hydrogel in a biphasic microfluidic regime, and show a non-destructive separation that has a quantitative sorting efficiency, as well as the system's stability and amenability to multiple solution recycling.

- Binding configurations and intramolecular strain in single-molecule devices
  Rascón-Ramos, H.; Artés, J. M.; Li, Y.; Hihath, J. *Nature Mater.* **2015**, *14*, 517-522.
  Abstract:



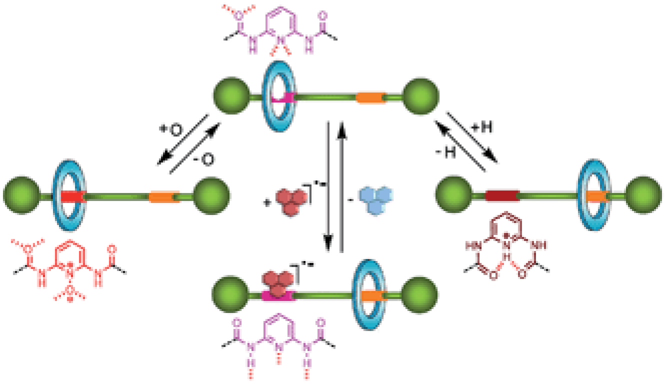
The development of molecular-scale electronic devices has made considerable progress over the past decade, and single-molecule transistors, diodes and wires have all been demonstrated. Despite this remarkable progress, the agreement between theoretically predicted conductance values and those measured experimentally remains limited. One of the primary reasons for these discrepancies lies in the difficulty to experimentally determine the contact geometry and binding configuration of a single-molecule junction. In this Article, we apply a small-amplitude, high-frequency, sinusoidal mechanical signal to a series of single-molecule devices during junction formation and breakdown. By measuring the current response at this frequency, it is possible to determine the most probable binding and contact configurations for the molecular junction at room temperature in solution, and to obtain information about how an applied strain is distributed within the molecular junction. These results provide insight into the complex configuration of single-molecule devices, and are in excellent agreement with previous predictions from theoretical models.

- Induction of targeted necrosis with HER2-targeted platinum(IV) anticancer prodrugs
  Wong, D. Y. Q.; Lima, J. H.; Ang, W. H. *Chem. Sci.* **2015**, *6*, 3051-3056.
  Abstract:



It is well-recognized that the failure of many chemotherapeutics arises due to an inability to induce apoptosis. Most cancers acquire a myriad of pro-survival adaptations, and the vast heterogeneity and accumulation of multiple often unrelated anti-apoptotic signaling pathways have been a major stumbling block towards the development of conventional chemotherapeutics, which can overcome drug resistance. We have developed highly potent and selective HER2-targeted Pt(IV) prodrugs bearing anti-HER2/neu peptides that induce *targeted necrosis* as a novel strategy to circumvent apoptosis-resistance. These Pt(IV)–peptide conjugates exhibit a unique biphasic mode of cytotoxicity comprising rapid killing of cancer cells via necrosis in the first phase followed by an extended and gradual phase of delayed cell death. We demonstrate that these Pt(IV)–peptide prodrugs are more potent than their Pt(II) congeners in direct cell-killing and exhibit comparable long-term inhibition of proliferative capacity and with greater selectivity against HER2-positive cancer cells.

- Versatile control of the submolecular motion of di(acylamino)pyridine-based [2]rotaxanes
  Martinez-Cuezva, A.; Pastor, A. ; Cioncoloni, G. ; Orenes, R.-A.; Alajarin, M.; Symes, M. D.; Berna, J. *Chem. Sci.* **2015**, *6*, 3087-3094.
  Abstract:

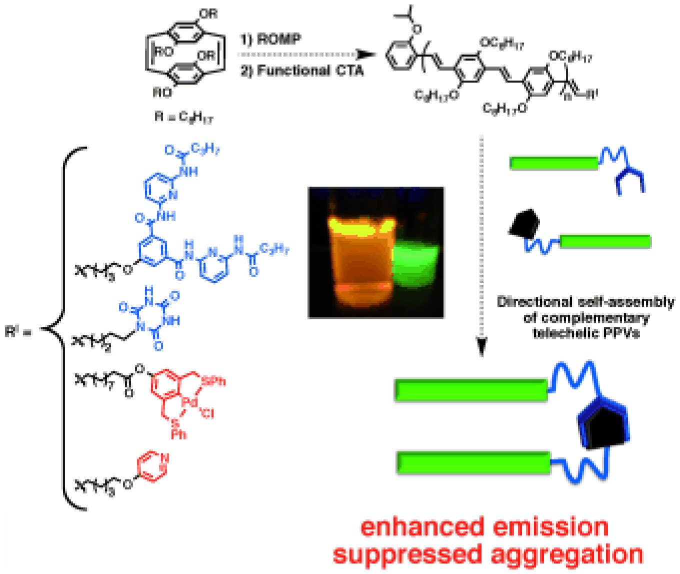


A cyclic network of chemical reactions has been conceived for exchanging the dynamic behaviour of di(acylamino)pyridine-based rotaxanes and surrogates. X-ray diffraction studies revealed the intercomponent interactions in these interlocked compounds and were consistent with those found in solution by dynamic NMR experiments. This particular binding site was incorporated into a molecular shuttle enabled for accessing two states with an outstanding positional discrimination through chemical manipulation. Furthermore, the ability of the di(acylamino)pyridine domain to associate with external binders with a complementary array of HB donor and acceptor sites was exploited for the advance of an unprecedented electrochemical switch operating through a reversible anion radical recognition process.

- Fabrication of Supramolecular Semiconductor Block Copolymers by Ring-Opening Metathesis Polymerization

  Elacqua, E.; Weck, M. *Chem. Eur. J.* **2015**, *21*, 7151–7158.

  Abstract:

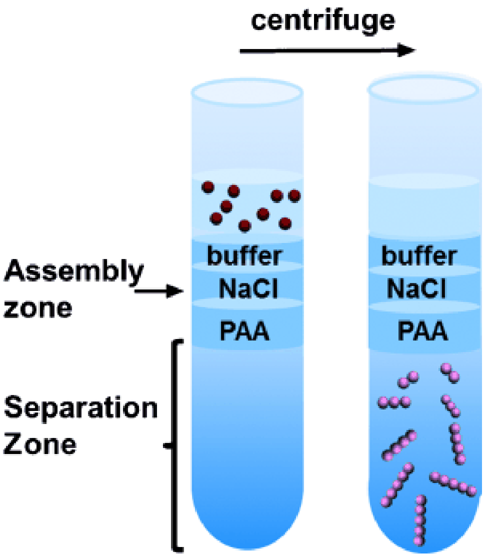


ω-Telechelic poly(*p*-phenylene vinylene) species (PPVs) are prepared by living ring-opening metathesis polymerization of a [2.2]paracyclophane-1,9-diene in the presence of Hoveyda–Grubbs 2nd generation initiator, with terminating agents based on N^1,N^3-bis(6-butyramidopyridin-2-yl)-5-hydroxyisophthalamide (Hamilton wedge), cyanuric acid, Pd^{II}–SCS-pincer, or pyridine moieties installing the supramolecular motifs. The resultant telechelic polymers are self-assembled into supramolecular block copolymers (BCPs) via metal coordination or hydrogen bonding and analyzed by ^{1}H NMR spectroscopy. The optical properties are examined, whereby individual PPVs exhibit similar properties regardless of the nature of the end group. Upon self-assembly, different behaviors emerge: the hydrogen-bonding BCP behaves similarly to the parent PPVs whereas the metallosupramolecular BCP demonstrates a hypsochromic shift and a more intense emission owing to the suppression of aggregation. These results demonstrate that directional self-assembly can be a facile method to construct BCPs with semiconducting networks, while combating solubility and aggregation.

- Controllable Assembly and Separation of Colloidal Nanoparticles through a One-Tube Synthesis Based on Density Gradient Centrifugation

Qi, X.; Li, M.; Kuang, Y.; Wang, C.; Cai, Z.; Zhang, J.; You, S.; Yin, M.; Wan, P.; Luo, L.; Sun, X. *Chem. Eur. J.* **2015**, *21*, 7211–7216.

Abstract:

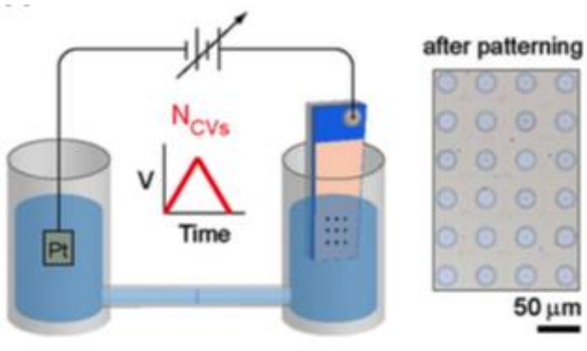


Self-assembly of gold nanoparticles into one-dimensional (1D) nanostructures with finite primary units was achieved by introducing a thin salt (NaCl) solution layer into density gradient before centrifugation. The electrostatic interactions between Au nanoparticles would be affected and cause 1D assembly upon passing through the salt layer. A negatively charged polymer such as poly(acrylic acid) was used as an encapsulation/stabilization layer to help the formation of 1D Au assemblies, which were subsequently sorted according to unit numbers at succeeding separation zones. A centrifugal field was introduced as the external field to overcome the random Brownian motion of NPs and benefit the assembly effect. Such a facile "one-tube synthesis" approach couples assembly and separation in one centrifuge tube by centrifuging once. The method can be tuned by changing the concentration of interference salt layer, encapsulation layer, and centrifugation rate. Furthermore, positively charged fluorescent polymers such as perylenediimide-poly(N,N-diethylaminoethyl methacrylate) could encapsulate the assemblies to give tunable fluorescence properties.

- High-throughput patterning of photonic structures with tunable periodicity

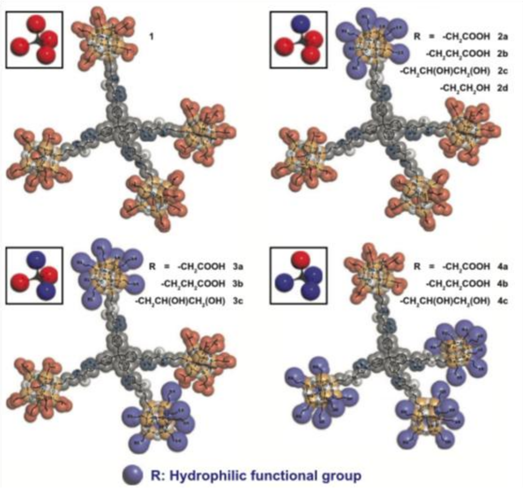
  Kempa, T. J.; Bediako, D. K.; Kim, S.-K.; Park, H.-G.; Nocera, D. G. *Proc. Nat. Acad. Sci. USA* **2015**, *112,* 5309-5313.

  Abstract:



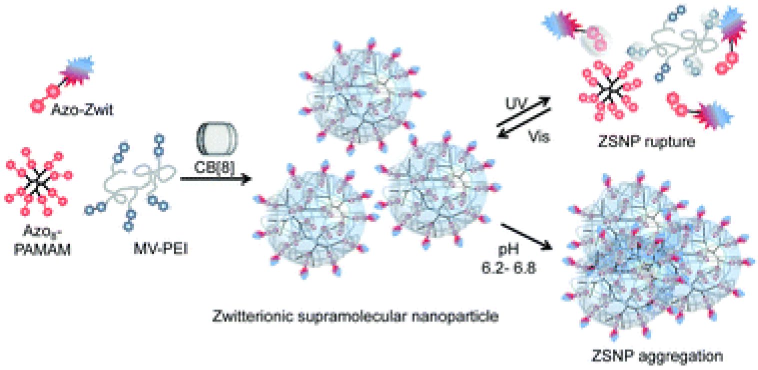
A patterning method termed RIPPLE (reactive interface patterning promoted by lithographic electrochemistry) is applied to the fabrication of arrays of dielectric and metallic optical elements. This method uses cyclic voltammetry to impart patterns onto the working electrode of a standard three-electrode electrochemical setup. Using this technique and a template stripping process, periodic arrays of Ag circular Bragg gratings are patterned in a high-throughput fashion over large substrate areas. By varying the scanrate of the cyclically applied voltage ramps, the periodicity of thegratings can be tuned in situ over micrometer and submicrometerlength scales. Characterization of the periodic arrays of periodic gratings identified point-like and annular scattering modes at different planes above the structured surface. Facile, reliable, and rapid patterning techniques like RIPPLE may enable the high-throughput and low-cost fabrication of photonic elements and metasurfaces for energy conversion and sensing applications.

- Selective assemblies of giant tetrahedra via precisely controlled positional interactions
  Huang, M.; Hsu, C.-H.; Wang, J.; Mei, S.; Dong, X.; Li, Y.; Li, M.; Liu, H.; Zhang, W.; Aida, T.; Zhang, W.-B.; Yue, K.; Cheng, S. Z. D. *Science* **2015**, *348*, 424-428.
  Abstract:



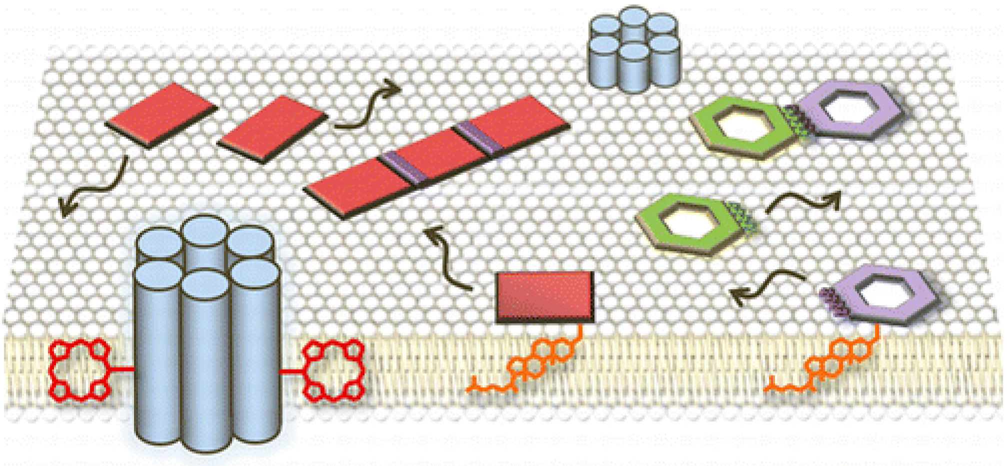
Self-assembly of rigid building blocks with explicit shape and symmetry is substantially influenced by the geometric factors and remains largely unexplored. We report the selective assembly behaviors of a class of precisely defined, nanosized giant tetrahedra constructed by placing different polyhedral oligomeric silsesquioxane (POSS) molecular nanoparticles at the vertices of a rigid tetrahedral framework. Designed symmetry breaking of these giant tetrahedra introduces precise positional interactions and results in diverse selectively assembled, highly ordered supramolecular lattices including a Frank-Kasper A15 phase, which resembles the essential structural features of certain metal alloys but at a larger length scale. These results demonstrate the power of persistent molecular geometry with balanced enthalpy and entropy in creating thermodynamically stable supramolecular lattices with properties distinct from those of other self-assembling soft materials.

- Zwitterionic supramolecular nanoparticles: self-assembly and responsive properties
  Stoffelena, C.; Huskens, J. *Nanoscale* **2015**, *7*, 7915 – 7919.
  Abstract:



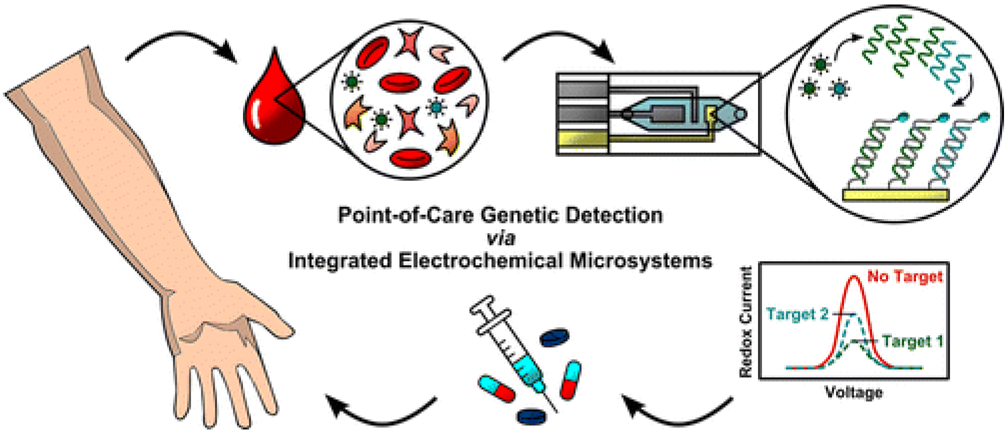
Supramolecular nanoparticles (SNPs) are of high interest in both nanoscience and molecular diagnostics and therapeutics, because of their reversible and designable properties. To ensure colloidal stabilization and biocompatibility, most reported strategies require the use of hydrophilic long-chain polymers such as poly(ethylene glycol). Here, we show the formation of zwitterionic supramolecular nanoparticles (ZSNPs) from appropriately functionalized mono- and multivalent components, based on the hetero-ternary host–guest complexation between cucurbit[8]uril (CB[8]), methyl viologen (MV), and azobenzene (Azo), while using the monovalent, small-molecule, non-fouling Azo-carboxybetaine analog (Azo-Zwit) as the shell-forming component. Even though steric shell stabilization is absent, the zwitterionic Azo-Zwit ensures stability of the ZSNPs in water, in PBS (pH 7.4) at ionic strengths ranging from 0–700 mM, and in PBS containing BSA. Size tuning by control over the stoichiometry of the components, as well as reversible assembly and disassembly by photoisomerization of the Azo moieties were observed. Surprisingly, the ZSNPs exhibited aggregation at the narrow pH range of 6.2–6.8.

- Mimicking Membrane-Related Biological Events by DNA Origami Nanotechnology
  Suzuki, Y.; Endo, M.; Sugiyama, H. *ACS Nano* **2015**, *9*, 3418 – 3420.
  Abstract:



One of the potential applications of DNA nanotechnology is the construction of two- or three-dimensional nanostructures that mimic the function of existing biological molecules. In this issue of ACS Nano, Kocabey et al. demonstrate that lipid-bilayer-anchored DNA origami structures can be assembled into prescribed superstructures in a programmed manner. The reported DNA-based artificial system can mimic the dynamic assembly of membrane-associated protein clusters that play an essential role in deformation of cellular membranes.

- Integrated Electrochemical Microsystems for Genetic Detection of Pathogens at the Point of Care
  Hsieh, K.; Ferguson, B. S.; Eisenstein, M.; Plaxco, K. W.; Soh, H. T. *Acc. Chem. Res.* **2015**, *48*, 900-910.
  Abstract:



The capacity to achieve rapid, sensitive, specific, quantitative, and multiplexed genetic detection of pathogens via a robust, portable, point-of-care platform could transform many diagnostic applications. And while contemporary technologies have yet to effectively achieve this goal, the advent of microfluidics provides a potentially viable approach to this end by enabling the integration of sophisticated multistep biochemical assays (e.g., sample preparation, genetic amplification, and quantitative detection) in a monolithic, portable device from relatively small biological samples.

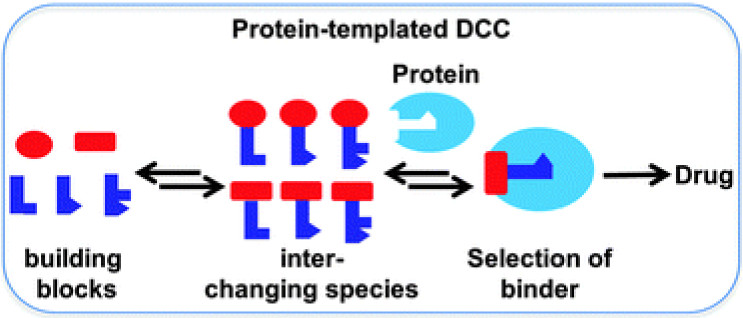
Integrated electrochemical sensors offer a particularly promising solution to genetic detection because they do not require optical instrumentation and are readily compatible with both integrated circuit and microfluidic technologies. Nevertheless, the development of generalizable microfluidic electrochemical platforms that integrate sample preparation and amplification as well as quantitative and multiplexed detection remains a challenging and unsolved technical problem. Recognizing this unmet need, we have developed a series of microfluidic electrochemical DNA sensors that have progressively evolved to encompass each of these critical functionalities.

For DNA detection, our platforms employ label-free, single-step, and sequence-specific electrochemical DNA (E-DNA) sensors, in which an electrode-bound, redox-reporter-modified DNA “probe” generates a current change after undergoing a hybridization-induced conformational change. After successfully integrating E-DNA sensors into a microfluidic chip format, we subsequently incorporated on-chip genetic amplification techniques including polymerase chain reaction (PCR) and loop-mediated isothermal amplification (LAMP) to enable genetic detection at clinically relevant target concentrations. To maximize the potential point-of-care utility of our platforms, we have further integrated sample preparation via immunomagnetic separation, which allowed the detection of influenza virus directly from throat swabs and developed strategies for the multiplexed detection of related bacterial strains from the blood of septic mice. Finally, we developed an alternative electrochemical detection platform based on real-time LAMP, which not is only capable of detecting across a broad dynamic range of target concentrations, but also greatly simplifies quantitative measurement of nucleic acids.

These efforts represent considerable progress toward the development of a true sample-in–answer-out platform for genetic detection of pathogens at the point of care. Given the many advantages of these systems, and the growing interest and innovative contributions from researchers in this field,

we are optimistic that iterations of these systems will arrive in clinical settings in the foreseeable future.

- Dynamic combinatorial chemistry: a tool to facilitate the identification of inhibitors for protein targets
  Mondal, M.; Hirsch, A. K. H. *Chem. Soc. Rev.* **2015**, *44*, 2455-2488.
  Abstract:



Dynamic combinatorial chemistry (DCC) has emerged as a powerful strategy to identify ligands for biological targets given that it enables the target to direct the synthesis and amplification of its strongest binder(s) from the library of interconverting compounds. Since the first report of DCC applied to the discovery of binders for a protein, this elegant tool has been employed on a range of protein targets at various stages of medicinal-chemistry projects. A series of suitable, reversible reactions that are biocompatible have been established and the portfolio of analytical techniques is growing. Despite progress, in most cases, the libraries employed remain of moderate size. We present here the most recent advances in the field of DCC applied to protein targets, paying particular attention to the experimental conditions and analytical methods chosen.