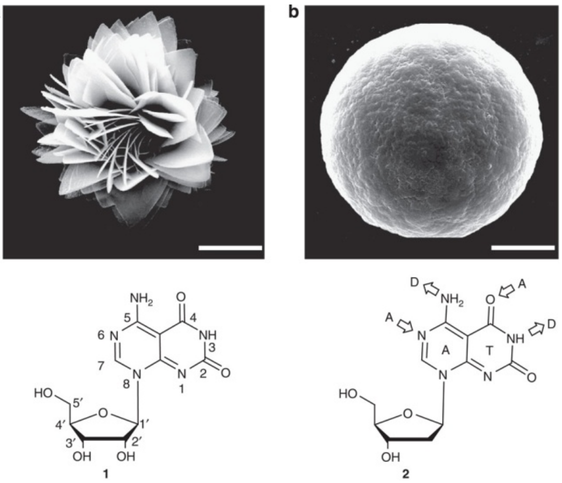
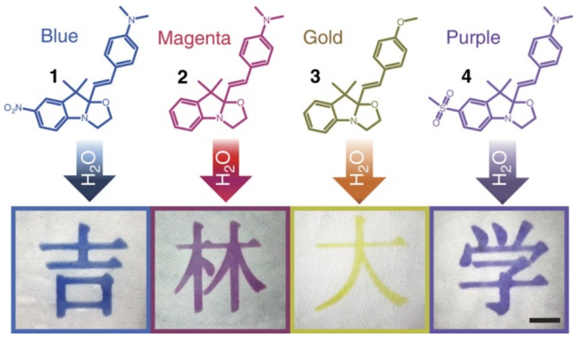
- Complex self-assembly of pyrimido[4,5-d]pyrimidine nucleoside supramolecular structures
  Zhao, H.; Guo, X.; He, S.; Zeng, X.; Zhou, X.; Zhang, C.; Hu, J.; Wu, X.; Xing, Z.; Chu, L.; He, Y.; Chen, Q. *Nature Commun.* **2014**, *5*, 3108.
  Abstract:



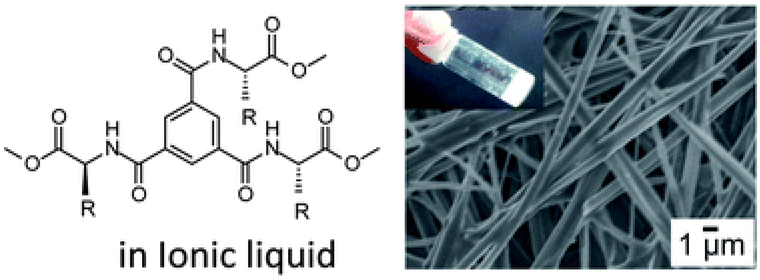
Supramolecular self-assembly is not only one of the chemical roots of biological structure but is also drawing attention in different industrial fields. Here we study the mechanism of the formation of a complex flower-shaped supramolecular structure of pyrimido[4,5-d]pyrimidine nucleosides by dynamic light scattering, scanning electron microscopy, differential scanning calorimetry, nuclear magnetic resonance and X-ray analysis. Upon removing the hydroxyl group of sugars, different flower-shaped superstructures can be produced. These works demonstrate that complex self-assembly can indeed be attained through hierarchical non-covalent interactions of single molecules. Furthermore, chimerical structures built from molecular recognition by these monomers indicate their potential in other fields if combined with other chemical entities.

- Hydrochromic molecular switches for water-jet rewritable paper
  Sheng, L.; Li, M.; Zhu, S.; Li, H.; Xi, G.; Li, Y.-G.; Wang, Y.; Li, Q.; Liang, S.; Zhong, K.; Zhang, S. X.-A. *Nature Commun.* **2014**, *5*, 3044.
  Abstract:



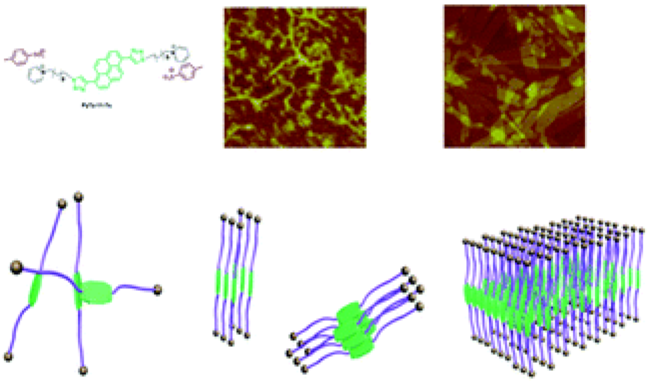
The days of rewritable paper are coming, printers of the future will use water-jet paper. Although several kinds of rewritable paper have been reported, practical usage of them is rare. Herein, a new rewritable paper for ink-free printing is proposed and demonstrated successfully by using water as the sole trigger to switch hydrochromic dyes on solid media. Water-jet prints with various colours are achieved with a commercial desktop printer based on these hydrochromic rewritable papers. The prints can be erased and rewritten dozens of times with no significant loss in colour quality. This rewritable paper is promising in that it can serve an eco-friendly information display to meet the increasing global needs for environmental protection.

- Supramolecular gelators based on benzenetricarboxamides for ionic liquids
  Ishioka, Y.; Minauchi, N.; Mizuhata, M.; Maruyama, T. *Soft Matter* **2014**, *10,* 965-971.
  Abstract:



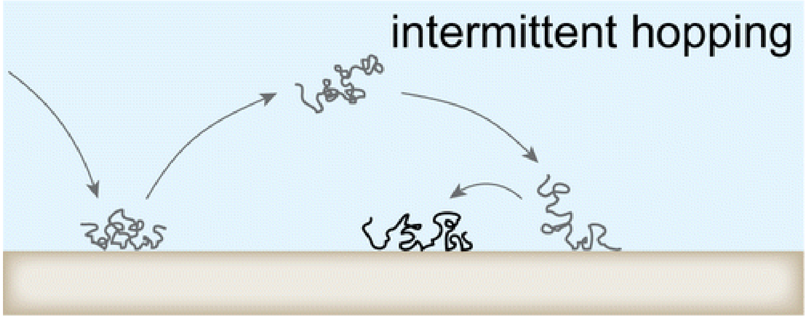
Supramolecular gelators comprising 1,3,5-benzenetricarboxylic acids and amino acid methyl esters (glycine, L-alanine, L-valine, L-leucine, L-methionine, and L-phenylalanine) for ionic liquids were developed. Ten types of ionic liquids were gelated using the above-mentioned gelators at relatively low concentrations. Field emission-scanning electron microscopy and confocal laser scanning microscopy analyses revealed that these gelators self-assembled into an entangled fibrous structure in ionic liquids, leading to the gelation of the ionic liquids. Comparison studies, involving compounds analogous to the gelators, and Fourier transform infrared spectroscopy measurements suggested that hydrogen bonding played a key role in the self-assembly of the gelator molecules. The ionogels displayed reversible thermal transition characteristics and viscoelastic properties typical of a gel. The gelation of the ionic liquids studied under a wide range of gelator concentrations did not affect the intrinsic conductivity of the ionic liquids.

- Mono-molecule-layer nano-ribbons formed by self-assembly of bolaamphiphiles
  Huang, J.; Wang, S.; Wu, G.; Yan, L.; Dong, L.; Lai, X.; Yin, S.; Song, B. *Soft Matter* **2014**, *10,* 1018-1023.
  Abstract:



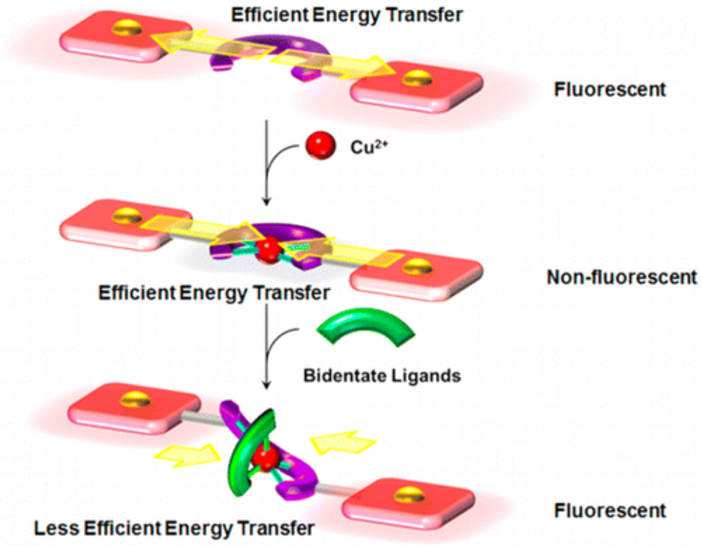
Amphiphilic molecules generally tend to organize spontaneously into spherical or cylindrical micelles/vesicles in appropriate liquid media and conditions, and seldom form two dimensional (2D) planar structures with a regular shape, due to their energetically unfavorable state. Herein, the self-assembly of a new bolaamphiphile bearing a bistriazole-pyrene unit leads to the formation of mono-molecule-layer nano-ribbons. The π–π stacking interaction between the rigid bistriazole-pyrene units and electrostatic screening contributed by the aromatic counterion tosyl groups are responsible for the 2D alignment of the molecules in the aggregate. Partial replacement of the tosyl groups causes a reduction in the width of the nano-ribbons and the coordination of triazole with Pd^{2+} ions results in the collapse of the self-assembled structure. This study supplies new clues for fabricating molecular level 2D nanostructures by bottom-up supramolecular assembly.

- Single-Molecule Tracking of Polymer Surface Diffusion
  Skaug, M. J.; Mabry, J. N.; Schwartz, D. K. *J. Am. Chem. Soc.* **2014**, *136*, 1327-1332.
  Abstract:



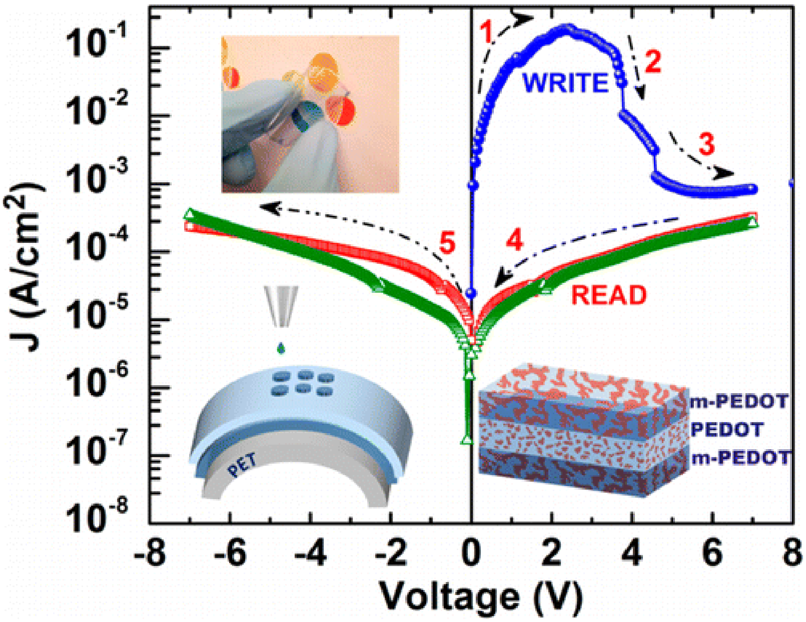
The dynamics of polymers adsorbed to a solid surface are important in thin-film formation, adhesion phenomena, and biosensing applications, but they are still poorly understood. Here we present tracking data that follow the dynamics of isolated poly(ethylene glycol) chains adsorbed at a hydrophobic solid-liquid interface. We found that molecules moved on the surface via a continuous-time random walk mechanism, where periods of immobilization were punctuated by desorption-mediated jumps. The dependence of the surface mobility on molecular weight (2, 5, 10, 20, and 40 kg/mol were investigated) suggested that surface-adsorbed polymers maintained effectively three-dimensional surface conformations. These results indicate that polymer surface diffusion, rather than occurring in the two dimensions of the interface, is dominated by a three-dimensional mechanism that leads to large surface displacements and significant bulk-surface coupling.

- A Porphyrin-Based Molecular Tweezer: Guest-Induced Switching of Forward and Backward Photoinduced Energy Transfer
  Yoon, H.; Lim, J. M.; Gee, H.-C.; Lee, C.-H.; Jeong, Y.-H.; Kim, D.; Jang, W.-D. *J. Am. Chem. Soc.* **2014**, *136*, 1672-1679.
  Abstract:



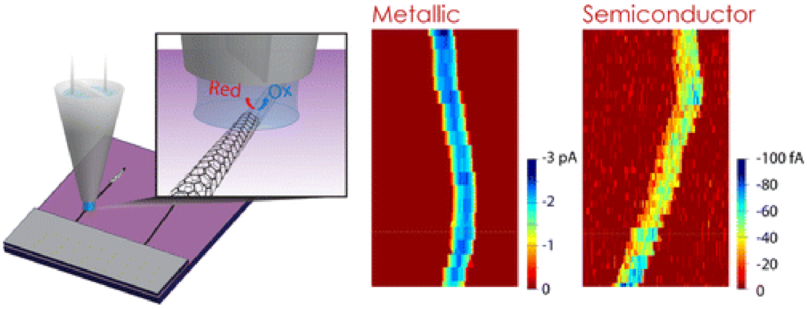
A bisindole-bridged-porphyrin tweezer (1), a pair of zinc porphyrins (P_{Zn}'s) connected to bisindole bridge (BB) via the CuI-mediated alkyne-azide click chemistry, exhibited unique switching in forward and backward photoinduced energy transfer by specific guest bindings. The addition of Cu^{2+} caused a change in electronic absorption and fluorescence quenching of 1. MALDI-TOF-MS and FT-IR analyses indicated the formation of stable coordination complex between 1 and Cu^{2+} (1-Cu(II)). Without Cu^{2+} coordination, the excitation energy flows from BB to P_{Zn}'s with significantly high energy transfer efficiency. In contrast, the direction of energy flow in 1 was completely reversed by the coordination of Cu^{2+}. The difference in fluorescence quantum yield between 1 and 1-Cu(II) indicates that more than 95% of excitation energy of P_{Zn} flows into Cu(II)-coordinated BB. The energy transfer efficiency was further controlled by bidentate ligand coordination onto 1-Cu(II). When pyrophosphate ion was added to 1-Cu(II), the recovery of fluorescence emission from P_{Zn} was observed. The quantum mechanical calculations indicated that the Cu(II)-coordinated BB has square planar geometry, which can be distorted to form octahedral geometry due to the coordination of bidentate ligands.

- Metal-Free, Single-Polymer Device Exhibits Resistive Memory Effect
  Bhansali, U. S.; Khan, M. A.; Cha, D.; AlMadhoun, M. N.; Li, R.; Chen, L.; Amassian, A.; Odeh, I. N.; Alshareef, H. N. *ACS Nano* **2013**, *7*, 10518–10524.
  Abstract:



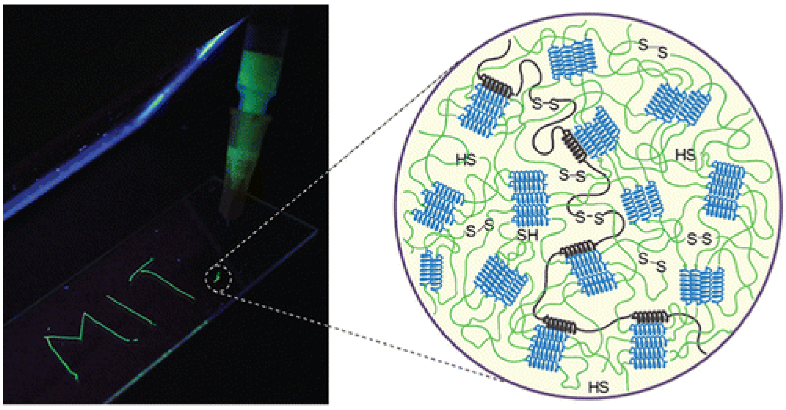
All-polymer, write-once-read-many times resistive memory devices have been fabricated on flexible substrates using a single polymer, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). Spin-cast or inkjet-printed films of solvent-modified PEDOT:PSS are used as electrodes, while the unmodified or as-is PEDOT:PSS is used as the semiconducting active layer. The all-polymer devices exhibit an irreversible but stable transition from a low resistance state (ON) to a high resistance state (OFF) at low voltages caused by an electric-field-induced morphological rearrangement of PEDOT and PSS at the electrode interface. However, in the metal–PEDOT:PSS–metal devices, we have shown a metal filament formation switching the device from an initial high resistance state (OFF) to the low resistance state (ON). The all-PEDOT:PSS memory device has low write voltages (<3 V), high ON/OFF ratio (>103), good retention characteristics (>10□000 s), and stability in ambient storage (>3 months).

- Mapping Nanoscale Electrochemistry of Individual Single-Walled Carbon Nanotubes
  Güell, A. G.; Meadows, K. E.; Dudin, P. V.; Ebejer, N.; Macpherson, J. V.; Unwin, P. R. *Nano Lett.* **2014**, *14*, 220–224.
  Abstract:



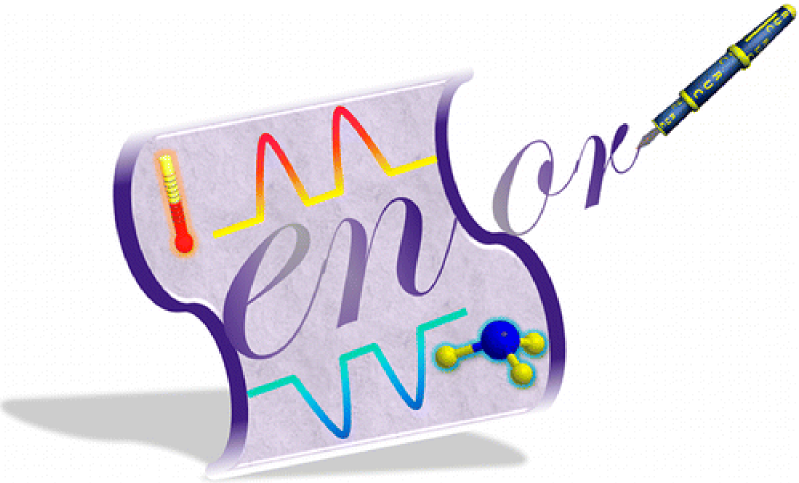
We introduce a multiprobe platform for the investigation of single-walled carbon nanotubes (SWNTs) that allows the electrochemical response of an individual SWNT to be mapped at high spatial resolution and correlated directly with the intrinsic electronic and structural properties. With this approach, we develop a detailed picture of the factors controlling electrochemistry at SWNTs and propose a definitive model that has major implications for future architectures of SWNT electrode devices.

- Oxidatively Responsive Chain Extension to Entangle Engineered Protein Hydrogels
  Tang, S.; Glassman, M. J.; Li, S.; Socrate, S.; Olsen, B. D. *Macromolecules* **2014**, *47*, 791–799.
  Abstract:



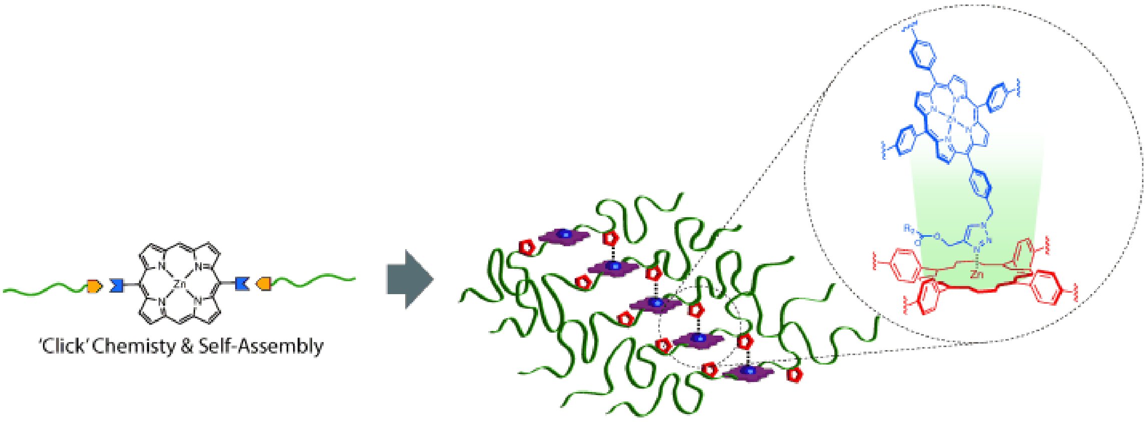
Engineering artificial protein hydrogels for medical applications requires precise control over their mechanical properties, including stiffness, toughness, extensibility, and stability in the physiological environment. Here we demonstrate topological entanglement as an effective strategy to robustly increase the mechanical tunability of a transient hydrogel network based on coiled-coil interactions. Chain extension and entanglement are achieved by coupling the cysteine residues near the N- and C-termini, and the resulting chain distribution is found to agree with the Jacobson–Stockmayer theory. By exploiting the reversible nature of the disulfide bonds, the entanglement effect can be switched on and off by redox stimuli. With the presence of entanglements, hydrogels exhibit a 7.2-fold enhanced creep resistance and a suppressed erosion rate by a factor of 5.8, making the gels more mechanically stable in a physiologically relevant open system. While hardly affecting material stiffness (only resulting in a 1.5-fold increase in the plateau modulus), the entanglements remarkably lead to hydrogels with a toughness of 65 000 J m^{-3} and extensibility to approximately 3000% engineering strain, which enables the preparation of tough yet soft tissue simulants. This improvement in mechanical properties resembles that from double-network hydrogels but is achieved with the use of a single associating network and topological entanglement. Therefore, redox-triggered chain entanglement offers an effective approach for constructing mechanically enhanced and responsive injectable hydrogels.

- Pen-Writing Polypyrrole Arrays on Paper for Versatile Cheap Sensors
  Jia, H.; Wang, J.; Zhang, X.; Wang, Y. *ACS Macro Lett.* **2014**, *3*, 86–90.
  Abstract:



A simple and low-cost "pen-writing" method is exploited for integrating conducting polymer on cellulosic paper. The pen-written paper chip not only possesses excellent mechanical and electrical properties, but also serves as a versatile sensor, fulfilling several real-time and in situ detections for ammonia gas, thermal heating, and NIR light. The theoretical detection limit of ammonia gas can be as low as 1.2 ppm, which is a promising performance for industrial application. In addition, this "pen-writing" technique can be extended to generate wearable electrical textiles in a large scale.

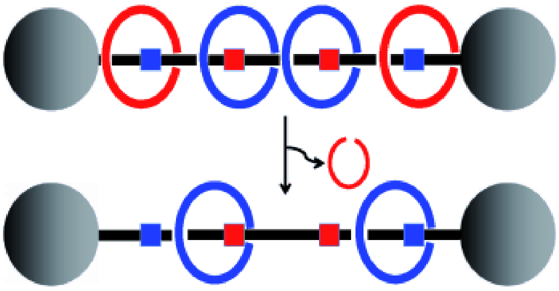
- Tunable Self-Assembly of Triazole-Linked Porphyrin–Polymer Conjugates
  Roberts, D. A.; Schmidt, T. W.; Crossley, M. J.; Perrier, S. *Chem. Eur. J.* **2013**, *19*, 12759–12770.
  Abstract:



The convergence of supramolecular chemistry and polymer science offers many powerful approaches for building functional nanostructures with well-defined dynamic behaviour. Herein we report the efficient "click" synthesis and self-assembly of AB_2- and AB_4-type multitopic porphyrin–polymer conjugates (PPCs). PPCs were prepared using the copper(I)-catalysed azide–alkyne cycloaddition (CuAAC) reaction, and consisted of linear polystyrene, poly(butyl acrylate), or poly(*tert*-

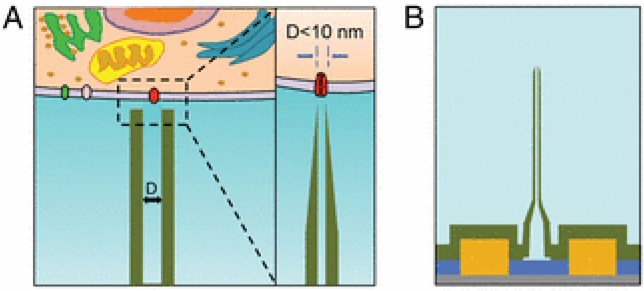
butyl acrylate) arms attached to a zinc(II) porphyrin core via triazole linkages. We exploit the presence of the triazole groups obtained from CuAAC coupling to direct the self-assembly of the PPCs into short oligomers (2–6 units in length) via intermolecular porphyrinatozinc–triazole coordination. By altering the length and grafting density of the polymer arms, we demonstrate that the association constant of the porphyrinatozinc–triazole complex can be systematically tuned over two orders of magnitude. Self-assembly of the PPCs also resulted in a 6 K increase in the glass transition temperature of the bulk material compared to a non-assembling PPC. The modular synthesis and tunable self-assembly of the triazole-linked PPCs thus represents a powerful supramolecular platform for building functional nanostructured materials.

- Use of Cleavable Coordinating Rings as Protective Groups in the Synthesis of a Rotaxane with an Axis that Incorporates More Chelating Groups Than Threaded Macrocycles
  Joosten, A.; Trolez, Y.; Heitz, V.; Sauvage, J.-P. *Chem. Eur. J.* **2013**, *19*, 12815–12823.
  Abstract:



A new methodology allowing preparation of a linear “unsaturated” [3]rotaxane consisting of an axis incorporating more coordination sites than threaded rings was developed. It was based on the preliminary synthesis of a “saturated” [5]rotaxane consisting of a four-chelating site axis threaded through four macrocyclic components, two of them being cleavable rings incorporating a lactone function and the two others being “secure” non-cleavable rings. The stoppering reaction was based on click chemistry. Subsequently, cleavage and removal of the two lactone-containing macrocycles from the [5]rotaxane in basic medium afforded the desired “unsaturated” [3]rotaxane in quantitative yield.

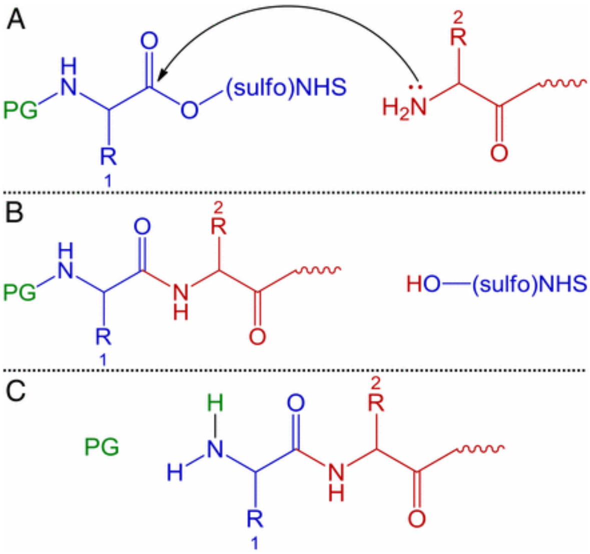
- Sub-10-nm intracellular bioelectronic probes from nanowire–nanotube heterostructures
  Fu, T.-M.; Duan, X.; Jiang, Z.; Dai, X.; Xie, P.; Cheng, Z.; Lieber, C. M. *Proc. Nat. Acad. Sci. USA* **2014**, *111,* 1259-1264.
  Abstract:



The miniaturization of bioelectronic intracellular probes with a wide dynamic frequency range can open up opportunities to study biological structures inaccessible by existing methods in a minimally invasive manner. Here, we report the design, fabrication, and demonstration of intracellular bioelectronic devices with probe sizes less than 10 nm. The devices are based on a nanowire–

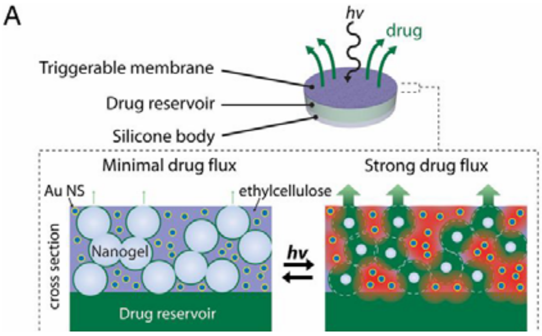
nanotube heterostructure in which a nanowire field-effect transistor detector is synthetically integrated with a nanotube cellular probe. Sub-10-nm nanotube probes were realized by a two-step selective etching approach that reduces the diameter of the nanotube free-end while maintaining a larger diameter at the nanowire detector necessary for mechanical strength and electrical sensitivity. Quasi-static water-gate measurements demonstrated selective device response to solution inside the nanotube, and pulsed measurements together with numerical simulations confirmed the capability to record fast electrophysiological signals. Systematic studies of the probe bandwidth in different ionic concentration solutions revealed the underlying mechanism governing the time response. In addition, the bandwidth effect of phospholipid coatings, which are important for intracellular recording, was investigated and modeled. The robustness of these sub-10-nm bioelectronics probes for intracellular interrogation was verified by optical imaging and recording the transmembrane resting potential of HL-1 cells. These ultrasmall bioelectronic probes enable direct detection of cellular electrical activity with highest spatial resolution achieved to date, and with further integration into larger chip arrays could provide a unique platform for ultra-high-resolution mapping of activity in neural networks and other systems.

- Efficient and directed peptide bond formation in the gas phase via ion/ion reactions
  McGee, W. M.; McLuckey, S. A. *Proc. Nat. Acad. Sci. USA* **2014**, *111,* 1288-1292.
  Abstract:



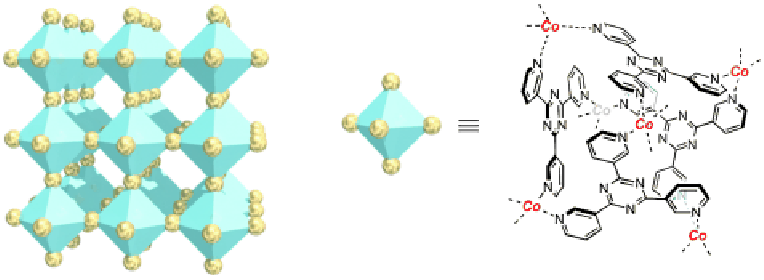
Amide linkages are among the most important chemical bonds in living systems, constituting the connections between amino acids in peptides and proteins. We demonstrate the controlled formation of amide bonds between amino acids or peptides in the gas phase using ion/ion reactions in a mass spectrometer. Individual amino acids or peptides can be prepared as reagents by (*i*) incorporating gas phase–labile protecting groups to silence otherwise reactive functional groups, such as the N terminus; (*ii*) converting the carboxyl groups to the active ester of *N*-hydroxysuccinimide; and (*iii*) incorporating a charge site. Protonation renders basic sites (nucleophiles) unreactive toward the *N*-hydroxysuccinimide ester reagents, resulting in sites with the greatest gas phase basicities being, in large part, unreactive. The N-terminal amines of most naturally occurring amino acids have lower gas phase basicities than the side chains of the basic amino acids (i.e., those of histidine, lysine, or arginine). Therefore, reagents may be directed to the N terminus of an existing "anchor" peptide to form an amide bond by protonating the anchor peptide's basic residues, while leaving the N-terminal amine unprotonated and therefore reactive. Reaction efficiencies of greater than 30% have been observed. We propose this method as a step toward the controlled synthesis of peptides in the gas phase.

- Near-infrared–actuated devices for remotely controlled drug delivery
  Timko, B. P.; Arruebo, M.; Shankarappa, S. A.; McAlvin, J. B.; Okonkwo, O. S.; Mizrahi, B.; Stefanescu, C. F.; Gomez, L.; Zhu, J.; Zhu, A.; Santamaria, J.; Langer, R.; Kohane, D. S. *Proc. Nat. Acad. Sci. USA* **2014**, *111,* 1349-1354.
  Abstract:



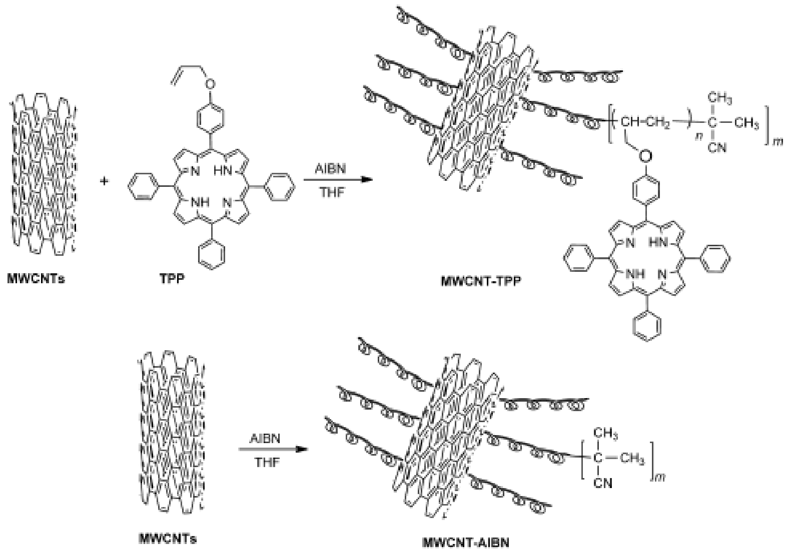
A reservoir that could be remotely triggered to release a drug would enable the patient or physician to achieve on-demand, reproducible, repeated, and tunable dosing. Such a device would allow precise adjustment of dosage to desired effect, with a consequent minimization of toxicity, and could obviate repeated drug administrations or device implantations, enhancing patient compliance. It should exhibit low off-state leakage to minimize basal effects, and tunable on-state release profiles that could be adjusted from pulsatile to sustained in real time. Despite the clear clinical need for a device that meets these criteria, none has been reported to date to our knowledge. To address this deficiency, we developed an implantable reservoir capped by a nanocomposite membrane whose permeability was modulated by irradiation with a near-infrared laser. Irradiated devices could exhibit sustained on-state drug release for at least 3 h, and could reproducibly deliver short pulses over at least 10 cycles, with an on/off ratio of 30. Devices containing aspart, a fast-acting insulin analog, could achieve glycemic control after s.c. implantation in diabetic rats, with reproducible dosing controlled by the intensity and timing of irradiation over a 2-wk period. These devices can be loaded with a wide range of drug types, and therefore represent a platform technology that might be used to address a wide variety of clinical indications.

- Stable Encapsulation of Acrylate Esters in Networked Molecular Capsules
  Ning, G.-H.; Inokuma, Y.; Fujita, M. *Chem. Asian J.* **2014,** *9*, 466-468.
  Abstract:



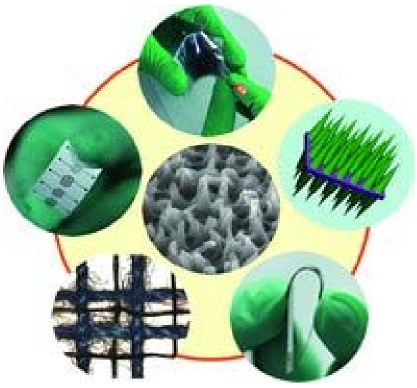
Reactive acrylate esters were encapsulated in the cavity of networked molecular capsules in a single-crystal-to-single-crystal fashion. Owing to the encapsulation effect, acrylates inside the capsules do not undergo polymerization upon irradiation with UV light or heating, while the guest molecules can be quantitatively extracted by treatment with toluene.

- Allyloxyporphyrin-Functionalized Multiwalled Carbon Nanotubes: Synthesis by Radical Polymerization and Enhanced Optical-Limiting Properties
  Wang, A.; Fang, Y.; Yu, W.; Long, L.; Song, Y.; Zhao, W.; Cifuentes, M. P.; Humphrey, M. G.; Zhang, C. *Chem. Asian J.* **2014,** *9*, 639-648.
  Abstract:



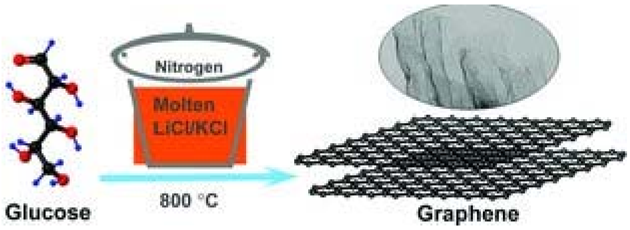
Allyloxyporphyrin-functionalized multiwalled carbon nanotubes (MWCNT-TPP) were synthesized by radical polymerization and characterized by FTIR, UV/Vis absorption, and X-ray photoelectron spectroscopy; elemental analysis; TEM; and thermogravimetric analysis. Z-scan studies revealed that this nanohybrid exhibits enhanced nonlinear optical (NLO) properties compared to a control sample consisting of a covalently unattached physical blend of MWCNTs and porphyrin, as well as to the separate MWCNTs and porphyrin. At the wavelengths used, the mechanism of enhanced optical limiting likely involves reverse saturable absorption, nonlinear scattering, and photoinduced electron/energy transfer between the MWCNTs and the porphyrin. The role of electron/energy transfer in the NLO performance of MWCNT-TPP was investigated by Raman and fluorescence spectroscopy.

- Conducting Polymer Nanowire Arrays for High Performance Supercapacitors
  Wang, K.; Wu, H.; Meng, Y.; Wei, Z. *Small* **2014**, *1*, 14-31.
  Abstract:



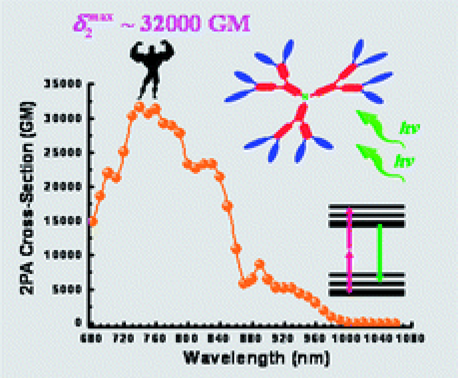
This Review provides a brief summary of the most recent research developments in the fabrication and application of one-dimensional ordered conducting polymers nanostructure (especially nanowire arrays) and their composites as electrodes for supercapacitors. By controlling the nucleation and growth process of polymerization, aligned conducting polymer nanowire arrays and their composites with nano-carbon materials can be prepared by employing in situ chemical polymerization or electrochemical polymerization without a template. This kind of nanostructure (such as polypyrrole and polyaniline nanowire arrays) possesses high capacitance, superior rate capability ascribed to large electrochemical surface, and an optimal ion diffusion path in the ordered nanowire structure, which is proved to be an ideal electrode material for high performance supercapacitors. Furthermore, flexible, micro-scale, threadlike, and multifunctional supercapacitors are introduced based on conducting polyaniline nanowire arrays and their composites. These prototypes of supercapacitors utilize the high flexibility, good processability, and large capacitance of conducting polymers, which efficiently extend the usage of supercapacitors in various situations, and even for a complicated integration system of different electronic devices.

- A Facile Molten-Salt Route to Graphene Synthesis
  Liu, X.; Giordano, C.; Antonietti, M. *Small* **2014**, *1*, 193-200.
  Abstract:



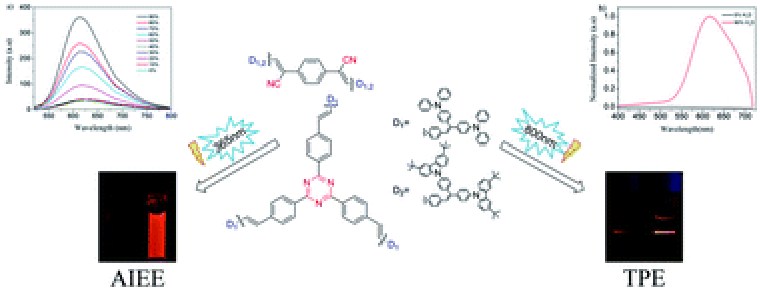
Efficient synthetic routes are continuously pursued for graphene in order to implement its applications in different areas. However, direct conversion of simple monomers to graphene through polymerization in a scalable manner remains a major challenge for chemists. Herein, a molten-salt (MS) route for the synthesis of carbon nanostructures and graphene by controlled carbonization of glucose in molten metal chloride is reported. In this process, carbohydrate undergoes polymerization in the presence of strongly interacting ionic species, which leads to nanoporous carbon with amorphous nature and adjustable pore size. At a low precursor concentration, the process converts the sugar molecules (glucose) to rather pure few-layer graphenes. The MS-derived graphenes are strongly hydrophobic and exhibit remarkable selectivity and capacity for absorption of organics. The methodology described may open up a new avenue towards the synthesis and manipulation of carbon materials in liquid media.

- Synthesis and characterization of a highly two-photon active dendrimer derived from 2,3,8-trifunctionalized indenoquinoxaline units
  Lin, T.-C.; Liu, C.-Y.; Li, M.-H.; Liu, Y.-Y.; Tseng, S.-Y.; Wang, Y.-T.; Tseng, Y.-H.; Chu, H.-H.; Luo, C.-W. *J. Mater. Chem. C* **2014***, 2*, 821–828.
  Abstract:



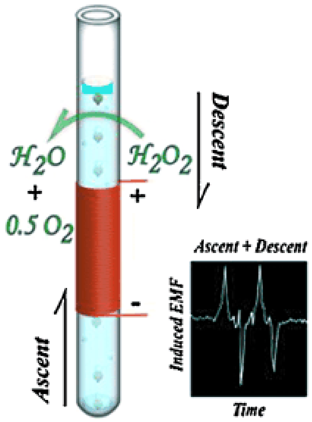
A dendritic chromophore derived from 2,3,8-trifunctionalized indenoquinoxaline units was synthesized and experimentally shown to manifest very strong and widely-dispersed two-photon absorption (2PA) across the dynamic tuning range of a Ti:sapphire laser. The maximum 2PA of the studied chromophore was found to reach ≈31 700 GM, indicating that 2,3,8-trifuctionalized indenoquinoxaline units are useful building moieties for the construction of highly active 2PA-dyes. In addition, this dendritic structure was also demonstrated to effectively regulate the optical power of femtosecond laser pulses at 800 nm.

- Large cyano- and triazine-substituted D–π–A–π–D structures as efficient AIEE solid emitters with large two-photon absorption cross sections
  Huang, W.; Tang, F.; Li, B.; Su, J.; Tian, H. *J. Mater. Chem. C* **2014**, *2*, 1141–1148.
  Abstract:



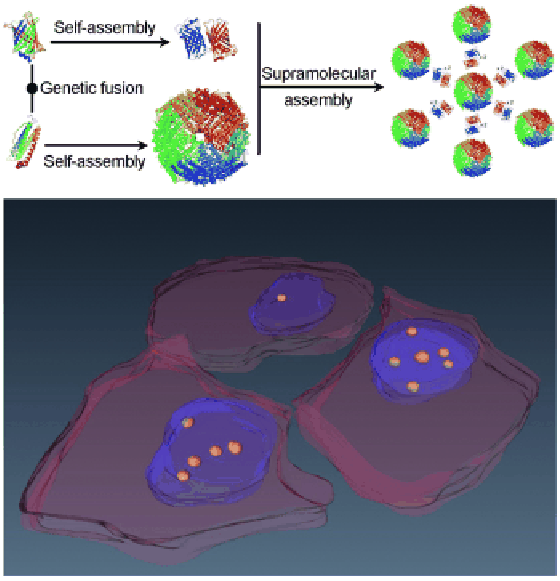
A series of new large π-conjugated molecules including diphenylamine and carbazole have been synthesized and characterized (3a–c). All compounds display aggregation-induced emission enhancement (AIEE) characteristics: exhibiting weak fluorescence in pure THF, while a significant AIEE effect is observed in mixtures with a water fraction (fw) of 90% with a sharp increase in fluorescence intensity. Combining intramolecular charge transfer (ICT) characteristics and AIEE features, 3a–c are intense solid emitters (589 nm, 546 nm and 556 nm, respectively) with high quantum efficiencies of 18.1%, 27.4% and 14.9%, respectively. Their two-photon absorption (2PA) properties have been investigated using the open-aperture Z-scan technique, and the values of the 2PA cross section at 800 nm for 3a–c are 1363 GM, 413 GM and 5782 GM, respectively. Their excellent 2PA properties and solid quantum efficiencies pave the way for their potential use in biophotonic and optoelectronic applications.

- Induction of Electromotive Force by an Autonomously Moving Magnetic Bot
  Sailapu, S. K.; Chattopadhyay, A. *Angew. Chem. Int. Ed.* **2014**, *53,* 1521–1524.
  Abstract:



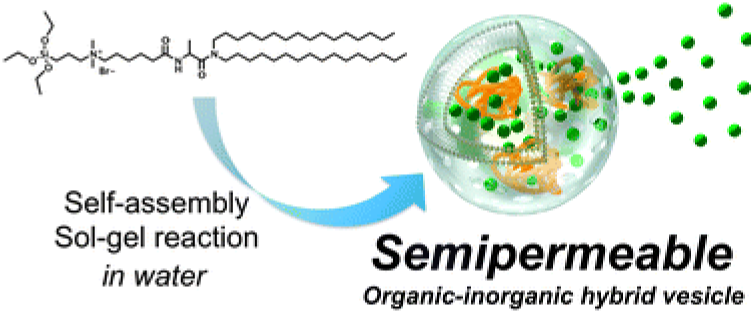
We report the observation of the induction of electromotive force (emf) into a Faraday coil by an autonomously moving composite magnetic particle in aqueous medium. The particle consisted of a micron-sized polymer sphere, which was decorated with catalytic Pd nanoparticles (NPs) and attached to a micron-scale (N-42 grade) rare-earth magnet. The Pd NPs catalytically decomposed H_2O_2 to generate O_2, resulting in buoyancy-driven vertical motion of the particle, while the micromagnet induced emf during the flight. Because a small volume of ethanol was layered on top of the liquid, the bubble burst when the particle ascended to the top and thus nearly continuous vertical motion was achieved. Spikes of alternating electrical signal could be observed up to 20 times per minute. The signal was sufficiently strong to illuminate light-emitting diodes following appropriate amplification. This distinctive approach is expected to pave the way to developing synthetic bots which are autonomously propelled, generating their own signal for running complex circuitry.

- Supramolecular Protein Assemblies in the Nucleus of Human Cells
  Bellapadrona, G.; Elbaum, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 1534–1537.
  Abstract:



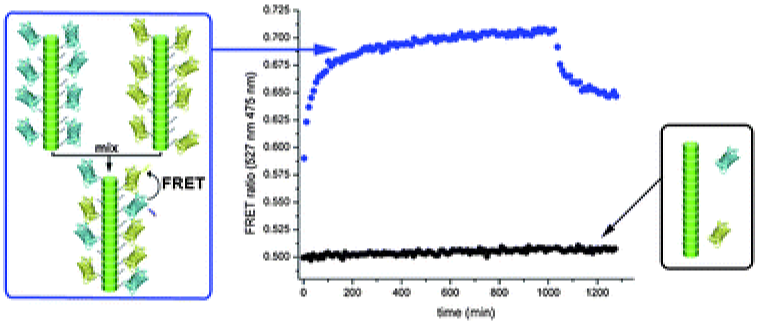
Genetically encoded supramolecular protein assemblies (SMPAs) are induced to form in living cells by combination of distinct self-assembly properties. A single fusion construct contains genes encoding the heavy chain (H) of human ferritin and the citrine fluorescent protein, the latter exposing a weak dimerization interface, as well as a nuclear localization signal. Upon expression in HeLa cells, in vivo confocal fluorescence and differential interference contrast imaging revealed extended SMPA structures exclusively in the nuclei. Assemblies were typically round and took alveolar, shell-like, or hybrid structure. Transmission electron microscopy revealed a crystalline packing. Site-specific mutagenesis of the citrine dimerization interface clarified the mechanism of SMPA formation. The constituent proteins retained their activity in iron binding and fluorescence emission, thus suggesting a general strategy for formation of synthetic cellular bodies with specific biochemical function.

- Spontaneously formed semipermeable organic-inorganic hybrid vesicles permitting molecular weight selective transmembrane passage
  Yasuhara, K.; Kawataki, T.; Okuda, S.; Oshima, S.; Kikuchi, J. *Chem. Commun.* **2013**, *49,* 665-667.
  Abstract:



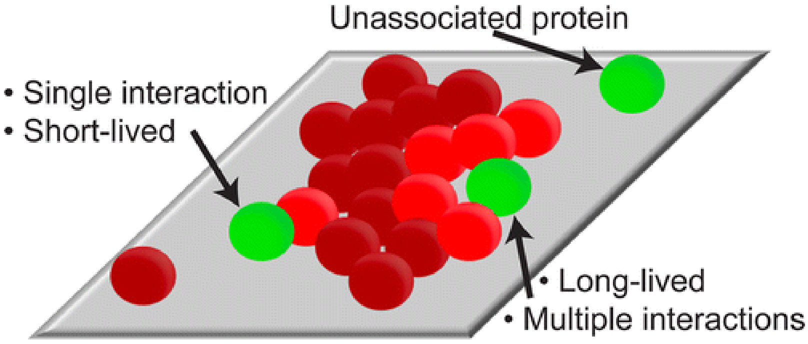
Semipermeable organic-inorganic hybrid vesicles coated with a siloxane surface were spontaneously formed by simple dispersion of an organoalkoxysilane lipid in water. The hybrid vesicles allow the permeation of hydrophilic small molecules across the membrane without an introduction of a pore-forming protein.

- Dynamic and bio-orthogonal protein assembly along a supramolecular polymer
  Petkau-Milroy, K.; Uhlenheuer, D. A.; Spiering, A. J. H.; Vekemans, J. A. J. M.; Brunsveld, L. *Chem. Sci.* **2013**, *4*, 2886-2891.
  Abstract:



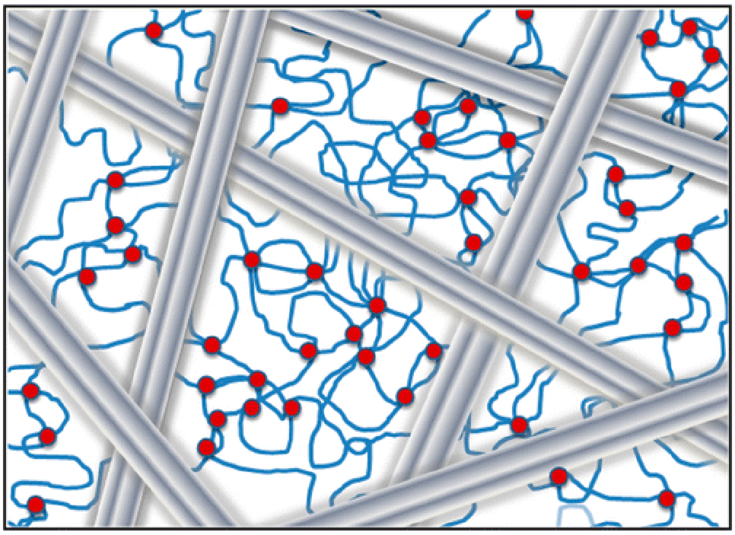
Dynamic protein assembly along supramolecular columnar polymers has been achieved through the site specific covalent attachment of different SNAP-tag fusion proteins to self-assembled benzylguanine-decorated discotics. The self-assembly of monovalent discotics into supramolecular polymers creates a multivalent, bio-orthogonal and self-regulating framework for protein assembly. The intrinsic reversibility of supramolecular interactions results in reorganization and exchange of building blocks allowing for dynamic intermixing of protein-functionalized discotics between different self-assembled polymers, leading to self-optimization of protein arrangement and distance as evidenced by efficient energy transfer between fluorescent proteins.

- Interfacial Protein–Protein Associations
  Langdon, B. B.; Kastantin, M.; Walder, R.; Schwartz, D. K. *Biomacromolecules* **2014**, *15*, 66–74.
  Abstract:



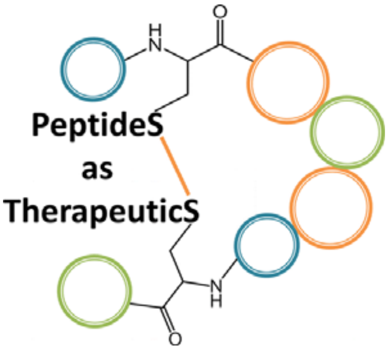
While traditional models of protein adsorption focus primarily on direct protein–surface interactions, recent findings suggest that protein–protein interactions may play a central role. Using high-throughput intermolecular resonance energy transfer (RET) tracking, we directly observed dynamic, protein–protein associations of bovine serum albumin on polyethylene glycol modified surfaces. The associations were heterogeneous and reversible, and associating molecules resided on the surface for longer times. The appearance of three distinct RET states suggested a spatially heterogeneous surface – with areas of high protein density (i.e., strongly interacting clusters) coexisting with mobile monomers. Distinct association states exhibited characteristic behavior, i.e., partial-RET (monomer–monomer) associations were shorter-lived than complete-RET (protein-cluster) associations. While the fractional surface area covered by regions with high protein density (i.e., clusters) increased with increasing concentration, the distribution of contact times between monomers and clusters was independent of solution concentration, suggesting that associations were a local phenomenon, and independent of the global surface coverage.

- Evidence for the Coexistence of Interpenetrating Permanent and Transient Networks of Hydroxypropyl Methyl Cellulose
  Shahin, A.; Nicolai, T.; Benyahia, L.; Tassin, J.-F.; Chassenieux, C. *Biomacromolecules* **2014**, *15*, 311–318.
  Abstract:



Dynamic mechanical properties of aqueous solutions of hydroxypropyl methyl cellulose (HPMC) were investigated using oscillatory shear measurements. The structure was investigated with light scattering. A systematic investigation of the frequency dependence of the shear moduli showed that HPMC forms two distinct interpenetrating networks. A transient network is formed above about 0.3 wt % by reversible cross-linking of the chains. The elastic modulus of this network is independent of the temperature, but increases linearly with the concentration. An independent permanent network is formed involving a small fraction of the polymers and has an elastic modulus that increases with increasing temperature. Its elastic modulus is history dependent and evolves slowly with time. The transient network collapses at a critical temperature where micro phase separation occurs, but the permanent network is not influenced by this phenomenon. Light scattering showed that the pore size of the transient network is less than 40 nm, while probe diffusion measurements showed that the pore size of the permanent network is larger than 1 µm.

- Multifaceted Roles of Disulfide Bonds. Peptides as Therapeutics
  Góngora-Benítez, M.; Tulla-Puche, J.; Albericio, F. *Chem. Rev.* ***2014**, 114*, 901-926.
  <u>Abstract:</u>



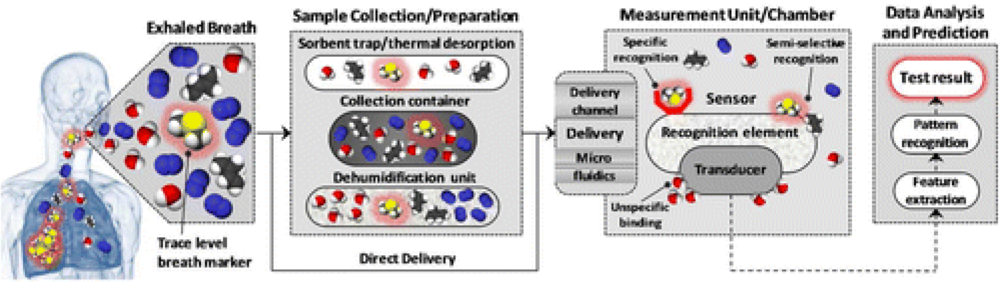
After a long period of disinterest on the part of a large number of pharmaceutical companies, peptides as therapeutics have re-emerged with force during recent years. Macrocycles and constrained peptides, in particular, have generated great expectation as prospective drug candidates, owing to their intrinsic high stability and potency.

In this review, we have focused on the multifaceted roles of disulfide bonds as constrained structural elements involved in both the oxidative folding and conformational stabilization of peptides, along with the participation of these motifs in the improvement of the drug-like properties of peptides. Thus, given the multiple roles played by cystine residues, we propose to browse through the most relevant and novel literature reported in the past decade regarding disulfide bonds in peptide therapeutics, from their biological role in oxidative folding and structure stability, to their capacity to enhance the pharmacological properties of peptides. Therefore, first we cover the in vivo and in vitro oxidative folding processes involved in the crucial disulfide bond formation. We also address the contribution of these structural elements to the stability of peptides and proteins. In addition, recent studies addressing the cyclization of peptide sequences through disulfide bond formation for stabilizing secondary structures, and the enhancement of activity, selectivity, and stability against proteases, as well as the elucidation of active peptide conformations, are covered in this review. Furthermore, a particular use of disulfide bonds as reversible covalent linkages for enhancing the cell permeability of peptides has been also considered.

Moreover, we have placed special emphasis on small, disulfide-rich peptides, privileged architectures with promising pharmacological properties that have gained a foothold as templates in drug design over recent years. These naturally occurring molecules have attracted our attention because they have been revealed as structures with prospective pharmacological properties that display high chemical and biological stability. Interestingly, some disulfide-rich peptides may address two main unresolved issues for peptides as therapeutics, namely oral delivery and cell uptake. In addition, recent studies have also covered the use of some of these structures as scaffolds for peptide drug design and development.

Finally, we have provided a brief perspective of the major considerations and tools available—strategies and techniques—for the synthesis and successive characterization of disulfide-rich peptides. Thus, an overview of novel recombinant techniques for the preparation of disulfide-rich peptides has been provided, as well as the main considerations for the chemical synthesis of these compounds. Herein, we highlight the difficulties that need to be tackled during the chemical synthesis of these complex macromolecules and describe the catalog of the most commonly used synthetic tools and the analytical methods and techniques employed for the characterization of multiple-disulfide peptides.

- Sensors for Breath Testing: From Nanomaterials to Comprehensive Disease Detection
  Konvalina, G.; Haick, H. *Acc. Chem. Res.* **2014**, *47*, 66-76.
  Abstract:



The analysis of volatile organic compounds in exhaled breath samples represents a new frontier in medical diagnostics because it is a noninvasive and potentially inexpensive way to detect illnesses. Clinical trials with spectrometry and spectroscopy techniques, the standard volatile-compound detection methods, have shown the potential for diagnosing illnesses including cancer, multiple sclerosis, Parkinson's disease, tuberculosis, diabetes, and more via breath tests. Unfortunately, this approach requires expensive equipment and high levels of expertise to operate the necessary instruments, and the tests must be done quickly and use preconcentration techniques, all of which impede its adoption.

Sensing matrices based on nanomaterials are likely to become a clinical and laboratory diagnostic tool because they are significantly smaller, easier-to-use, and less expensive than spectrometry or spectroscopy. An ideal nanomaterial-based sensor for breath testing should be sensitive at very low concentrations of volatile organic compounds, even in the presence of environmental or physiological confounding factors. It should also respond rapidly and proportionately to small changes in concentration and provide a consistent output that is specific to a given volatile organic compound. When not in contact with the volatile organic compounds, the sensor should quickly return to its baseline state or be simple and inexpensive enough to be disposable.

Several reviews have focused on the methodological, biochemical, and clinical aspects of breath analysis in attempts to bring breath testing closer to practice for comprehensive disease detection. This Account pays particular attention to the technological gaps and confounding factors that impede nanomaterial-sensor-based breath testing, in the hope of directing future research and development efforts towards the best possible approaches to overcome these obstacles. We discuss breath testing as a complex process involving numerous steps, each of which has several possible technological alternatives with advantages and drawbacks that might affect the performance of the nanomaterial-based sensors in a breath-testing system. With this in mind, we discuss how to choose nanomaterial-based sensors, considering the profile of the targeted breath markers and the possible limitations of the approach, and how to design the surrounding breath-testing setup. We also discuss how to tailor the dynamic range and selectivity of the applied sensors to detect the disease-related volatile organic compounds of interest. Finally, we describe approaches to overcome other obstacles by improving the sensing elements and the supporting techniques such as preconcentration and dehumidification.