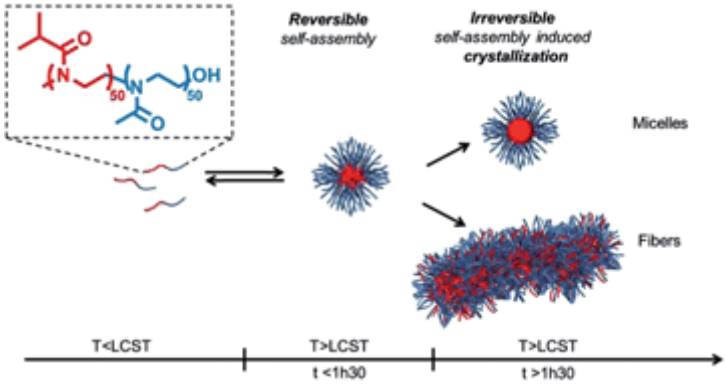
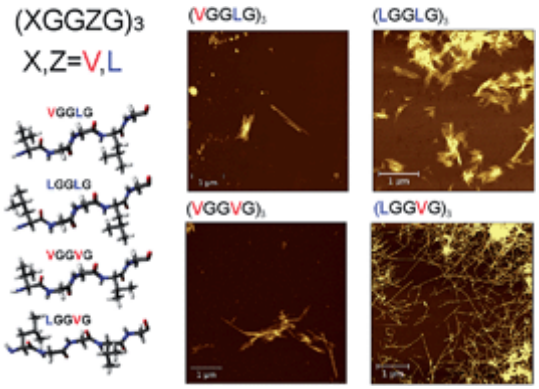
- Crystallisation-driven self-assembly of poly(2-isopropyl-2-oxazoline)-block-poly(2-methyl-2-oxazoline) above the LCST
  Legros, C.; De Pauw-Gillet, M.-C.; Tam, K. C.; Taton, D.; Lecommandoux, S. *Soft Matter* **2015**, *11*, 3354-3359.
  Abstract:



The solution behaviour in water of a polyoxazoline-type block copolymer, namely poly(2-isopropyl-2-oxazoline)-*block*-poly(2-methyl-2-oxazoline), denoted as P(iPrOx-*b*-MeOx), above the lower critical solution temperature (LCST) of the PiPrOx block was exploited to induce a temporary or permanent self-assembly. Spherical micelles were first obtained and could be disassembled in a reversible manner when kept for a short period of time (*i.e.* t < 90 min) above the LCST, and cooled down to room temperature. In contrast, annealing the copolymer solution for more than 90 min at 65 °C induced the crystallisation of the PiPrOx block, as evidenced by wide angle X-ray scattering (WAXS) experiments. This crystallisation-driven self-assembly phenomenon resulted in different morphologies, including spherical and distorted crystallised micelles and micron-size fibers, their relative proportion varies with the annealing time. Formation of micron-size range fiber-like structures might be explained by the re-organization of parent crystallised micelles. The crystal structure, as determined by WAXS, appeared to be identical to that of the PiPrOx homopolymer.

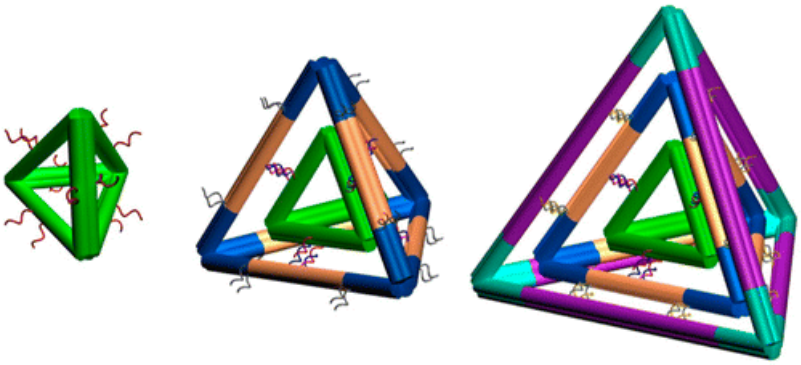
- Tuning self-assembly in elastin-derived peptides
  Bochicchio, B.; Pepe, A.; Crudele, M.; Belloy, N.; Baud, S.; Dauche, M. *Soft Matter* **2015**, *11,* 3385-3395.
  Abstract:



Elastin-derived peptides are gaining increasing interest as potential biomaterials. Previous studies have demonstrated that short elastin-derived peptides are able to self-assemble into fibrils as the entire elastin protein. The motif responsible for that is the XGGZG motif at least three-fold repeated. In this work we have synthesized and studied, at molecular and supramolecular levels, four pentadecapeptides obtained by switching the X and Z residue with leucine and/or valine. We found

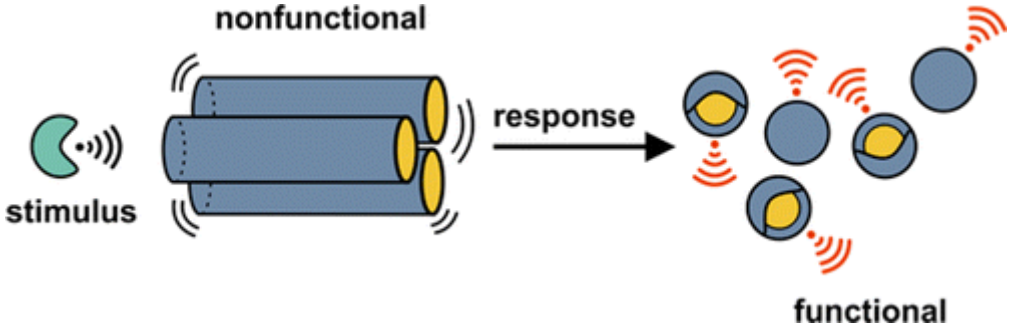
that the four peptides formed different supramolecular structures corresponding to specific molecular conformations. Our results show that not only the residue type but also the exact position occupied by the residue in the motif is crucial in driving the self-aggregation. The aim of this work is to provide the basis for designing elastin-derived peptides with tunable supramolecular architecture.

- Self-Assembly of Responsive Multilayered DNA Nanocages
  Liu, Z.; Tian, C.; Yu, J.; Li, Y.; Jiang, W.; Mao, C. *J. Am. Chem. Soc.* **2015**, *137*, 1730-1733.
  Abstract:



Here we report the assembly of multilayered DNA nanocages. The layers can be separated in response to a chemical cue, ATP. This is an effort to increase the structural complexity of DNA nanocages. The structures have been characterized by native polyacrylamide gel electrophoresis, atomic force microscopy, and cryogenic electron microscopy. We envision that the layerby-layer assembly strategy used in this study can be easily applied to other DNA nanocages to form Russian-doll-like semisolid structures, while the chemically activated layer separation makes a contribution to the development of “smart” DNA nanocages.

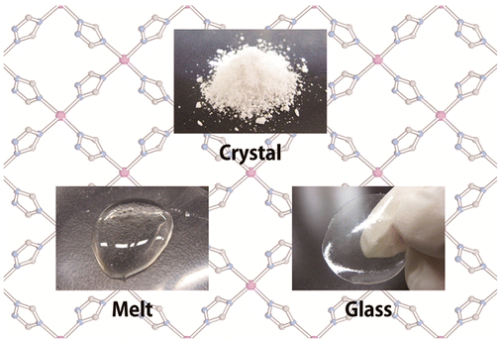
- Stimuli-Responsive Nanomaterials for Biomedical Applications
  Blum, A. P.; Kammeyer, J. K.; Rush, A., M.; Callmann, C. E.; Hahn, M. E.; Gianneschi, N. C. *J. Am. Chem. Soc.* **2015**, *137*, 2140-2154.
  Abstract:



Nature employs a variety of tactics to precisely time and execute the processes and mechanics of life, relying on sequential sense and response cascades to transduce signaling events over multiple length and time scales. Many of these tactics, such as the activation of a zymogen, involve the direct manipulation of a material by a stimulus. Similarly, effective therapeutics and diagnostics require the selective and efficient homing of material to specific tissues and biomolecular targets with appropriate temporal resolution. These systems must also avoid undesirable or toxic side effects and evade unwanted removal by endogenous clearing mechanisms. Nanoscale delivery vehicles have been developed to package materials with the hope of delivering them to select locations with rates of accumulation and clearance governed by an interplay between the carrier and its cargo. Many modern approaches to drug delivery have taken inspiration from natural activatable materials like

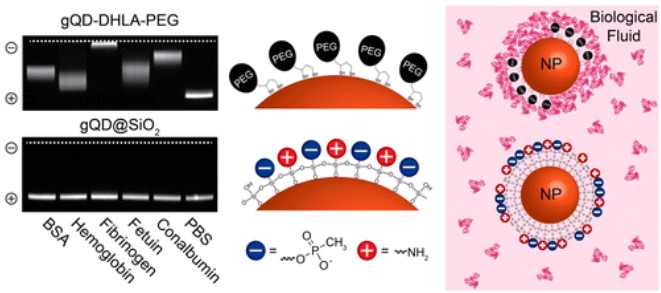
zymogens, membrane proteins, and metabolites, whereby stimuli initiate transformations that are required for cargo release, prodrug activation, or selective transport. This Perspective describes key advances in the field of stimuli-responsive nanomaterials while highlighting some of the many challenges faced and opportunities for development. Major hurdles include the increasing need for powerful new tools and strategies for characterizing the dynamics, morphology, and behavior of advanced delivery systems in situ and the perennial problem of identifying truly specific and useful physical or molecular biomarkers that allow a material to autonomously distinguish diseased from normal tissue.

- Reversible Solid-to-Liquid Phase Transition of Coordination Polymer Crystals
  Umeyama, D.; Horike, S.; Inukai, M.; Itakura, T.; Kitagawa, S. *J. Am. Chem. Soc.* **2015**, *137*, 864-870.
  Abstract:



The solid-to-liquid phase transition, a fundamental process commonly observed for various types of substances with significant potential for application, has been given little attention in the field of coordination polymers (CPs) despite the rich functionality of these compounds. In this article, we report the reversible solid-to-liquid phase transition of crystalline CPs. These CPs are composed of zinc ions, phosphate, and azoles, and a well-balanced composition, ionicity, and bond strength afford “melting” CPs. We examined the structure of one such melting framework in the liquid and glass states and found that the coordination bonds are not fully preserved in the liquid state but are re-formed in the glass state. As a demonstration, we fabricated, via phase transition, a thin film with an aligned crystal orientation and a monolith crystal of the CP.

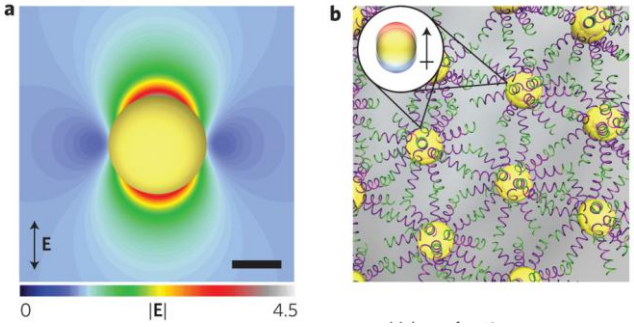
- Discovery of Protein- and DNA-Imperceptible Nanoparticle Hard Coating Using Gel-Based Reaction Tuning
  Welsher, K.; McManus, S. A.; Hsia, C.-H.; Yin, S.; Yang, H. *J. Am. Chem. Soc.* **2015**, *137*, 580-583.
  Abstract:



The seemingly inevitable protein corona appears to be an insurmountable obstacle to wider application of functional nanomaterials in biotechnology. The accumulation of serum proteins can block targeting functionalities and alter the in vivo fate of these nanomaterials. Here we

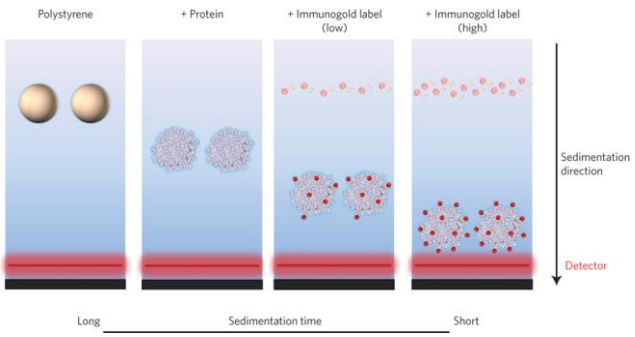
demonstrate a method to generate non-stick, robustly passivated functional nanoparticles (NPs) using a tailored silica coating. We apply agarose gel electrophoresis to sensitively evaluate protein binding to NPs with different surface chemistry. Using gel banding and retardation as a read-out for protein adsorption, we optimize the surface chemistry to yield a mixed charge surface which displays remarkable binding resistance to a wide range of serum proteins and nucleic acids. The hard silica shell also protects the functional NP core in harsh environments (down to pH 1) while still showing the ability to be targeted for cellular uptake with little or no non-specific binding.

- Nanoscale form dictates mesoscale function in plasmonic DNA–nanoparticle superlattices
  Ross, M. B.; Ku, J. C.; Vaccarezza, V. M.; Schatz, G. C.; Mirkin, C. A. *Nature Nanotech.* **2015**, *10*, 453–458.
  Abstract:



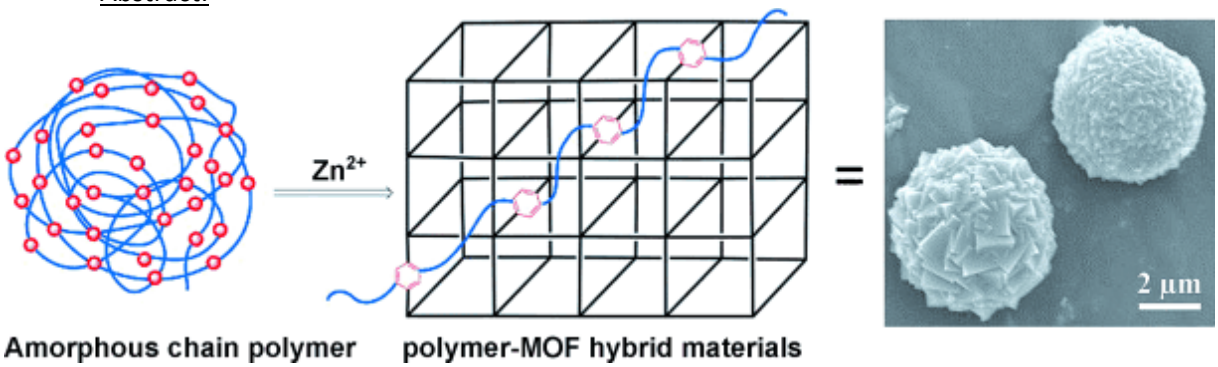
The nanoscale manipulation of matter allows properties to be created in a material that would be difficult or even impossible to achieve in the bulk state. Progress towards such functional nanoscale architectures requires the development of methods to precisely locate nanoscale objects in three dimensions and for the formation of rigorous structure–function relationships across multiple size regimes (beginning from the nanoscale). Here, we use DNA as a programmable ligand to show that two- and three-dimensional mesoscale superlattice crystals with precisely engineered optical properties can be assembled from the bottom up. The superlattices can transition from exhibiting the properties of the constituent plasmonic nanoparticles to adopting the photonic properties defined by the mesoscale crystal (here a rhombic dodecahedron) by controlling the spacing between the gold nanoparticle building blocks. Furthermore, we develop a generally applicable theoretical framework that illustrates how crystal habit can be a design consideration for controlling far-field extinction and light confinement in plasmonic metamaterial superlattices.

- Mapping protein binding sites on the biomolecular corona of nanoparticles
  Kelly, P. M.; Åberg, C.; Polo, E.; O'Connell, A.; Cookman, J.; Fallon, J.; Krpetić , Ž.; Dawson, K. A. *Nature Nanotech.* **2015**, *10*, 472–479.
  Abstract:



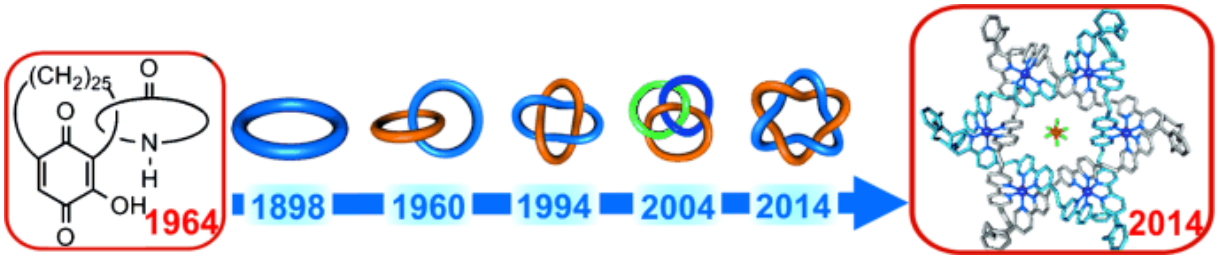
Nanoparticles in a biological milieu are known to form a sufficiently long-lived and well-organized 'corona' of biomolecules to confer a biological identity to the particle. Because this nanoparticle–biomolecule complex interacts with cells and biological barriers, potentially engaging with different biological pathways, it is important to clarify the presentation of functional biomolecular motifs at its interface. Here, we demonstrate that by using antibody-labelled gold nanoparticles, differential centrifugal sedimentation and various imaging techniques it is possible to identify the spatial location of proteins, their functional motifs and their binding sites. We show that for transferrin-coated polystyrene nanoparticles only a minority of adsorbed proteins exhibit functional motifs and the spatial organization appears random, which is consistent, overall, with a stochastic and irreversible adsorption process. Our methods are applicable to a wide array of nanoparticles and can offer a microscopic molecular description of the biological identity of nanoparticles.

- polyMOFs: A Class of Interconvertible Polymer-Metal-Organic-Framework Hybrid
  Zhang, Z.; Nguyen, H. T. H.; Miller, S. A.; Cohen, S. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 6152 – 6157.
  Abstract:



Preparation of porous materials from one-dimensional polymers is challenging because the packing of polymer chains results in a dense, non-porous arrangement. Herein, we demonstrate the remarkable adaptation of an amorphous, linear, non-porous, flexible organic polymer into a three-dimensional, highly porous, crystalline solid, as the organic component of a metal–organic framework (MOF). A polymer with aromatic dicarboxylic acids in the backbone functioned as a polymer ligand upon annealing with Zn^{II}, generating a polymer–metal–organic framework (polyMOF). These materials break the dogma that MOFs must be prepared from small, rigid ligands. Similarly, polyMOFs contradict conventional polymer chemistry by demonstrating that linear and amorphous polymers can be readily coaxed into a highly crystalline, porous, three-dimensional structure by coordination chemistry.

- Catenanes: Fifty Years of Molecular Links
  Gil-Ramírez, G.; Leigh, D. A.; Stephens, A. J. *Angew. Chem. Int. Ed*. **2015**, 54, 6110 –6150.
  Abstract:



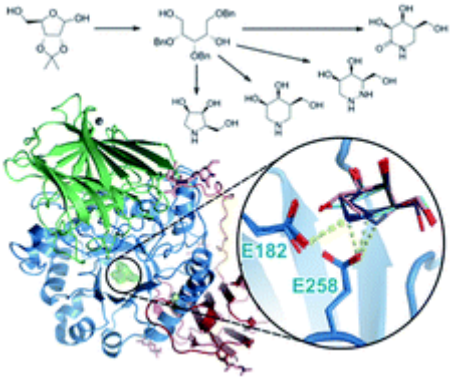
Half a century after Schill and Lüttringhaus carried out the first directed synthesis of a [2]catenane, a plethora of strategies now exist for the construction of molecular Hopf links (singly interlocked rings), the simplest type of catenane. The precision and effectiveness with which suitable templates

and/or noncovalent interactions can arrange building blocks has also enabled the synthesis of intricate and often beautiful higher order interlocked systems, including Solomon links, Borromean rings, and a Star of David catenane. This Review outlines the diverse strategies that exist for synthesizing catenanes in the 21st century and examines their emerging applications and the challenges that still exist for the synthesis of more complex topologies.

- Sulfonyl fluorides as privileged warheads in chemical biology
  Narayanan, A.; Jones, L. H. *Chem. Sci.* **2015**, *6*, 2650-2659.
  Abstract:

Sulfonyl fluoride electrophiles have found significant utility as reactive probes in chemical biology and molecular pharmacology. As warheads they possess the right balance of biocompatibility (including aqueous stability) and protein reactivity. Their functionality is privileged in this regard as they are known to modify not only reactive serines (resulting in their common use as protease inhibitors), but also context-specific threonine, lysine, tyrosine, cysteine and histidine residues. This review describes the application of sulfonyl fluoride probes across various areas of research and explores new approaches that could further enhance the chemical biology toolkit. We believe that sulfonyl fluoride probes will find greater utility in areas such as covalent enzyme inhibition, target identification and validation, and the mapping of enzyme binding sites, substrates and protein–protein interactions.

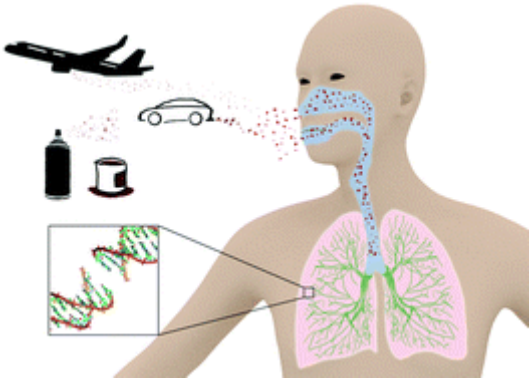
- Azasugar inhibitors as pharmacological chaperones for Krabbe disease
  Hill, C. H.; Viuff, A. H.; Spratley, S. J.; Salamone, S.; Christensen, S. H.; Read, R. J.; Moriarty, N. W.; Jensen, H. H.; Deane, J. E. *Chem. Sci.* **2015**, *6*, 3075-3086.
  Abstract:



Krabbe disease is a devastating neurodegenerative disorder characterized by rapid demyelination of nerve fibers. This disease is caused by defects in the lysosomal enzyme β-galactocerebrosidase (GALC), which hydrolyzes the terminal galactose from glycosphingolipids. These lipids are essential components of eukaryotic cell membranes: substrates of GALC include galactocerebroside, the primary lipid component of myelin, and psychosine, a cytotoxic metabolite. Mutations of GALC that cause misfolding of the protein may be responsive to pharmacological chaperone therapy (PCT), whereby small molecules are used to stabilize these mutant proteins, thus correcting trafficking defects and increasing residual catabolic activity in cells. Here we describe a new approach for the synthesis of galacto-configured azasugars and the characterization of their interaction with GALC using biophysical, biochemical and crystallographic methods. We identify that the global stabilization

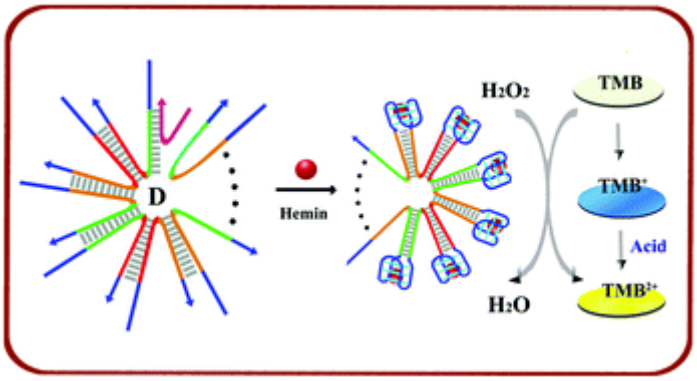
of GALC conferred by azasugar derivatives, measured by fluorescence-based thermal shift assays, is directly related to their binding affinity, measured by enzyme inhibition. X-ray crystal structures of these molecules bound in the GALC active site reveal which residues participate in stabilizing interactions, show how potency is achieved and illustrate the penalties of aza/iminosugar ring distortion. The structure–activity relationships described here identify the key physical properties required of pharmacological chaperones for Krabbe disease and highlight the potential of azasugars as stabilizing agents for future enzyme replacement therapies. This work lays the foundation for new drug-based treatments of Krabbe disease.

- Genotoxic effects of zinc oxide nanoparticles
  Heim, J.; Felder, E.; Tahir, M. N.; Kaltbeitzel, A.; Heinrich, U. R.; Brochhausen, C.; Mailänder, V.; Tremel, W.; Brieger, J. *Nanoscale* **2015**, *7*, 8931 – 8938.
  Abstract:



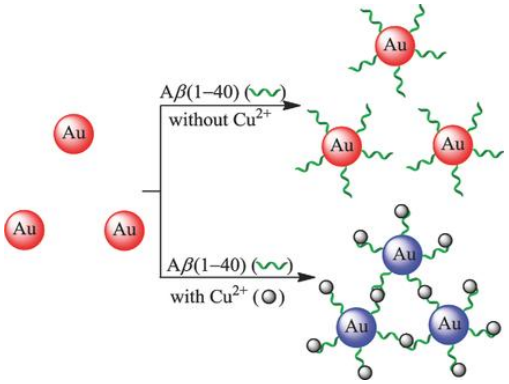
The potential toxicity of nanoparticles has currently provoked public and scientific discussions, and attempts to develop generally accepted handling procedures for nanoparticles are under way. The investigation of the impact of nanoparticles on human health is overdue and reliable test systems accounting for the special properties of nanomaterials must be developed. Nanoparticular zinc oxide (ZnO) may be internalised through ambient air or the topical application of cosmetics, only to name a few, with unpredictable health effects. Therefore, we analysed the determinants of ZnO nanoparticle (NP) genotoxicity. ZnO NPs (15–18 nm in diameter) were investigated at concentrations of 0.1, 10 and 100 μg mL^{-1} using the cell line A549. Internalised NPs were only infrequently detectable by TEM, but strongly increased Zn^{2+} levels in the cytoplasm and even more in the nuclear fraction, as measured by atom absorption spectroscopy, indicative of an internalised zinc and nuclear accumulation. We observed a time and dosage dependent reduction of cellular viability after ZnO NP exposure. $ZnCl_2$ exposure to cells induced similar impairments of cellular viability. Complexation of Zn^{2+} with diethylene triamine pentaacetic acid (DTPA) resulted in the loss of toxicity of NPs, indicating the relevant role of Zn^{2+} for ZnO NP toxicity. Foci analyses showed the induction of DNA double strand breaks (DSBs) by ZnO NPs and increased intracellular reactive oxygen species (ROS) levels. Treatment of the cells with the ROS scavenger *N*-acetyl-L-cysteine (NAC) resulted in strongly decreased intracellular ROS levels and reduced DNA damage. However, a slow increase of ROS after ZnO NP exposure and reduced but not quashed DSBs after NAC-treatment suggest that Zn^{2+} may exert genotoxic activities without the necessity of preceding ROS-induction. Our data indicate that ZnO NP toxicity is a result of cellular Zn^{2+} intake. Subsequently increased ROS-levels cause DNA damage. However, we found evidence for the assumption that DNA-DSBs could be caused by Zn^{2+} without the involvement of ROS.

- MicroRNA-triggered, cascaded and catalytic self-assembly of functional "DNAzyme ferris wheel" nanostructures for highly sensitive colorimetric detection of cancer cells
  Zhou, W.; Liang, W.; Li, X.; Chai, Y.; Yuan, R.; Xiang, Y. *Nanoscale* **2015**, *7*, 9055 – 9061.
  Abstract:



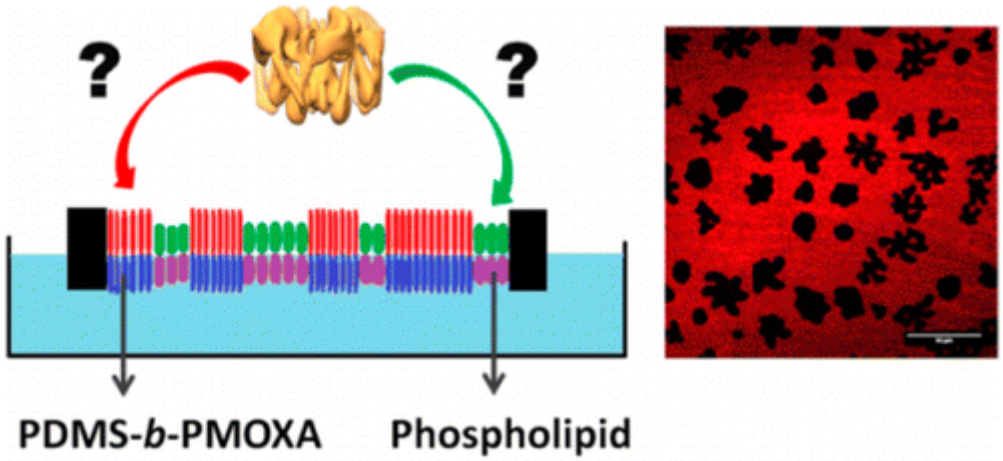
The construction of DNA nanostructures with various sizes and shapes has significantly advanced during the past three decades, yet the application of these DNA nanostructures for solving real problems is still in the early stage. On the basis of microRNA-triggered, catalytic self-assembly formation of the functional "DNAzyme ferris wheel" nanostructures, we show here a new signal amplification platform for highly sensitive, label-free and non-enzyme colorimetric detection of a small number of human prostate cancer cells. The microRNA (miR-141), which is catalytically recycled and reused, triggers isothermal self-assembly of a pre-designed, G-quadruplex sequence containing hairpin DNAs into "DNAzyme ferris wheel"-like nanostructures (in association with hemin) with horseradish peroxidase mimicking activity. These DNAzyme nanostructures catalyze an intensified color transition of the probe solution for highly sensitive detection of miR-141 down to 0.5 pM with the naked eye, and the monitoring of as low as 283 human prostate cancer cells can also, theoretically, be achieved in a colorimetric approach. The work demonstrated here thus offers new opportunities for the construction of functional DNA nanostructures and for the application of these DNA nanostructures as an effective signal amplification means in the sensitive detection of nucleic acid biomarkers.

- Simple Colorimetric Detection of Amyloid β -peptide (1–40) based on Aggregation of Gold Nanoparticles in the Presence of Copper Ions
  Zhou, Y.; Dong, H.; Liu, L.; Xu, M. *Small* **2015**, *11*, 2144-2149.
  Abstract:



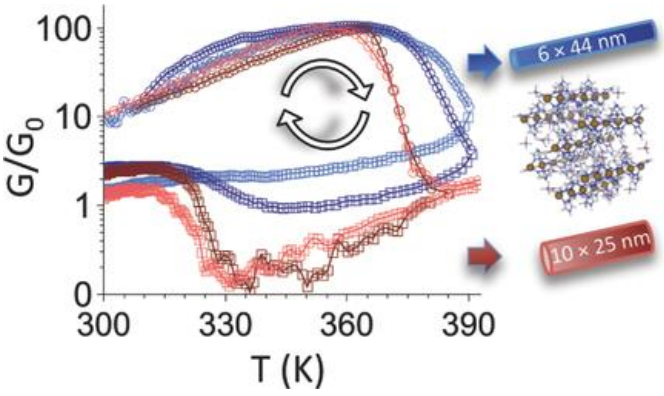
A simple method for specific colorimetric sensing of Alzheimer's disease related amyloid-βpeptide (Aβ) is developed based on the aggregation of gold nanoparticles in the presence of copper ion. The detection of limit for Aβ(1–40) is 0.6 nm and the promising results from practical samples (human serum) indicate the great potential for the routine detection.

- Hybrid Polymer–Lipid Films as Platforms for Directed Membrane Protein Insertion
  Kowal, J.; Wu, D.; Mikhalevich, V.; Palivan, C. G.; Meier, W. *Langmuir* **2015**, *31*, 4868-4877.
  Abstract:



Hybrids composed of amphiphilic block copolymers and lipids constitute a new generation of biological membrane-inspired materials. Hybrid membranes resulting from self-assembly of lipids and polymers represent adjustable models for interactions between artificial and natural membranes, which are of key importance, e.g., when developing systems for drug delivery. By combining poly(dimethylsiloxane)-*block*-poly(2-methyl-2-oxazoline) amphiphilic copolymers (PDMS-*b*-PMOXA) with various phospholipids, we obtained hybrid films with modulated properties and topology, based on phase separation, and the formation of distinct domains. By understanding the factors driving the phase separation in these hybrid lipid–polymer films, we were able to use them as platforms for directed insertion of membrane proteins. Tuning the composition of the polymer–lipids mixtures favored successful insertion of membrane proteins with desired topological distributions (in polymer or/and lipid regions). Controlled insertion and location of membrane proteins in hybrid films make these hybrids ideal candidates for numerous applications where specific spatial functionality is required.

- Spin Switching in Electronic Devices Based on 2D Assemblies of Spin-Crossover Nanoparticles
  Dugay, J.; Giménez-Marqués, M.; Kozlova, T.; Zandbergen, H. W.; Coronado, E.; van der Zant, H. S. J. *Adv. Mater.* **2015**, *27*, 1288–1293.
  Abstract:

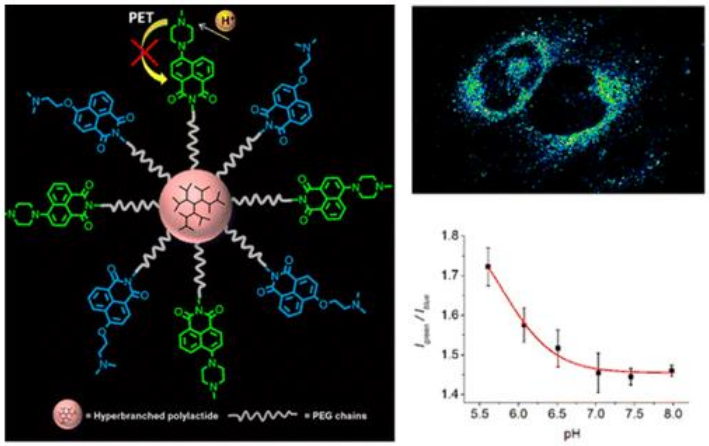


Two-dimensional assemblies of triazole-based spin-crossover nanoparticles (SCO NPs) presenting different morphologies are prepared and electrically characterized. The thermal hysteresis loop in the electrical conductance near room temperature correlates with the NP morphologies and their 2D organization. The unprecedentedly large difference – up to two orders of magnitude – in the electrical conductance of the two spin states is of interest for applications.

- Hydrogen-Terminated Si Nanowires as Label-Free Colorimetric Sensors in the Ultrasensitive and Highly Selective Detection of Fluoride Anions in Pure Water Phase
  Wang, H.; Fan, P.-H.; Tong, B.; Dong, Y.-P.; Ou, X.-M.; Li, F.; Zhang, X.-H. *Adv. Funct. Mater.* **2015**, *25*, 1506–1510.
  Abstract:

The detection of anions in pure water phase with colorimetric sensor is a long standing challenge. As one of the most important anions, F^- is associated with nerve gases and the refinement of uranium for nuclear weapons. However, limited by its anions nature, few of the reported colorimetric sensors can successfully applied to detect F^{-1} in pure water phase. This work designs a colorimetric sensor for F^{-1} pure water phase detection by taking the advantages of the strong specific binding between F and Si, as well as the color-changing property of H-terminated Si nanowires (SiNWs). The sensor demonstrates ultra-sensitivity, high selectivity, and good stability. The results reveal particular interest for the development of new type aqueous phase anions sensors with SiNWs.

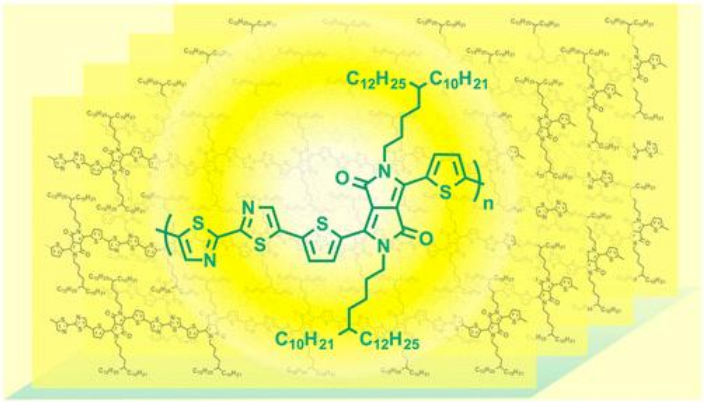
- Tunable Ratiometric Fluorescence Sensing of Intracellular pH by Aggregation-Induced Emission-Active Hyperbranched Polymer Nanoparticles
  Bao, Y.; De Keersmaecker, H.; Corneillie, S.; Yu, F.; Mizuno, H.; Zhang, G.; Hofkens, J.; Mendrek, B.; Kowalczuk, A.; Smet, M. *Chem. Mater.* **2015,** *27*, 3450-3455.
  Abstract:



Recently, ratiometric pH nanosensors have emerged as a robust tool for the fluorescence sensing and imaging, but there is no report of ratiometric sensors based on hyperbranched polymers for intracellular pH sensing. Herein, we describe the first example of hyperbranched polymer-based tunable fluorescent pH nanosensor with aggregation-induced emission activity, which exhibits great potential for ratiometric sensing of intracellular pH. These polymer nanoparticles can selectively accumulate in the acidic organelles of living cells by endocytosis process, and no obvious cytotoxicity was observed. The quantitative analysis of the intracellular pH values in HeLa cells was successfully conducted based on this new sensing platform. This platform provides a new choice for future

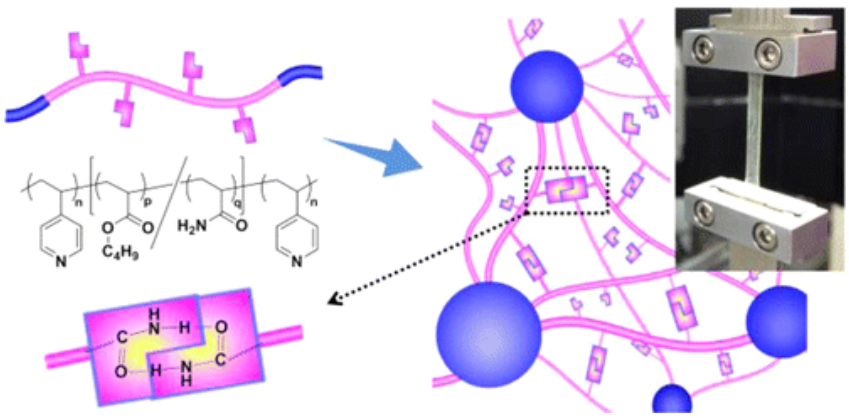
developments of ratiometric fluorescent nanosensors, targeting not only protons but also a variety of other analytes of biological interest, such as metal ions, anions, and other biomolecules.

- Molecular Engineering of Nonhalogenated Solution-Processable Bithiazole-Based Electron-Transport Polymeric Semiconductors
  Fu, B.; Wang, C.-Y.; Rose, B. D.; Jiang, Y.; Chang, M.; Chu, P.-H.; Yuan, Z.; Fuentes-Hernandez, C.; Kippelen, B.; Brédas, J.-L.; Collard, D. M.; Reichmanis, E. *Chem. Mater.* **2015,** *27*, 2928-2937.
  Abstract:



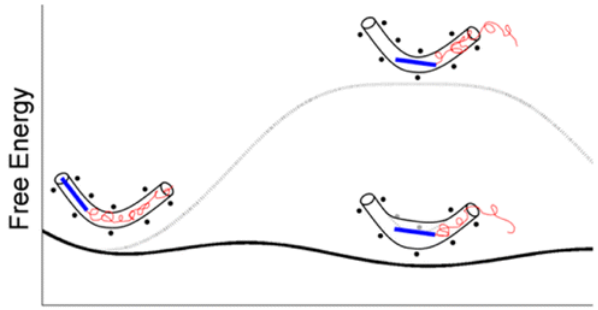
The electron deficiency and trans-planar conformation of bithiazole is potentially beneficial for the electron-transport performance of organic semiconductors. However, the incorporation of bithiazole into polymers through a facile synthetic strategy remains a challenge. Herein, 2,2′-bithiazole was synthesized in one step and copolymerized with dithienyldiketopyrrolopyrrole to afford poly(dithienyldiketopyrrolopyrrole-bithiazole), **PDBTz**. **PDBTz** exhibited electron mobility reaching 0.3 $cm^2 V^{-1} s^{-1}$ in organic field-effect transistor (OFET) configuration; this contrasts with a recently discussed isoelectronic conjugated polymer comprising an electron-rich bithiophene and dithienyldiketopyrrolopyrrole, which displays merely hole-transport characteristics. This inversion of charge-carrier transport characteristics confirms the significant potential for bithiazole in the development of electron-transport semiconducting materials. Branched 5-decylheptacyl side chains were incorporated into **PDBTz** to enhance polymer solubility, particularly in nonhalogenated, more environmentally compatible solvents. **PDBTz** cast from a range of nonhalogenated solvents exhibited film morphologies and field-effect electron mobility similar to those cast from halogenated solvents.

- Mechanical Property Enhancement of ABA Block Copolymer-Based Elastomers by Incorporating Transient Cross-Links into Soft Middle Block
  Hayashi, M.; Matsushima, S.; Noro, A.; Matsushita, Y. *Macromolecules* **2015**, *48*, 421–431.
  Abstract:



We propose a new strategy to enhance mechanical properties of ABA triblock copolymer-based elastomers by incorporating transient cross-links into the soft middle block. An ABA triblock-type copolymer, poly(4-vinylpyridine)-*b*-[(poly(butyl acrylate)-*co*-polyacrylamide]-*b*-poly(4-vinylpyridine) (P–Ba–P), was synthesized via RAFT polymerization. In the molecular design, the poly(4-vinylpyridine) (P) end blocks with a high T_g formed pseudo-cross-link domains due to segregation against the soft Ba middle block, while acrylamide units on the middle block formed self-complementary hydrogen bonding, serving as transient cross-links. According to tensile tests, the Young's modulus, elongation at break, maximum stress, and material toughness were 1.9 MPa, 200%, 2.6 MPa, and 2.8 MJ/m^3, respectively. Comparison between mechanical properties of P–Ba–P and those of another triblock copolymer, poly(4-vinylpyridine)-*b*-poly(butyl acrylate)-*b*-poly(4-vinylpyridine) (P–B–P), revealed that P–Ba–P showed larger Young's modulus, longer elongation at break, and larger maximum tensile stress than P–B–P. Particularly, the material toughness of P–Ba–P (2.8 MJ/m^3) was more than 100 times larger than that of P–B–P (0.02 MJ/m^3). Rheological analysis on the basis of sticky Rouse relaxation of Ba middle block of P–Ba–P suggested that the hydrogen bonds on the middle block serve as dynamic stickers in elastic strands of elastomers under stress. Such dynamic behavior of the hydrogen bonds could prevent local concentration of applied stress for activating break/failure of the materials during elongation, leading to mechanical property enhancement of the materials. In addition, zinc chloride was blended with P–Ba–P to form metal–ligand coordination in the P end block domains, which also affected the mechanical properties of the elastomers.

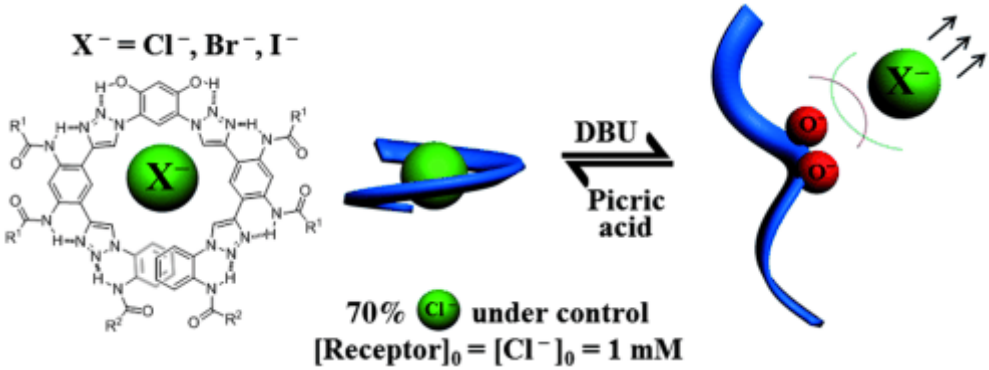
- Self-Diffusion and Constraint Release in Isotropic Entangled Rod− Coil Block Copolymers
  Wang, M.; Timachova, K.; Olsen, B. D.
  Abstract:



Understanding dynamic relaxation mechanisms in self-diffusion and constraint release processes of rod−coil block copolymers is important for many technological applications that employ neat melts or concentrated solutions. Using a model system composed of poly(alkoxyphenylenevinylene) rods and polyisoprene coils, reptation theories of entangled rod−coil block copolymers are investigated in the isotropic melt state. Self-diffusion was measured by forced Rayleigh scattering using a red laser line and a new blue photoswitchable dye that allow operation above the bandgap of most semiconducting polymers. In contrast to previous tracer studies where the diffusion of rod−coils through a coil homopolymer matrix is slowed relative to coil homopolymers because of a mismatch in the curvature of the rod and coil entanglement tubes, slowed diffusion is only present in self-diffusion measurements above a critical molecular weight. An activated reptation mechanism with constraint release is proposed as a modification to the description of entangled rod−coil block copolymer dynamics, where the slowing occurs when the time scale of rod block reptation is faster than the reorganization of the surrounding entanglement tube. This mechanism is supported by additional tracer diffusion experiments on polyalanine-b-poly(ethylene oxide) diblocks in aqueous entangled poly(ethylene oxide) matrix solutions and Kremer−Grest simulations where the matrix

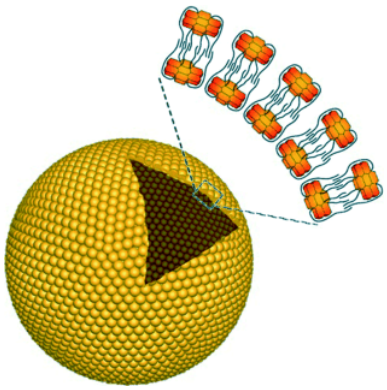
molecular weight is varied. The slowing of tracer diffusion in rod−coil block copolymers relative to coil homopolymers is significantly weaker for smaller matrix polymers, confirming the proposed constraint release effects.

- Acid/Base-Mediated Uptake and Release of Halide Anions with a Preorganized Aryl-Triazole Foldamer
  Zhao, W.; Wang, Y.; Shang, J.; Che, Y.; Jiang, H. *Chem. Eur. J.* **2015**, *21*, 7731–7735.
  Abstract:



A new approach for the construction of artificial receptors capable of selectively uptake and release of halides to mimic the biological halide ions pumps is developed, in which the preorganized aryl-triazole foldamer was designed to bear a resorcinolic group in the central strand as a switch regulator. By using 1,8-diazabicyclo[5.4.0]undec-7-ene/picric acid as the trigger, the foldamer can be switched between “w”-shape and helical conformation. Due to the large, half-open cavity as well as the additional electrostatic repulsion between oxyanions and guest halide, the foldamer in “w”-shape possesses a much weaker affinity for chloride, bromide, and iodide anions than those in the helical conformation in 6:94 (v/v) $[D_6]$DMSO/$CDCl_3$. When the foldamer and chloride ions have the same initial concentrations of 1 mM, 70 % chloride ions in the solution could be reversibly bound or released upon switching.

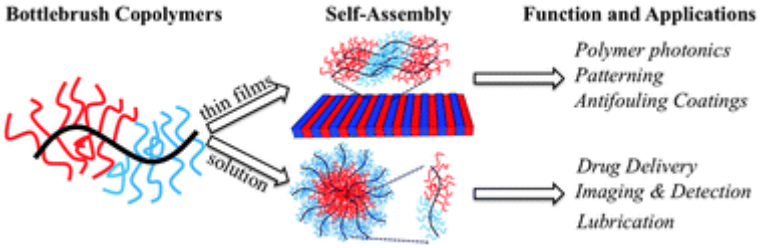
- Unilamellar Vesicles from Amphiphilic Graphene Quantum Dots
  Nandi, S.; Kolusheva, S.; Malishev, R.; Trachtenberg, A.; Vinod, T. P.; Jelinek , R *Chem. Eur. J.* **2015**, *21*, 7755–7759.
  Abstract:



Graphene quantum dots (GQDs) have attracted considerable interest due to their unique physicochemical properties and various applications. For the first time it is shown that GQDs surface-functionalized with hydrocarbon chains (i.e., amphiphilic GQDs) self-assemble into unilamellar spherical vesicles in aqueous solution. The amphiphilic GQD vesicles exhibit multicolor luminescence that can be readily exploited for membrane studies by fluorescence spectroscopy and microscopy.

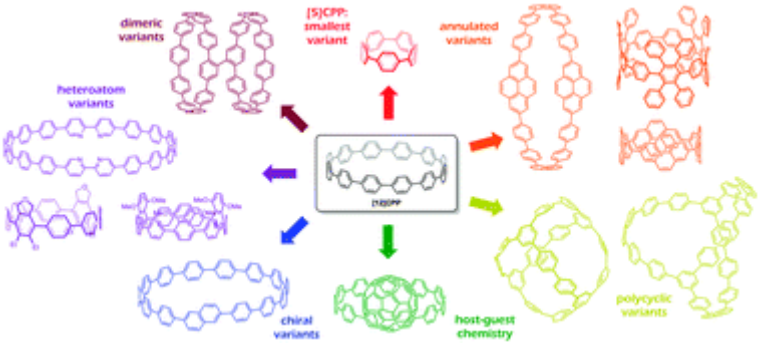
The GQD vesicles were used for microscopic analysis of membrane interactions and disruption by the peptide beta-amyloid.

- Structure, function, self-assembly, and applications of bottlebrush copolymers
  Verduzco, R.; Li, X.; Pesek, S. L.; Stein, G. E. *Chem. Soc. Rev.* **2015**, *44*, 2405-2420.
  Abstract:



Bottlebrush polymers are a type of branched or graft polymer with polymeric side-chains attached to a linear backbone, and the unusual architectures of bottlebrushes provide a number of unique and potentially useful properties. These include a high entanglement molecular weight, enabling rapid self-assembly of bottlebrush block copolymers into large domain structures, the self-assembly of bottlebrush block copolymer micelles in a selective solvent even at very low dilutions, and the functionalization of bottlebrush side-chains for recognition, imaging, or drug delivery in aqueous environments. This review article focuses on recent developments in the field of bottlebrush polymers with an emphasis on applications of bottlebrush copolymers. Bottlebrush copolymers contain two (or more) different types of polymeric side-chains. Recent work has explored the diverse properties and functions of bottlebrush polymers and copolymers in solutions, films, and melts, and applications explored include photonic materials, bottlebrush films for lithographic patterning, drug delivery, and tumor detection and imaging. We provide a brief introduction to bottlebrush synthesis and physical properties and then discuss work related to: (i) bottlebrush self-assembly in melts and bulk thin films, (ii) bottlebrushes for photonics and lithography, (iii) bottlebrushes for small molecule encapsulation and delivery in solution, and (iv) bottlebrush micelles and assemblies in solution. We briefly discuss three potential areas for future research, including developing a more quantitative model of bottlebrush self-assembly in the bulk, studying the properties of bottlebrushes at interfaces, and investigating the solution assembly of bottlebrush copolymers.

- Cycloparaphenylenes and related nanohoops
  Lewis, S. E. *Chem. Soc. Rev.* **2015**, *44*, 2221-2304.
  Abstract:



The first synthesis of a cyclic oligophenylene possessing a radial π system was reported in 2008. In the short period that has elapsed since, there has been an ever-increasing level of interest in molecules of this type, as evidenced by the volume of publications in this area. This interest has been driven by the highly unusual properties of these molecules in comparison to their linear

oligoarene analogues, as well as the diverse array of potential applications for them. Notably, CPPs and related structures were proposed as viable templates for the bottom-up synthesis of single-walled carbon nanotubes (SWCNTs), a proposition which has recently been realised. This review gives a comprehensive and strictly chronological (by date of first online publication) treatment of literature reports from the inception of the field, with emphasis on both synthesis and properties of CPPs and related nanohoops. (The scope of this review is restricted to molecules possessing a radial π system consisting entirely of subunits which are aromatic in isolation, *e.g.* CPPs, but not cycloparaphenyleneacetylenes or cyclopolyacetylenes).