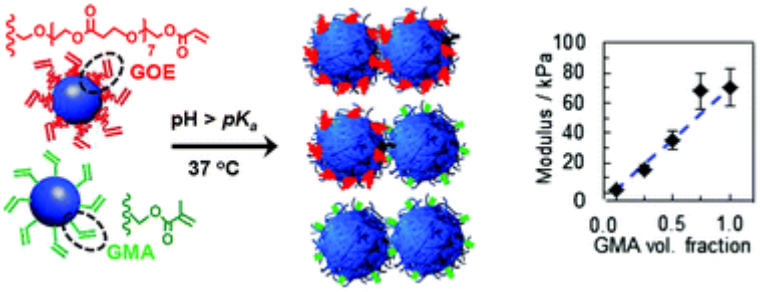
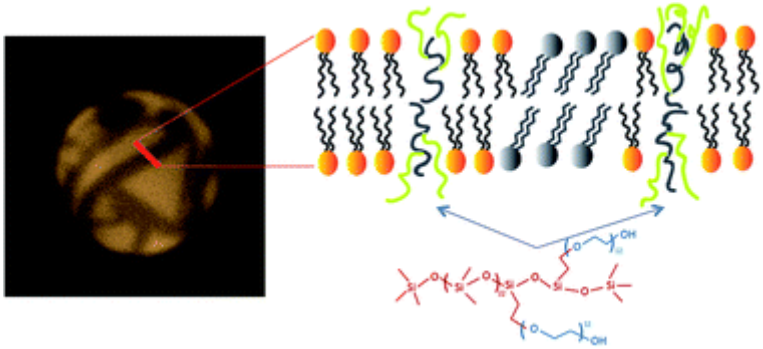
- Swelling and mechanical properties of hydrogels composed of binary blends of inter-linked pH-responsive microgel particles
  Milani, A. H.; Bramhill, J.; Freemont, A. J.; Saunders, B. R. *Soft Matter* **2015**, *11*, 2586-2595.
  Abstract:



We show that a new type of hydrogel can be prepared by covalently inter-linking binary blends of microgel (MG) particles and that the swelling ratio and modulus of the gels can be predicted from their composition. In previous work we established that physical gels of glycidyl methacrylate (GMA) functionalised poly(methyl methacrylate-co-methacrylic acid-co-ethyleneglycol dimethacrylate) microgel particles (GMA-MG) could be covalently inter-linked to give hydrogels, termed doubly crosslinked microgels, DX MGs. We build on this concept here by investigating the properties of DX MGs containing binary blends of GMA-MG particles and glycidyl oligo(ether ester) acrylate-functionalised microgel particles (GOE-MG). These new hydrogels were assembled by inter-linking nanoscale MG building blocks in the absence of small molecule monomers or crosslinkers. The volume fraction of GMA-MG particles used to prepare the GOE–GMA DX MGs was systematically varied. Rheology data showed that inclusion of GMA-MG and GOE-MG within the GOE–GMA DX MGs increased the modulus and yield strain, respectively, compared to the values measured for the respective physical gels. The data for the covalent GOE–GMA DX MG gels showed that the ductility increased with increasing GOE-MG content. GOE provided covalent inter-linking of the MG particles and also acted as a lubricant between particles due to its low T_g. By demonstrating compositionally determined swelling and mechanical properties for DX MG gels prepared using binary blends of MG particles, this study introduces a new, widely applicable, hydrogel construction assembly concept that is not available for conventional hydrogels.

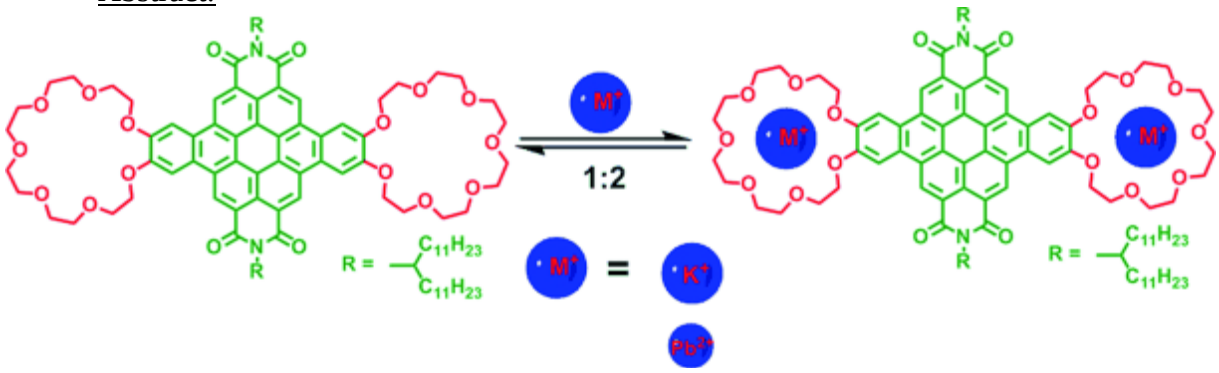
- Hybrid copolymer-phospholipid vesibles: phase separation resembling mixed phospholipid lamellae, but with mechanical stability and control
  Chen, D.; Santore, M. M. *Soft. Matter* **2015**, *11*, 2617-2626.
  Abstract:



Vesicles whose bilayer membranes contain phospholipids mixed with co-polymers or surfactants comprise new hybrid materials having potential applications in drug delivery, sensors, and biomaterials. Here we describe a model polymer–phospholipid hybrid membrane system exhibiting strong similarities to binary phospholipid mixtures, but with more robust

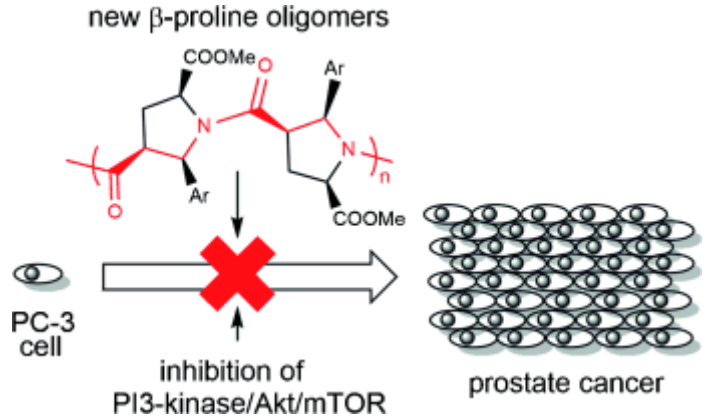
membrane mechanics. A lamella-forming graft copolymer, PDMS-*co*-PEO (polydimethylsiloxane-*co*-polyethylene oxide) was blended with a high melting temperature phospholipid, DPPC (1,2-dipalmitoyl-*sn*-*glycero*-3-phosphocholine), over a broad compositional range. The resulting giant hybrid unilamellar vesicles were compared qualitatively and quantitatively to analogous mixed phospholipid membranes in which a low melting temperature phospholipid, DOPC (1,2-dioleoyl-*sn*-*glycero*-3-phosphocholine), was blended with DPPC. The mechanical properties of the hybrid vesicles, even when phase separated, were robust with high lysis stresses and strains approaching those of the pure copolymer vesicles. The temperature-composition phase diagram of the hybrid vesicles closely resembled that of the mixed phospholipids; with only slightly greater nonidealities in the hybrid compared with DOPC/DPPC mixed membranes. In both systems, it was demonstrated that tension could be used to manipulate DPPC solidification into domains of patchy or striped morphologies that exhibited different tracer incorporation. The patch and stripe-shaped domains are thought to be different solid DPPC polymorphys: ripple and tilt (or gel). This work demonstrates that in mixed-phospholipid bilayers where a high-melting phospholipid solidifies on cooling, the lower-melting phospholipid may be substituted by an appropriate copolymer to improve mechanical properties while retaining the underlying membrane physics.

- A Crown Ether Decorated Dibenzocoronene Tetracarboxdiimide Chromophore: Synthesis, Sensing, and Self-Organization
  Ma, Y.; Marszalek, T.; Yuan, Z.; Stangenberg, R.; Pisula, W.; Chen, L.; Müllen, K. *Chem. Asian J.* **2015**, *10*, 139–143.
  Abstract:



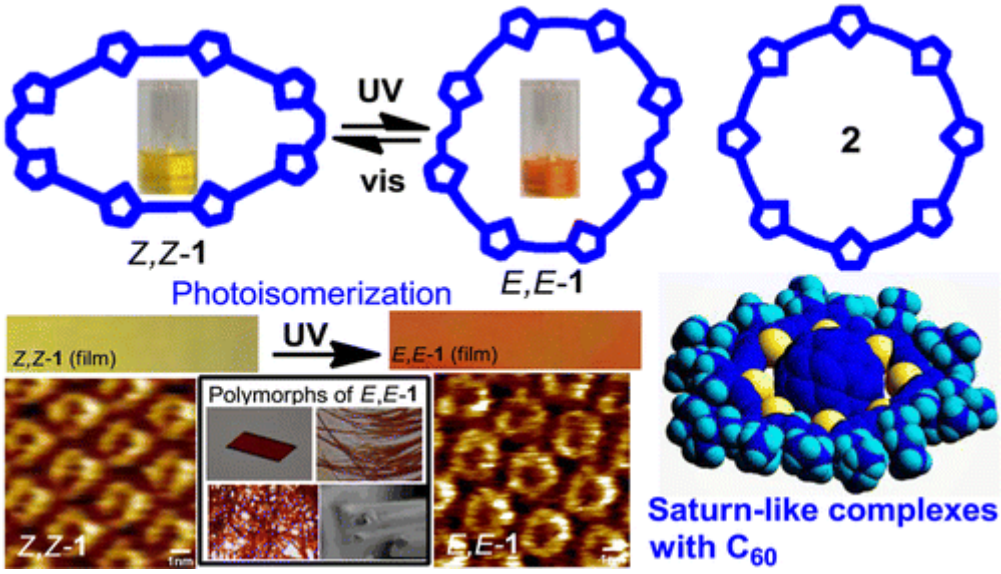
Sensing Sensibility: A macrocyclic dibenzocoronene tetracarboxdiimide containing two benzo-21-crown-7 groups has been synthesized. It shows liquid-crystalline behavior and selectively binds Pb^{2+} or K^{+} to form 1:2 complexes in solution. The complexation leads to a significant increase of fluorescence; the surface organization of discotic columnar structures, in the solid-state, can be controlled by selective ion binding.

- Structural Studies and Anticancer Activity of a Novel Class of β-Peptides
  Kudryavtsev, K. V.; Yu, C.-C.; Ivantcova, P. M.; Polshakov, V. I.; Churakov, A. V.; Bräse, S.; Zefirov, N. S.; Guh, J.-H. *Chem. Asian J.* **2015**, *10*, 383–389.
  Abstract:



Functionalized oligomeric organic compounds with well-defined β-proline scaffold have been synthesized by a cycloadditive oligomerization approach in racemic and enantiopure forms. The structure of the novel β-peptides was investigated by NMR spectroscopic and X-ray methods determining the conformational shapes of the β-proline oligomers in solution and solid states. The main structural elements subject to conformational switches are β-peptide bonds between 5-arylpyrrolidine-2-carboxylic acid units existing in *Z*/*E* configurations. The whole library of short β-peptides and intermediate acrylamides has been tested on antiproliferative activity towards the hormone-refractory prostate cancer cell line PC-3 revealing several oligomeric compounds with low micromolar and submicromolar activities. Bromine-substituted dimeric and trimeric acrylamides induced caspase-dependent apoptosis of PC-3 cells through cell-cycle arrest and mitochondrial damage.

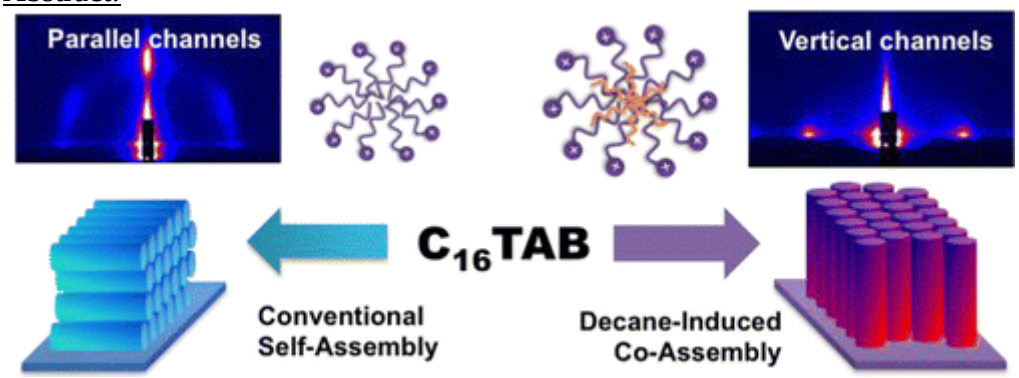
- Synthesis, Structures, and Photophysical Properties of π Expanded Oligothiophene 8-mers and Their Saturn-Like C_{60} Complexes
  Shimizu, H, González, J. D. C.; Hasegawa, M.; Nishinaga, T.; Haque, T.; Takase, M.; Otani, H.; Rabe, J. P.; Iyoda, M. *J. Am. Chem. Soc.* **2015**, *137*, 3877–3885.
  Abstract:



Two isomers of a multifunctional π-expanded macrocyclic oligothiophene 8-mer, *E*,*E*-**1** and *Z*,*Z*-**1**, were synthesized using a McMurry coupling of a dialdehyde composed of four 2,5-thienylene and three ethynylene units under high dilution conditions. On the other hand, cyclo[8](2,5-thienylene-ethynylene) **2** was synthesized by intramolecular Sonogashira cyclization of ethynyl bromide **5**. From STM measurements, both *E*,*E*-**1** and *Z*,*Z*-**1** formed self-assembled monolayers at the solid–liquid interface to produce porous networks, and from X-ray analyses of *E*,*E*-**1** and **2**, both compounds had a round shape with a honeycomb stacked

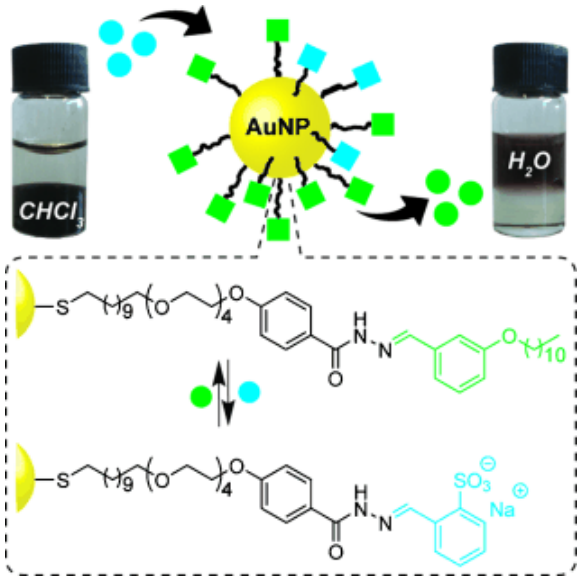
structure. *E*,*E*-**1** formed various fibrous polymorphs due to nanophase separation of the macrorings. *E*,*E*-**1** and *Z*,*Z*-**1** in solution exhibited photochromism upon irradiation with visible and UV light, respectively, and this photoisomerization was confirmed by using STM. Furthermore, amorphous films of *Z*,*Z*-**1** and *E*,*E*-**1** showed photoisomerization, although single crystals, fibers, and square tubes of *E*,*E*-**1** remained unchanged under similar conditions. *E*,*E*-**1** with a 12.5–14.7 Å inner cavity incorporated fullerene C_{60} in the cavity in solution and the solid state to produce a Saturn-like complex, whose structure was determined by X-ray analysis. **2** also formed a Saturn-like complex with C_{60} in the solid state. These Saturn-like complexes are stabilized by van der Waals interactions between the sulfur atoms of 8-mer and C_{60}. The complexes exhibited charge-transfer interactions in the solid state. Like *E*,*E*-**1**, Saturn-like complex *E*,*E*-**1**⊃C_{60} formed small cube and fiber structures depending on the solvent used, whereas those of Saturn-like complex **2**⊃C_{60} were limited due to the rigidity of the macroring of **2**.

- A General Method for Growing Large Area Mesoporous Silica Thin Films on Flat Substrates with Perpendicular Nanochannels
  Kao, K.-C.; Lin, C.-H.; Chen, T.-Y.; Liu, Y.-H.; Mou, C.-Y. *J. Am. Chem. Soc.* **2015**, *137*, 3779–3782.
  Abstract:



Here we introduce a new synthetic approach to grow mesoporous silica thin films with vertical mesochannels on centimeter-sized substrates via an oil-induced co-assembly process. Adding an oil, i.e., decane, into a CTAB−EtOH−TEOS ammonia solution leads to thin-film formation of mesoporous silica of controlled thickness between 20 and 100 nm with vertical mesochannels on various surfaces. The vertical mesoporous channels were evidenced by grazing incidence small-angle X-ray scattering (GISAXS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) characterizations. Decane played two roles: (a) as a pore expansion agent (up to 5.7 ± 0.5 nm) and (b) inducing vertically oriented hexagonal mesophases of micelle−silica composite. The production of periodic and vertical nanochannels is very robust, over many different substrate surfaces (from silicon to polystyrene), various silica precursors (TEOS, fumed silica, or zeolite seed), and many oils (decane, petroleum ether, or ethyl acetate). This wide robustness in the formation of vertical nanophases is attributed to a unique mechanism of confined synthesis of surfactant−silicate between two identical thin layers of oils on a substrate.

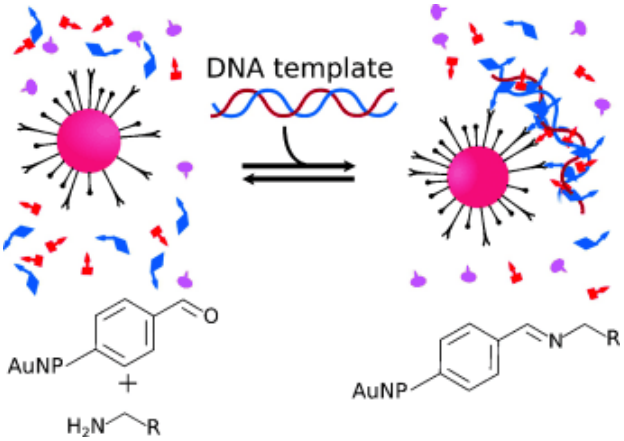
- Reversible Control of Nanoparticle Functionalization and Physicochemical Properties by Dynamic Covalent Exchange
  Sala, F.; Kay, E. R. *Angew.Chem. Int. Ed.* **2015**, *54*, 4187–4191.
  Abstract:



Ligand swap shop: Dynamic covalent hydrazone exchange within a homogeneous monolayer bound to the surface of gold nanoparticles is tracked in real time. The introduction of appropriately functionalized aldehyde exchange units allows reversible tuning of nanoparticle solvophilicity and presents a generalizable covalent approach to postsynthetic modification of nanoparticle functionalization and properties.

Existing methods for the covalent functionalization of nanoparticles rely on kinetically controlled reactions, and largely lack the sophistication of the preeminent oligonucleotide-based noncovalent strategies. Here we report the application of dynamic covalent chemistry for the reversible modification of nanoparticle (NP) surface functionality, combining the benefits of non-biomolecular covalent chemistry with the favorable features of equilibrium processes. A homogeneous monolayer of nanoparticle-bound hydrazones can undergo quantitative dynamic covalent exchange. The pseudomolecular nature of the NP system allows for the in situ characterization of surface-bound species, and real-time tracking of the exchange reactions. Furthermore, dynamic covalent exchange offers a simple approach for reversibly switching—and subtly tuning—NP properties such as solvophilicity.

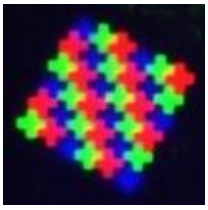
- Localized Template-Driven Functionalization of Nanoparticles by Dynamic Combinatorial Chemistry
  Nowak, P.; Saggiomo, V.; Salehian, F.; Colomb-Delsuc, M.; Han, Y.; Otto, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 4192–4197.
  Abstract:



We have developed a method for the localized functionalization of gold nanoparticles using imine-based dynamic combinatorial chemistry. By using DNA templates, amines were grafted

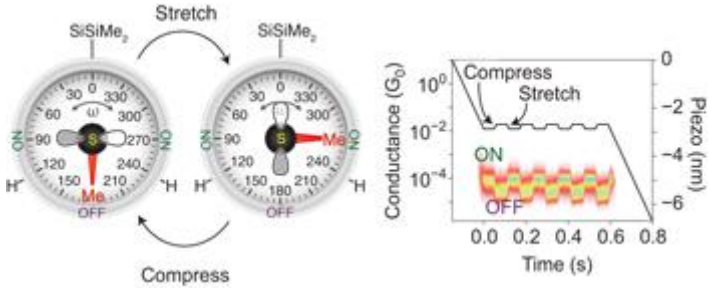
on the aldehyde-functionalized nanoparticles only if and where the nanoparticles interacted with the template molecules. Functionalization of the nanoparticles was controlled solely by the DNA template; only amines capable of interacting with DNA were bound to the surface. Interestingly, even though our libraries contained only a handful of simple amines, the DNA sequence influenced their attachment to the surface. Our method opens up new opportunities for the synthesis of multivalent, nanoparticle-based receptors for biomacromolecules.

- Trehalose glycopolymer resists allow direct writing of protein patterns by electron-beam lithography
  Bat, E.; Lee, J.; Lau, U. Y.; Maynard, H. D. *Nature Comm.* **2015**, *6*, 6654.
  Abstract:



Direct-write patterning of multiple proteins on surfaces is of tremendous interest for a myriad of applications. Precise arrangement of different proteins at increasingly smaller dimensions is a fundamental challenge to apply the materials in tissue engineering, diagnostics, proteomics and biosensors. Herein, we present a new resist that protects proteins during electron-beam exposure and its application in direct-write patterning of multiple proteins. Polymers with pendant trehalose units are shown to effectively crosslink to surfaces as negative resists, while at the same time providing stabilization to proteins during the vacuum and electron-beam irradiation steps. In this manner, arbitrary patterns of several different classes of proteins such as enzymes, growth factors and immunoglobulins are realized. Utilizing the high-precision alignment capability of electron-beam lithography, surfaces with complex patterns of multiple proteins are successfully generated at the micrometre and nanometre scale without requiring cleanroom conditions.

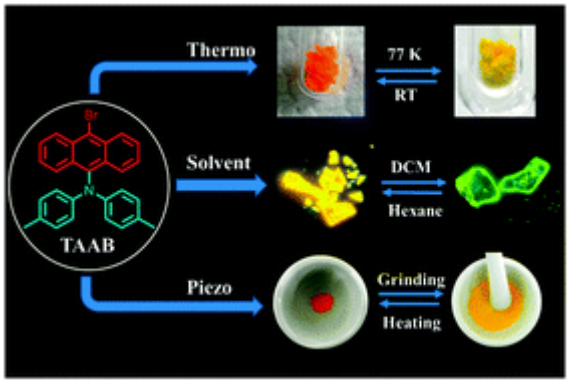
- Stereoelectronic switching in single-molecule junctions
  Su, T. A.; Li, H.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. *Nature Chem.* **2015**, *7*, 215-220.
  Abstract:



A new intersection between reaction chemistry and electronic circuitry is emerging from the ultraminiaturization of electronic devices. Over decades chemists have developed a nuanced understanding of stereoelectronics to establish how the electronic properties of molecules relate to their conformation; the recent advent of single-molecule break-junction techniques provides the means to alter this conformation with a level of control previously unimagined. Here we unite these ideas by demonstrating the first single-molecule switch that operates through a stereoelectronic effect. We demonstrate this behaviour in permethyloligosilanes with methylthiomethyl electrode linkers. The strong σ conjugation in the oligosilane backbone couples the stereoelectronic properties of the sulfur–methylene σ bonds that

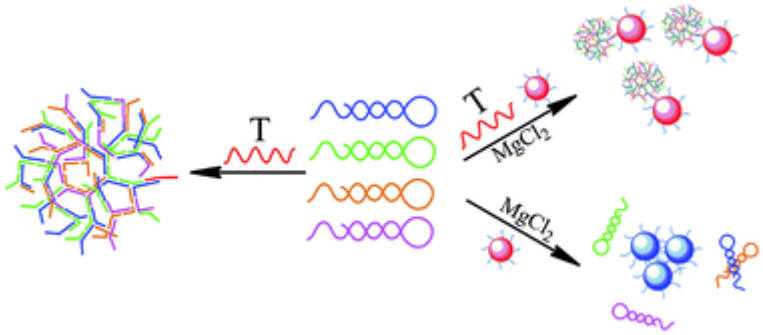
terminate the molecule. Theoretical calculations support the existence of three distinct dihedral conformations that differ drastically in their electronic character. We can shift between these three species by simply lengthening or compressing the molecular junction, and, in doing so, we can switch conductance digitally between two states.

- Bromo induced reversible distinct color switching of a structurally simple donor-acceptor molecule by vapo, piezo and thermal stimuli
  Rajamalli, P.; Gandeepan, P.; Huang, M.-J.; Cheng, C.-H. *J. Mater. Chem. C* **2015**, *3*, 3329-3335.
  Abstract:



Altering the luminescence properties of a material through external factors is an attractive feature that has the potential for various luminescence-related applications. Here, we report the synthesis and luminescence properties of two anthracene-based donor acceptor compounds, N,N-di-p-tolylanthracen-9-amine (**TAA**) and 10-bromo-N,N-di-p-tolylanthracen-9-amine (**TAAB**). In the solid state, the bromo-substituted compound **TAAB** shows reversible visible switching of the emission by external stimuli such as solvent, mechanical grinding and temperature. Single crystal X-ray studies, powder-XRD analysis and theoretical calculations reveal that switchable emission originated from the different stacking modes of **TAAB**. Furthermore, we have found that the bromo group interaction in the solid state plays a crucial role in this tunable emission. The other anthracene-based compound **TAA** does not show such switching of the emission by external stimuli. The observed changes in the luminescence of **TAAB** by external stimuli suggest potential applications in rewritable optical media, sensors, and optoelectronic devices.

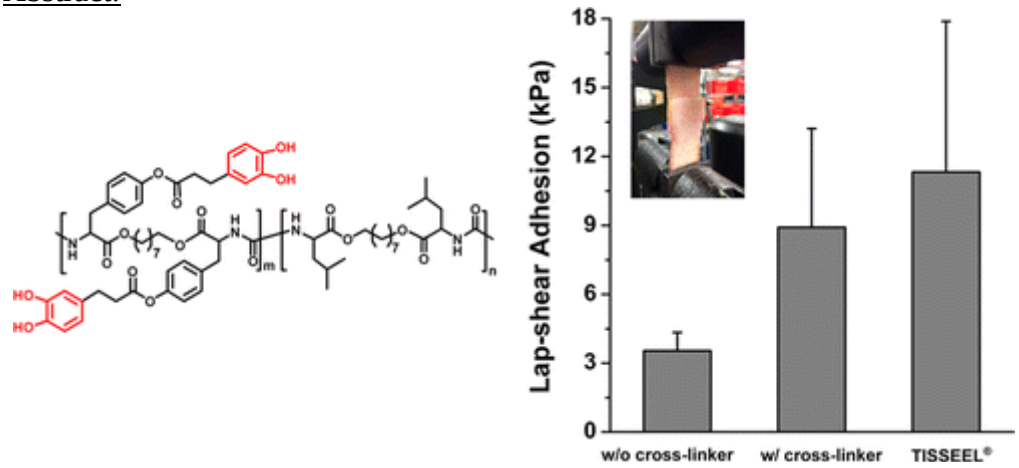
- Three-dimensional DNA nanostructures for colorimetric assay of nucleic acids
  Ma, C.; Wu, Z.; Wang, W.; Jiang, Q.; Shi, C. *J. Mater. Chem. B* **2015**, *3*, 2853-2857.
  Abstract:



Here, we propose a kinetically controlled DNA self-assembly pathway based on exponential hairpin assembly (EHA) to obtain a novel DNA network-like structure. This method is very simple over existing DNA self-assembly techniques, only requiring the input of four DNA hairpins to form dendritic nanostructures. AFM imaging reveals the expected dendritic

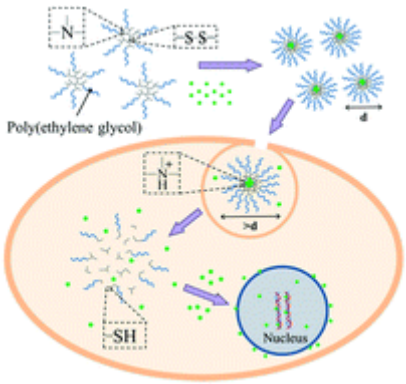
nanostructures, and they interweave to form a regular nanoporous structure that has a mesh size ranging from 200 to 400 nm. The network-like structure is very large and almost isotropic along all directions. At present, so large and regular self-assembly nanomaterials are very rare. The DNA network can potentially be used as a nanoporous material and a general signal carrier for bioanalytical application. As a model, the DNA nanomaterial has been successfully applied to detect nucleic acids coupled with the AuNP colorimetric strategy with a detection limit of 25 pM for the naked eye within 15 min.

- Adhesion Properties of Catechol-Based Biodegradable Amino AcidBased Poly(ester urea) Copolymers Inspired from Mussel Proteins
  Zhou, J.; Defante, A. P.; Lin, F.; Xu, Y.; Yu, J.; Gao, Y.; Childers, E.; Dhinojwala, A.; Becker, M. L. *Biomacromolecules* **2015**, *16*, 266–274.
  Abstract:



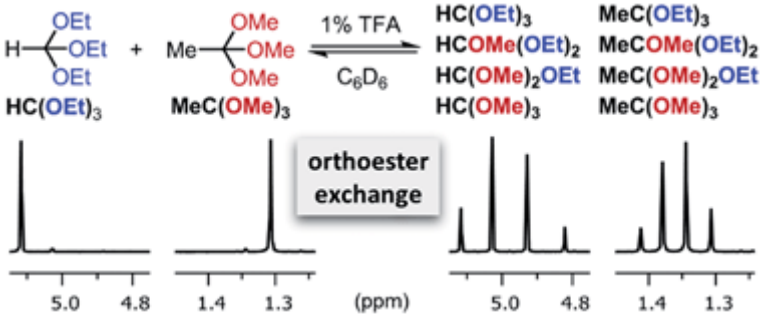
Amino acid-based poly(ester urea) (PEU) copolymers functionalized with pendant catechol groups that address the need for strongly adhesive yet degradable biomaterials have been developed. Lap-shear tests with aluminum adherends demonstrated that these polymers have lap-shear adhesion strengths near 1 MPa. An increase in lapshear adhesive strength to 2.4 MPa was achieved upon the addition of an oxidative cross-linker. The adhesive strength on porcine skin adherends was comparable with commercial fibrin glue. Interfacial energies of the polymeric materials were investigated via contact angle measurements and Johnson−Kendall−Roberts (JKR) technique. The JKR work of adhesion was consistent with contact angle measurements. The chemical and physical properties of PEUs can be controlled using different diols and amino acids, making the polymers candidates for the development of biological glues for use in clinical applications.

- pH- and redox-responsive self-assembly of amphiphilic hyperbranched poly(amido amine)s for controlled doxorubicin delivery
  Cheng, W.; Kumar, J. N.; Zhang, Y.; Liu, Y. *Biomater. Sci.* **2015**, *3*, 597-607.
  Abstract:



Vinyl-terminated hyperbranched poly(amido amine)s is obtained by Michael addition polymerization of 4-(aminomethyl)piperidine (AMPD) with a double molar N,N-cystaminebis(acrylamide) (BAC). Then an amphiphilic hyperbranched poly(BAC2-AMPD1)-PEG is produced via converting the vinyl groups to amines followed by PEGylation. Transmission electron microscopy (TEM), dynamic light scattering (DLS), and 1H nuclear magnetic resonance (NMR) results indicate that the micelles can be obtained via self-assembly of hyperbranched poly(BAC2-AMPD1)-PEG. Further an anti-cancer drug, doxorubicin (DOX), can be loaded into the micelles. pH- and redox-response of the micelles of hyperbranched poly(BAC2AMPD1)-PEG without and with DOX are investigated. The results of confocal microscopy and flow cytometry reflect that FITC tagged or DOX loaded micelles of hyperbranched poly(BAC2-AMPD1)-PEG can enter HepG2 and MCF-7 cells, and DOX can be observed in the nucleus of the cells. The cytotoxicity of the micelles without and with DOX is evaluated in HepG2 and MCF-7 cells, and the efficacy to kill the cancer cells is discussed in comparison with free DOX.

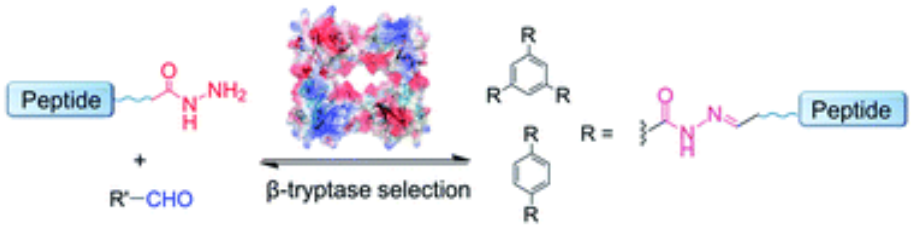
- Orthoester exchange: a tripodal tool for dynamic covalent and systems chemistry
  Brachvogel, R.-C.; von Delius, M. *Chem. Sci.* **2015**, *6*, 1399-1403.
  Abstract:



Reversible covalent reactions have become an important tool in supramolecular chemistry and materials science. Here we introduce the acid-catalyzed exchange of O,O,O-orthoesters to the toolbox of dynamic covalent chemistry. We demonstrate that orthoesters readily exchange with a wide range of alcohols under mild conditions and we disclose the first report of an orthoester metathesis reaction. We also show that dynamic orthoester systems give rise to pronounced metal template effects, which can best be understood by agonistic relationships in a three-dimensional network analysis. Due to the tripodal architecture of orthoesters, the exchange process described herein could find unique applications in dynamic polymers, porous materials and host–guest architectures.

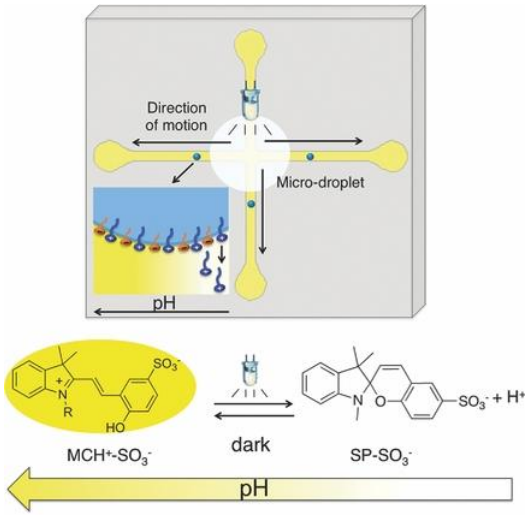
- Discovery of potent inhibitors of human β-tryptase from pre-equilibrated dynamic combinatorial libraries
  Jiang, Q.-Q.; Sicking, W.; Ehlers, M.; Schmuck, C. *Chem. Sci.* **2015**, *6*, 1792-1800.

Abstract:



Pre-equilibrated dynamic combinatorial libraries based on acyl hydrazone interchange of peptide-derived hydrazides and di- and tri-aldehydes have been used to discover potent inhibitors with nanomolar affinities for β-tryptase. To identify potent inhibitors the activity of the full library containing 95 members was compared with those of sub-libraries in which individual building blocks were missing. The most active library members contain a rigid central aromatic scaffold with three cationic peptide arms. The arms of the best inhibitors also contained a tailor-made GCP oxoanion binding motif attached to a lysine side chain. The most potent tri-armed hydrazones with peptide arms GKWR or GKWK(GCP) were shown to inhibit β-tryptase (Kica. 10–20 nM) reversibly, non-competitively and selectively (compared to related serine proteases, e.g. trypsin and chymotrypsin), most likely by binding to the protein surface, also in agreement with molecular modelling calculations. These new inhibitors are one order of magnitude more efficient than related tetravalent inhibitors obtained from previous work on a split-mix-combinatorial library and were identified with significantly less effort, demonstrating the usefulness of this approach for the identification of enzyme inhibitors in general.

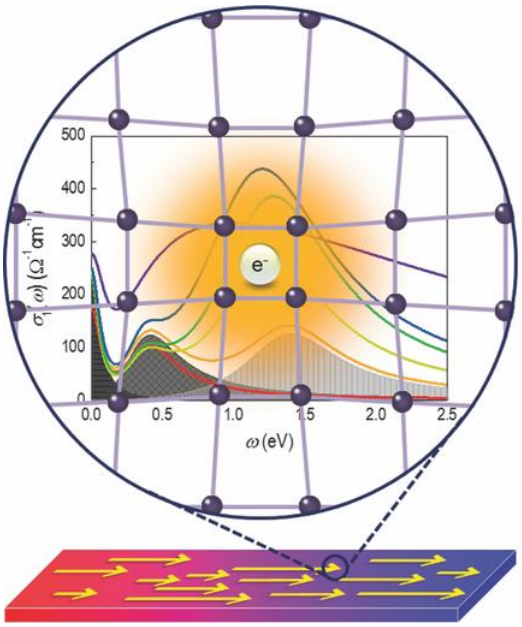
- Photo-Chemopropulsion – Light-Stimulated Movement of Microdroplets
  Florea, L.; Wagner, K.; Wagner, P.; Wallace, G. G.; Benito-Lopez, F.; Officer, D. L.; Diamond, D. *Adv. Mater.* **2014**, *26*, 7339–7345.
  Abstract:



The controlled movement of a chemical container by the light-activated expulsion of a chemical fuel, named here "photo-chemopropulsion", is an exciting new development in the array of mechanisms employed for controlling the movement of microvehicles, herein represented by lipid-based microdroplets. This "chemopropulsion" effect can be switched on and off, and is fully reversible.

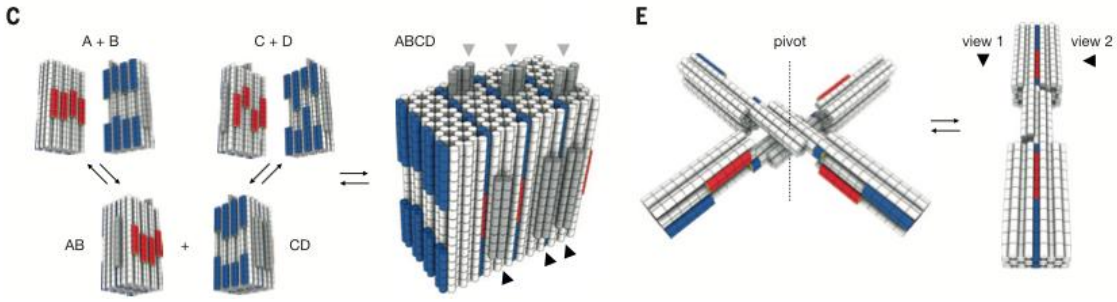
- Polaron Transport and Thermoelectric Behavior in La-Doped SrTiO3 Thin Films with Elemental Vacancies
  Choi, W. S.; Yoo, H. K., Ohta, H. *Adv. Funct. Mater.* **2015**, *25*, 799–804.

Abstract:



The electrodynamic properties of La-doped $SrTiO_3$ thin films with controlled elemental vacancies are investigated using optical spectroscopy and thermopower measurement. In particular, a correlation between the polaron formation and thermoelectric properties of the transition metal oxide (TMO) thin films is observed. With decreasing oxygen partial pressure during the film growth ($P(O_2)$), a systematic lattice expansion is observed along with the increased elemental vacancy and carrier density, experimentally determined using optical spectroscopy. Moreover, an absorption in the mid-infrared photon energy range is found, which is attributed to the polaron formation in the doped $SrTiO_3$ system. Thermopower of the La-doped $SrTiO_3$ thin films can be largely modulated from –120 to –260 μV K^{-1}, reflecting an enhanced polaronic mass of $\approx 3 < m_{polron}/m < \approx 4$. The elemental vacancies generated in the TMO films grown at various $P(O_2)$ influences the global polaronic transport, which governs the charge transport behavior, including the thermoelectric properties.

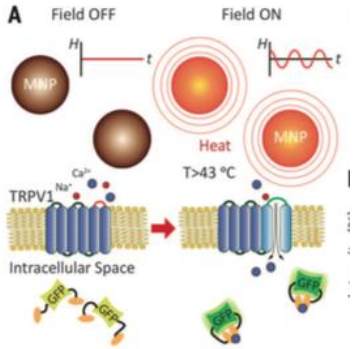
- Dynamic DNA devices and assemblies formed by shape-complementary, non–base pairing 3D components
  Gerling, T.; Wagenbauer, K. F.; Neuner, A. M.; Dietz, H. *Science* **2015**, *347*, 1446-1452.
  Abstract:



We demonstrate that discrete three-dimensional (3D) DNA components can specifically self-assemble in solution on the basis of shape-complementarity and without base pairing. Using this principle, we produced homo- and heteromultimeric objects, including micrometer-scale one- and two-stranded filaments and lattices, as well as reconfigurable devices, including an actuator, a switchable gear, an unfoldable nanobook, and a nanorobot. These multidomain assemblies were stabilized via short-ranged nucleobase stacking bonds that compete against

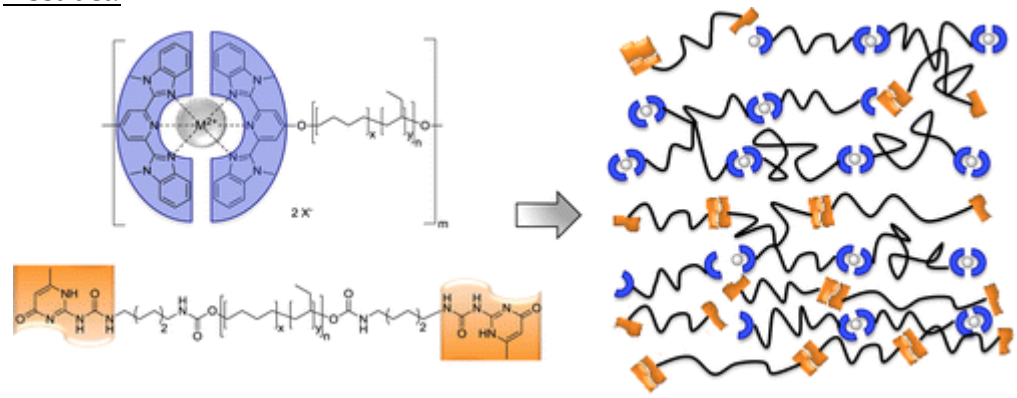
electrostatic repulsion between the components' interfaces. Using imaging by electron microscopy, ensemble and single-molecule fluorescence resonance energy transfer spectroscopy, and electrophoretic mobility analysis, we show that the balance between attractive and repulsive interactions, and thus the conformation of the assemblies, may be finely controlled by global parameters such as cation concentration or temperature and by an allosteric mechanism based on strand-displacement reactions.

- Wireless magnetothermal deep brain stimulation
  Chen, R.; Romero, G.; Christiansen, M. G.; Mohr, A.; Anikeeva, P. *Science* **2015**, *347*, 1477-1480.
  Abstract:



Wireless deep brain stimulation of well-defined neuronal populations could facilitate the study of intact brain circuits and the treatment of neurological disorders. Here, we demonstrate minimally invasive and remote neural excitation through the activation of the heat-sensitive capsaicin receptor TRPV1 by magnetic nanoparticles. When exposed to alternating magnetic fields, the nanoparticles dissipate heat generated by hysteresis, triggering widespread and reversible firing of TRPV1+ neurons. Wireless magnetothermal stimulation in the ventral tegmental area of mice evoked excitation in subpopulations of neurons in the targeted brain region and in structures receiving excitatory projections. The nanoparticles persisted in the brain for over a month, allowing for chronic stimulation without the need for implants and connectors.

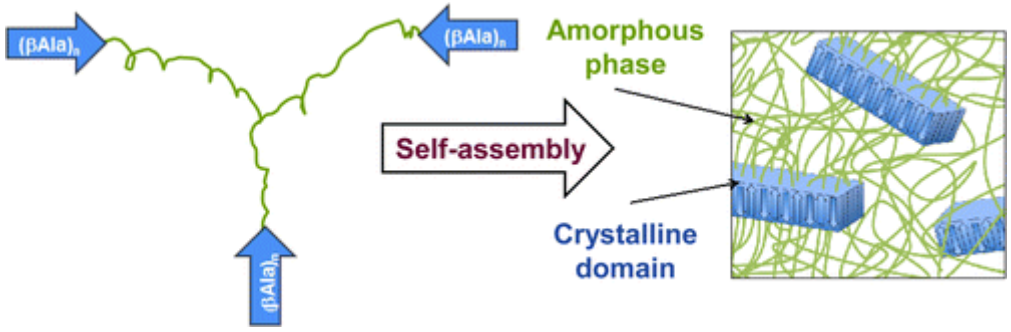
- Supramolecular Polymers with Orthogonal Functionality
  Coulibaly, S.; Heinzmann, C.; Beyer, F. L.; Balog, S.; Weder, C. *Macromolecules* **2014**, *27*, 8487-8496.
  Abstract:



Supramolecular polymers with orthogonal interactions are of broad interest, and reports on such materials with multifunctional stimuli-responsive behavior are rare. Polymer blends based on a poly(ethylene-*co*-butylene) core (PEB) terminated with either 2-ureido-4[1*H*]-pyrimidinone (UPy) hydrogen-bonding motifs (UPy-PEB-UPy) or 2,6-bis(1′-

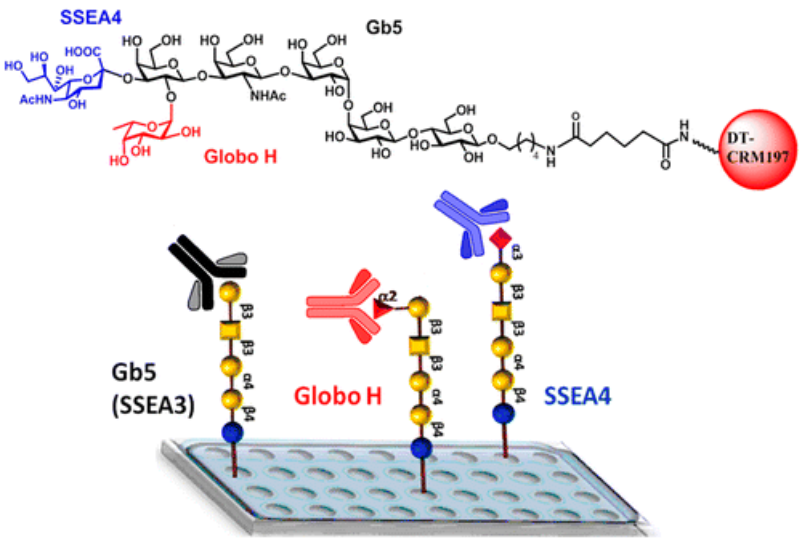
methylbenzimidazolyl)pyridine (Mebip) ligands coordinated to metal ions ([M(Mebip-PEB-Mebip)]$^{2+}$ (M = Zn, Fe)) were prepared. The degree of orthogonality of the supramolecular polymer blends was explored by UV–vis spectroscopy, small-angle X-ray scattering, and dynamic mechanical thermal analysis (DMTA). Polymer blends of [Zn(Mebip-PEB-Mebip)](NTf$_2$)$_2$ and UPy-PEB-UPy resulted in a statistical mixture of noncovalent interactions, whereas blends with [Fe(Mebip-PEB-Mebip)](ClO$_4$)$_2$ and UPy-PEB-UPy assembled in an orthogonal fashion. Additionally, the DMTA showed two transitions for the disassembly of UPy (ca. 60 °C) and Fe^{2+}-Mebip (ca. 180 °C) phases. The Fe^{2+}-Mebip interactions were selectively disrupted by the addition of a competitive ligand, demonstrating that each supramolecular motif can be targeted with either a thermal or chemical stimulus.

- Supramolecular Elastomers: Self-Assembling Star−Blocks of Soft Polyisobutylene and Hard Oligo(β-alanine) Segments
  Scavuzzo, J.; Tomita, S.; Cheng, S.; Liu, L.; Gao, M.; Kennedy, J. P.; Sakurai, S.; Cheng, S. Z. D.; Lia, L. *Macromolecules* **2015**, *48*, 1077-1086.
  Abstract:



A series of novel self-assembling star-blocks consisting of M_w = 29 000 g/mol 3-arm polyisobutylene (PIB) stars and oligo(β-alanine) end segments were synthesized and characterized. Star–blocks containing β-alanine dimers are viscous liquids, while those with tri-, tetra-, and penta(β-alanine)s are elastic solids. According to IR spectroscopy, the β-alanine dimer is partially hydrogen-bonded, while the trimer, tetramer, and pentamer are fully hydrogen-bonded and form β-sheets. DSC suggests crystalline β-alanine trimer tetramer and pentamer domains phase separated from the rubbery PIB. The melting temperature of the crystalline domains increases with the length of the oligo(β-alanine) segment. Transmission electron microscopy, wide-angle X-ray diffraction, and small-angle X-ray scattering of star-blocks containing tetra(β-alanine) indicate stacks of hydrogen-bonded β-sheets dispersed in a soft continuous PIB phase. The crystalline phases form fibrous lamellae with lengths up to ∼200 nm, widths up to ∼20 nm, and thicknesses of ∼2 nm, which is the length of β-alanine tetramer. Although the oligo(β-alanine) contents are very low (from 1.5 to 3.6 wt % in the series), the static and dynamic mechanical properties of the star–blocks are very different. The elastic moduli of the TPEs increase 5-fold with increasing β-alanine content. Evidently, the oligo(β-alanine) domains provide not only physical cross-links but also act as fillers.

- A Development of Globo-H Cancer Vaccine
  Danishefsky S. J.; Shue, Y. K.; Chang, M. N.; Wong, C.-H. *Acc. Chem. Res.* **2015**, *48*, 643-652.
  Abstract:

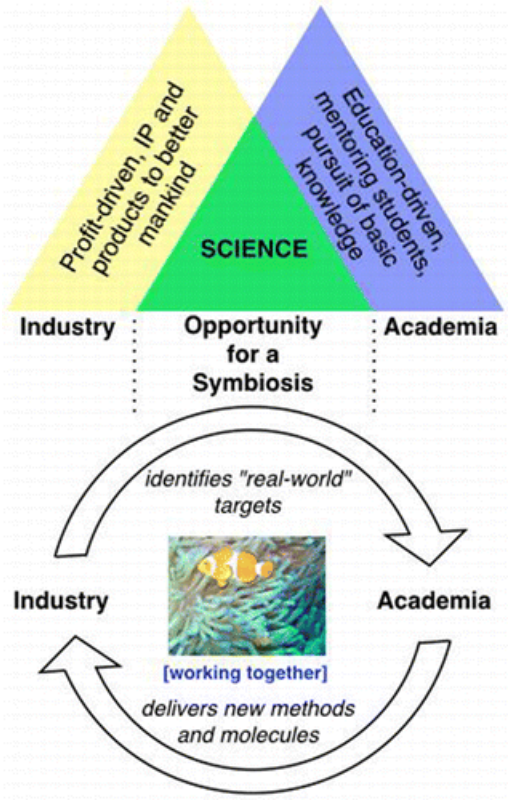


The development of anticancer vaccines requires the identification of unique epitope markers, preferably expressed exclusively on the surface of cancer cells. This Account describes the path of development of a carbohydrate-based vaccine for metastatic breast cancer, including the selection and synthesis of Globo-H as the target, the development of the vaccine conjugate and adjuvant design, the study of the immune response and consideration of class switch, and the analysis of Globo-H distribution on the surface of various cancer cells, cancer stem cells, and normal cells.

The first synthesis of Globo-H was accomplished through the use of glycal chemistry; this approach delivered sufficient material for evaluation in phase I human trials. The development of a programmable one-pot synthesis method rendered the synthesis more practical and enabled the midstage proof-of-concept phase II trial and late-stage phase III trial. Finally, enzymatic synthesis of Globo-H coupled with cofactor regeneration was used for the late-stage multicenter trials and manufacture of the product. Along this path of development, it was discovered that the vaccine induced antibodies to target not only Globo-H, but also SSEA3 and SSEA4. Moreover, these three glycolipids were found to be uniquely expressed not only on the cell surface of breast cancer but on 15 additional cancer types, suggesting the broad application of this vaccine in cancer treatment and perhaps cancer prevention. In addition, a new glycolipid adjuvant was designed to target the CD1d receptor on dendritic cells and B cells for presentation to and activation of T cells to modulate the immune response and induce a class switch from IgM to IgG, thereby overcoming the common problem of carbohydrate-based vaccines that often induce mainly IgM antibodies.

As demonstrated in this vaccine development, the chemical approach to the synthesis and conjugation of carbohydrate-based immunogens provides the flexibility for access to various structures and linkers to identify optimal compositions for development. The enzymatic method was then introduced to enable the practical synthesis of the vaccine candidate for clinical development and commercialization. Overall, this Account illustrates the path of development of a cancer vaccine, from selection of a unique glycan marker on breast cancer cells and the cancer stem cells as target to the use of chemistry in combination with immunology and cancer biology to enable the design and development of the Globo-H vaccine to target three specific glycan markers exclusively expressed on the cell surface of a number of different types of cancer.

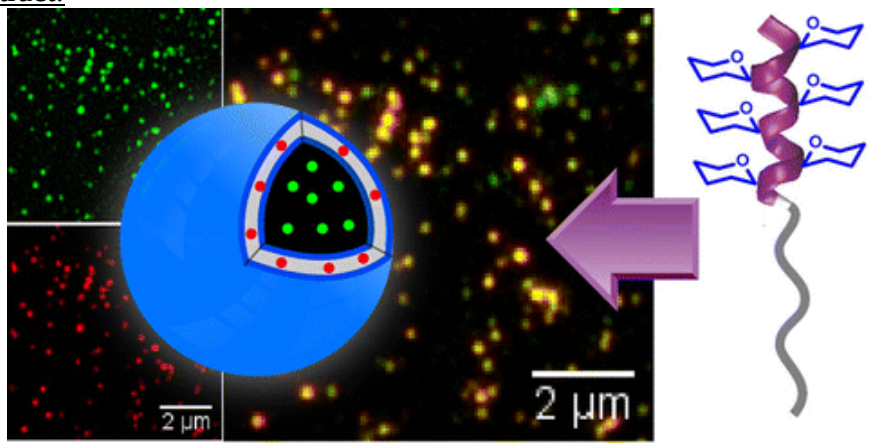
- Academia–Industry Symbiosis in Organic Chemistry
  Michaudel, Q.; Ishihara, Y; Baran, P. S. *Acc. Chem. Res.*, **2015**, *48*, 712–721.
  Abstract:



Collaboration between academia and industry is a growing phenomenon within the chemistry community. These sectors have long held strong ties since academia traditionally trains the future scientists of the corporate world, but the recent drastic decrease of public funding is motivating the academic world to seek more private grants. This concept of industrial "sponsoring" is not new, and in the past, some companies granted substantial amounts of money per annum to various academic institutions in exchange for prime access to all their scientific discoveries and inventions. However, academic and industrial interests were not always aligned, and therefore the investment has become increasingly difficult to justify from industry's point of view. With fluctuating macroeconomic factors, this type of unrestricted grant has become more rare and has been largely replaced by smaller and more focused partnerships. In our view, forging a partnership with industry can be a golden opportunity for both parties and can represent a true symbiosis. This type of project-specific collaboration is engendered by industry's desire to access very specific academic expertise that is required for the development of new technologies at the forefront of science. Since financial pressures do not allow companies to spend the time to acquire this expertise and even less to explore fundamental research, partnering with an academic laboratory whose research is related to the problem gives them a viable alternative. From an academic standpoint, it represents the perfect occasion to apply "pure science" research concepts to solve problems that benefit humanity. Moreover, it offers a unique opportunity for students to face challenges from the "real world" at an early stage of their career. Although not every problem in industry can be solved by research developments in academia, we argue that there is significant scientific overlap between these two seemingly disparate groups, thereby presenting an opportunity for a symbiosis. This type of partnership is challenging but can be a win–win situation if both parties agree on some general guidelines, including clearly defined goals and deliverables,

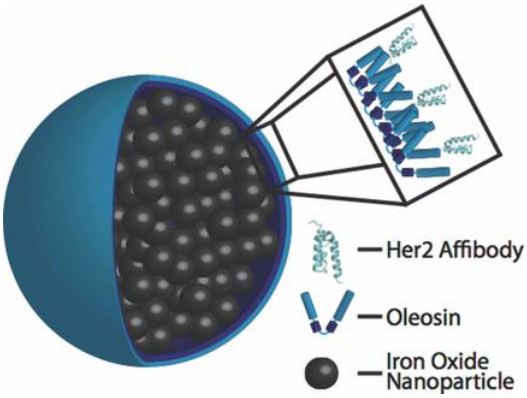
biweekly meetings to track research progress, and quarterly or annual meetings to recognize overarching, common objectives. This Account summarizes our personal experience concerning collaborations with various industrial groups and the way it impacted the research programs for both sides in a symbiotic fashion.

- Bioactive Polymersomes Self-Assembled from Amphiphilic PPO-GlycoPolypeptides: Synthesis, Characterization, and Dual-Dye Encapsulation
  Das, S.; Kumar Sharma, D.; Chakrabarty, S.; Chowdhury, A.; Sen Gupta, S. *Langmuir* **2015**, *31*, 3402–3412.
  Abstract:



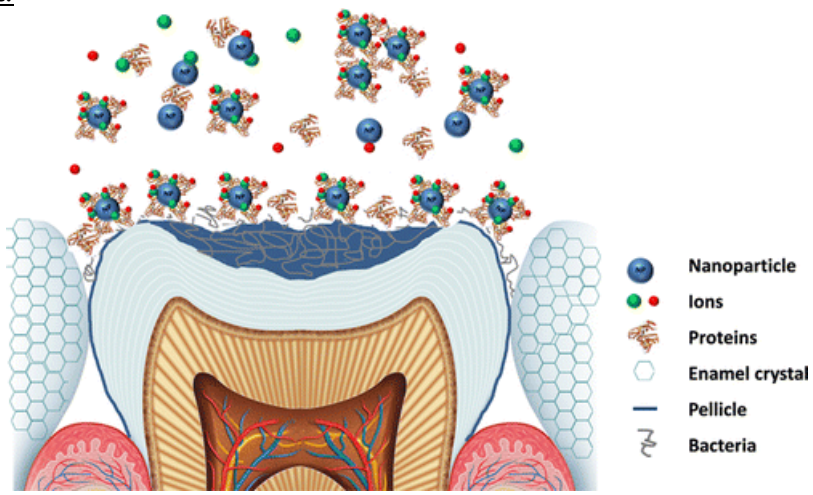
Glycopolypeptide-based polymersomes have promising applications as vehicles for targeted drug delivery because they are capable of encapsulating different pharmaceuticals of diverse polarity as well as interacting with specific cell surfaces due to their hollow structural morphology and bioactive surfaces. We have synthesized glycopolypeptide-*b*-poly(propylene oxide) by ROP of glyco-*N*-carboxyanhydride (NCA) using the hydrophobic amine-terminated poly(propylene oxide) (PPO) as the initiator. This block copolymer is composed of an FDA-approved PPO hydrophobic block in conjugation with hydrophilic glycopolypeptides which are expected to be biocompatible. We demonstrate the formation of glycopolypeptide-based polymersomes from the self-assembly of glycopolypeptide-*b*-poly(propylene oxide) in which the presence of an ordered helical glycopolypeptide segment is required for their self-assembly into spherical nanoscale (~50 nm) polymersomes. The polymersomes were characterized in detail using a variety of techniques such as TEM, AFM, cryo-SEM, and light-scattering measurements. As a model for drugs, both hydrophobic (RBOE) and hydrophilic (calcein) dyes have been incorporated within the polymersomes from solution. To substantiate the simultaneous entrapment of the two dyes, spectrally resolved fluorescence microscopy was performed on the glycopeptide polymersomes cast on a glass substrate. We show that it is possible to visualize individual nanoscale polymersomes and effectively probe the dyes' colocalization and energy-transfer behaviors therein as well as investigate the variation in dual-dye encapsulation over a large number of single polymersomes. Finally, we show that the galactose moieties present on the surface can specifically recognize lectin RCA_{120}, which reveals that the polymersomes' surface is indeed biologically active.

- Superparamagnetic Iron Oxide Nanoparticle Micelles Stabilized by Recombinant Oleosin for Targeted Magnetic Resonance Imaging
  Vargo, K. B.; Al Zaki, A.; Warden-Rothman, R.; Tsourkas, A.; Hammer, D. A. *Small* **2015**, *11*, 1409–1413.
  Abstract:



Recombinant surfactants present a new platform for stabilizing and targeting nanoparticle imaging agents. Superparamagnetic iron oxide nanoparticle-loaded micelles for MRI contrast are stabilized by an engineered variant of the naturally occurring protein oleosin and targeted using a Her2/neu affibody-oleosin fusion. The recombinant oleosin platform allows simple targeting and the ability to easily swap the ligand for numerous targets.

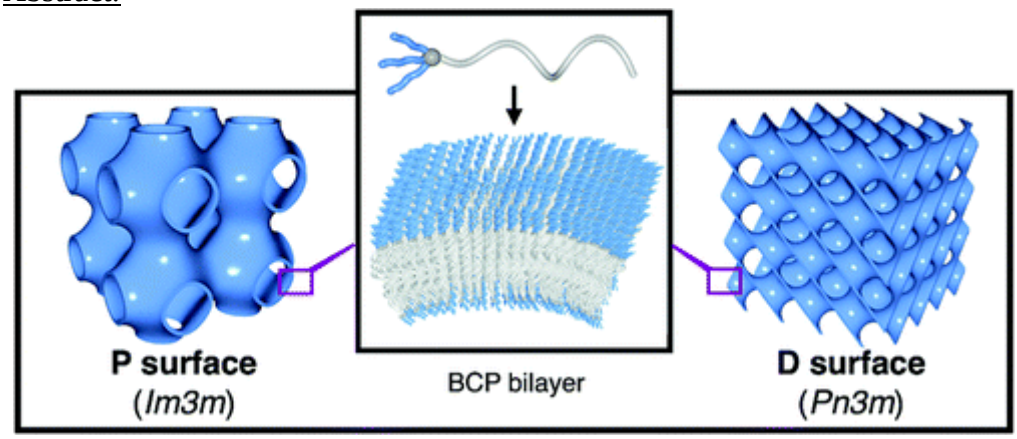
- Review of Nanomaterials in Dentistry: Interactions with the Oral Microenvironment, Clinical Applications, Hazards, and Benefits
  Besinis, A.; De Peralta, T.; Tredwin, C. J.; Handy, R. D. *ACS Nano* **2015**, *9*, 2255–2289.
  Abstract:



Interest in the use of engineered nanomaterials (ENMs) as either nanomedicines or dental materials/devices in clinical dentistry is growing. This review aims to detail the ultrafine structure, chemical composition, and reactivity of dental tissues in the context of interactions with ENMs, including the saliva, pellicle layer, and oral biofilm; then describes the applications of ENMs in dentistry in context with beneficial clinical outcomes versus potential risks. The flow rate and quality of saliva are likely to influence the behavior of ENMs in the oral cavity, but how the protein corona formed on the ENMs will alter bioavailability, or interact with the structure and proteins of the pellicle layer, as well as microbes in the biofilm, remains unclear. The tooth enamel is a dense crystalline structure that is likely to act as a barrier to ENM penetration, but underlying dentinal tubules are not. Consequently, ENMs may be used to strengthen dentine or regenerate pulp tissue. ENMs have dental applications as antibacterials for infection control, as nanofillers to improve the mechanical and bioactive properties of restoration materials, and as novel coatings on dental implants. Dentifrices and some related personal care products are already available for oral health applications. Overall, the clinical benefits generally outweigh the hazards of using

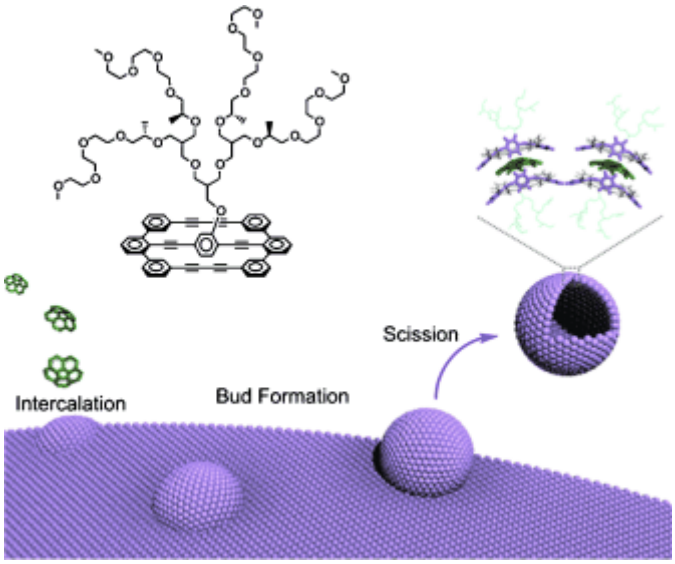
ENMs in the oral cavity, and the latter should not prevent the responsible innovation of nanotechnology in dentistry. However, the clinical safety regulations for dental materials have not been specifically updated for ENMs, and some guidance on occupational health for practitioners is also needed. Knowledge gaps for future research include the formation of protein corona in the oral cavity, ENM diffusion through clinically relevant biofilms, and mechanistic investigations on how ENMs strengthen the tooth structure.

- Solution Self-Assembly of Block Copolymers Containing a Branched Hydrophilic Block into Inverse Bicontinuous Cubic Mesophases
  An, T. H.; La, Y.; Cho, A.; Jeong, M. G.; Shin, T. J.; Park, C.; Kim, K. T. *ACS Nano* **2015**, *9*, 3084–3096.
  Abstract:



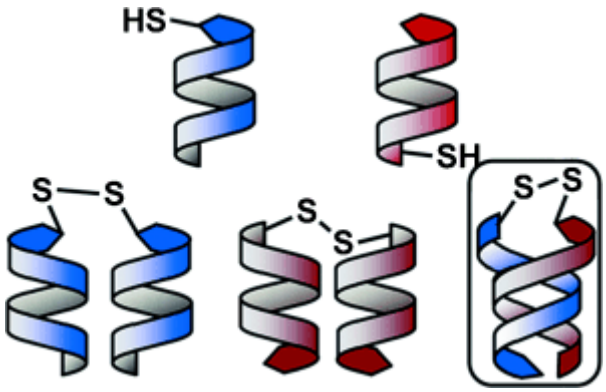
Solution self-assembly of amphiphilic block copolymers into inverse bicontinuous cubic mesophases is an emerging strategy for directly creating highly ordered triply periodic porous polymer nanostructures with large pore networks and desired surface functionalities. Although there have been recent reports on the formation of highly ordered triply periodic minimal surfaces of self-assembled block copolymer bilayers, the structural requirements for block copolymers in order to facilitate the preferential formation of such inverse mesophases in solution have not been fully investigated. In this study, we synthesized a series of model block copolymers, namely, branched poly(ethylene glycol)-block-polystyrene (bPEG-PS), to investigate the effect of the architecture of the block copolymers on their solution self-assembly into inverse mesophases consisting of the block copolymer bilayer. On the basis of the results, we suggest that the branched architecture of the hydrophilic block is a crucial structural requirement for the preferential self-assembly of the resulting block copolymers into inverse bicontinuous cubic phases. The internal crystalline lattice of the inverse bicontinuous cubic structure can be controlled via coassembly of branched and linear block copolymers. The results presented here provide design criteria for amphiphilic block copolymers to allow the formation of inverse bicontinuous cubic mesophases in solution. This may contribute to the direct synthesis of well-defined porous polymers with desired crystalline order in the porous networks and surface functionalities.

- Supramolecular Capsules from Bilayer Membrane Scission Driven by Corannulene
  Kim, Y.; Lee, M. *Chem. Eur. J.* **2015**, *21*, 5736–5740.
  Abstract:



Self-assembly of polyaromatic systems has proved to be a powerful technique to construct nanoscale optoelectronic materials. However, attempts to develop self-assembled nanomaterials guided by pristine polyaromatic molecules have been limited. Here the construction of photoactive nanocapsules through the scission of an aromatic bilayer membrane driven by curved corannulene intercalation is reported. The framework of the capsule consists of the lateral array of corannulene, a buckyball fragment. The supramolecular capsules exhibit photocatalytic activity to degrade encapsulated fluorescein dye molecules under sunlight irradiation.

- Dynamic Combinatorial Enrichment of Polyconformational D-/L-Peptide Dimers
  Jadhav, K. B.; Lichtenecker, R. J.; Bullach, A.; Mandal, B.; Arndt, H.-D. *Chem. Eur. J.* **2015**, *21*, 5898–5908.
  Abstract:



D-/L-Peptides such as gramicidin A (gA) adopt unique dimeric β-helical structures of different topologies. To overcome their conformational promiscuity and enrich individual components, a dynamic combinatorial approach assisted by thiol tags was developed. This method led to identification of the preferential formation of antiparallel dimers under a broad range of conditions, which was independent of peptide side-chain polarity. Exclusive formation of an antiparallel cyclic dimer was achieved in the presence of cesium ions.