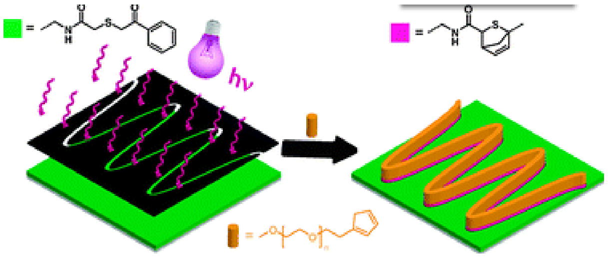
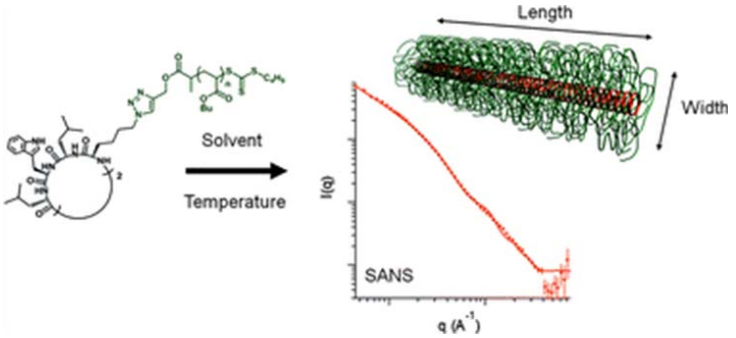
- Polymer surface patterning *via* Diels-Alder trapping of photo-generated thioaldehydes
  Glassner, M.; Oehlenschlaeger, K. K.; Welle, A.; Bruns, M.; Barner-Kowollik, C. *Chem. Commun.* **2013**, *49,* 633-635.
  Abstract:



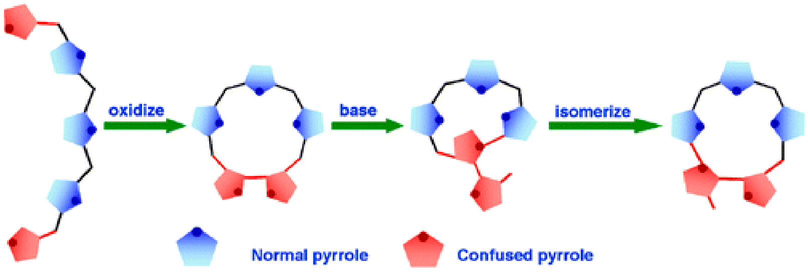
An efficient method for polymer surface patterning *via* Diels-Alder trapping of photo-generated thioaldehydes is presented. It is demonstrated that thioaldehyde end-groups generated by photolysis of phenacyl sulfides can be quantitatively trapped with various dienes. Poly(ethylene glycol) is immobilized on a surface in a spatially controlled fashion *via* irradiation through a shadow mask.

- Structure elucidation and control of cyclic peptide-derived nanotube assemblies in solution
  Chapman, R.; Koh, M. L.; Warr, G. G.; Jolliffe, K. A.; Perrier, S. *Chem. Sci.* **2013**, *4,* 2581-2589.
  Abstract:



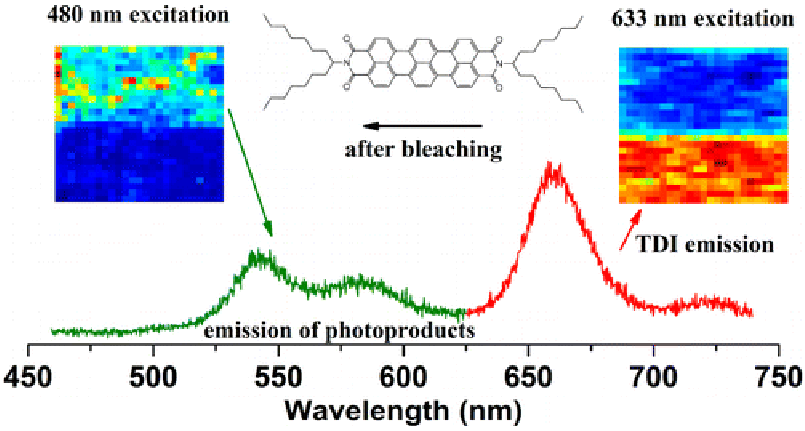
We describe the solution assembly of polymer-cyclic peptide conjugates into nanotubes, by direct *in situ* measurements. The conjugates were assembled by exploiting the β-sheet assembly of the *alt*(D,L) cyclic octapeptide core. The conjugated polymer permits solubilization of the peptide and the resulting nanotubes, thus allowing for the first time the direct study of the assembly mechanism of this system. The resulting materials present unique properties for a wide range of applications. We find that the polymer can act to both shield the peptide core from the solvent and put strain on the peptide core through steric repulsions. By controlling both the solvent mixture and the length of the polymer, control over the length of the resulting nanotubes can be obtained. In addition, monitoring the assembly with temperature allows the strength of the assembly to be probed, adding evidence for a co-operative mechanism of assembly. Finally, selective deuteration of the polymer component in SANS analyses leads to the precise measurement of the nanotubes core dimensions, and by cross-linking the polymeric shell, the structure of the nanotubes in solution are confirmed by transmission electron microscopy (TEM). This study establishes the fundamentals needed for the design and control of these new materials.

- Macrocycle Contraction and Expansion of a Dihydrosapphyrin Isomer
  Xie, Y.; Wei, P.; Li, X.; Hong, T.; Zhang, K.; Furuta, H. *J. Am. Chem. Soc.* **2013**, *135*, 19119-19122.
  Abstract:



Cyclization of a pentapyrrane with two terminal β-linked pyrroles afforded a dihydrosapphyrin isomer (1) with the pyrroles linked in a unique β,α–α,β mode, which was rather reactive, and thus it readily underwent a ring-contracted rearrangement to a pyrrolyl norrole (2), and succeeding ring expansion to a terpyrrole-containing isosmaragdyrin analogue (4). 1, 2, and 4 contain the internal ring pathways with a minimum of 17, 15, and 16 atoms, respectively. 1, 2, and 4 are almost nonfluorescent, whereas the complex of 2 with Zn^{2+} shows a distinct NIR emission peak at 741 nm. The unprecedented pyrrole transformation chemistry by confusion approach is illustrated.

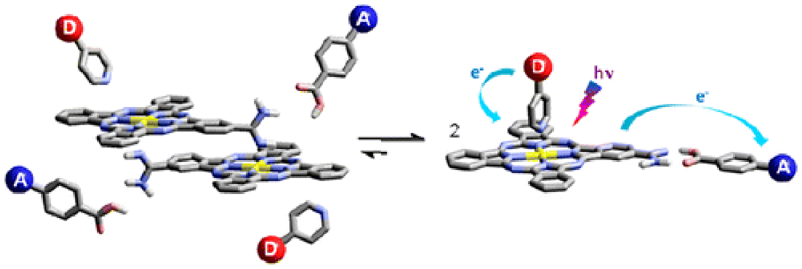
- Green Emitting Photoproducts from Terrylene Diimide after Red Illumination
  Liao, Z.; Hooley, E. N.; Chen, L.; Stappert, S.; Müllen, K.; Vosch, T. *J. Am. Chem. Soc.* **2013**, *135*, 19180-19185.
  Abstract:



The spectral properties of emissive photoproducts, formed upon 633 nm irradiation of a terrylene diimide dye, were investigated. Ensemble and single-molecule level experiments were conducted by immobilizing the TDI dye molecules in a polystyrene film. In the bulk experiments, green emission could be observed from the photobleached areas (photobleached with 633 nm light) when excited with 480 or 514 nm light. Similar phenomena were also observed at the single-molecule level. On the basis of the single-molecule experiments, a conversion efficiency of about 5% was estimated for the formation of emissive spectrally blue-shifted photoproducts. These green emissive photoproducts have spectral properties that resemble those of lower rylene homologues, e.g. perylene diimide or perylene monoimide. Our results indicate that the formation of blue-shifted emissive photoproducts can have implications for analyzing single-molecule FRET experiments or multiple color-labeled fluorescent systems.

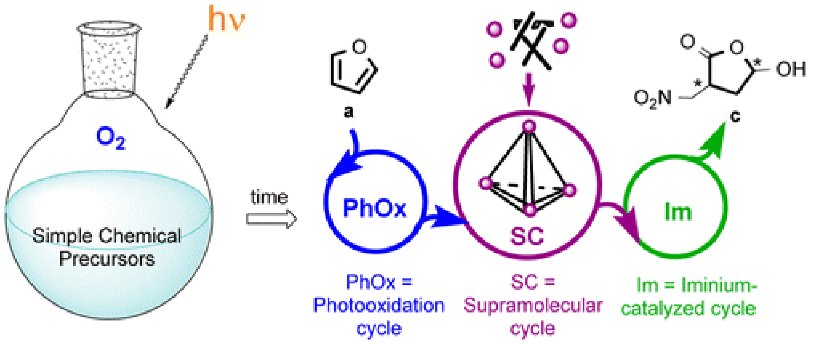
- Supramolecular Assembly of Multicomponent Photoactive Systems via Cooperatively Coupled Equilibria
  García-Iglesias, M.; Peuntinger, K.; Kahnt, A.; Krausmann, J.; Vázquez, P.; González-Rodríguez, D.; Guldi, D. M.; Torres, T. *J. Am. Chem. Soc.* **2013**, *135*, 19311–19318.

Abstract:



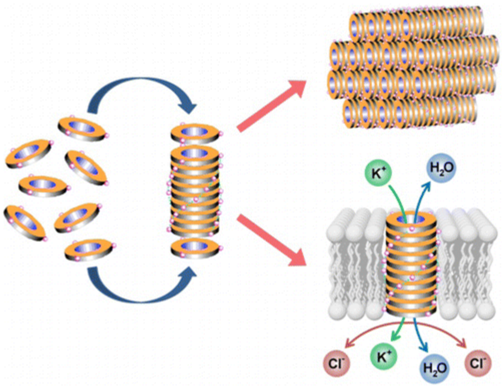
Here, we show that the synergistic interplay between two binding equilibria, acting at different sites of a (Zn)phthalocyanine-amidine molecule (**Pc1**), enables the dissociation of the photoinactive phthalocyanine dimer (**Pc1**)$_2$ into a three-component system, in which a sequence of light harvesting, charge separation, and charge shift is successfully proven. The aforementioned dimer is assembled by dual amidine-Zn(II) coordination between neighboring **Pc1** molecules and gives rise to high association constants ($K_D \approx 10^{11}$ M^{-1}). Such extraordinary stability hampers the individual binding of either carboxylic acid ligands through the amidine group or pyridine-type ligands through the Zn(II) metal atom to (**Pc1**)$_2$. However, the combined addition of both ligands, which cooperatively bind to different sites of **Pc1** through distinct noncovalent interactions, efficiently shifts the overall equilibrium toward a photoactive tricomponent species. In particular, when a fullerene-carboxylic acid (**C**$_{60}$**A**) and either a dimethylamino-pyridine (**DMAP**) or a phenothiazine-pyridine ligand (**PTZP)** are simultaneously present, the photoactivity is turned on and evidence is given for an electron transfer from photoexcited **Pc1** to the electron-accepting **C**$_{60}$**A** that affords the **DMAP-Pc1**$^{\bullet+}$**-C**$_{60}$**A**$^{\bullet-}$ or **PTZP-Pc1**$^{\bullet+}$**-C**$_{60}$**A**$^{\bullet-}$ radical ion pair states. Only in the latter case does a cascade of photoinduced electron transfer processes afford the **PTZP**$^{\bullet+}$**-Pc1-C**$_{60}$**A**$^{\bullet-}$ radical ion pair state. The latter is formed via a thermodynamically driven charge shift evolving from **PTZP-Pc1**$^{\bullet+}$**-C**$_{60}$**A**$^{\bullet-}$ and exhibits lifetimes that are notably longer than those of **DMAP-Pc1**$^{\bullet+}$**-C**$_{60}$**A**$^{\bullet-}$.

- A Self-Organizing Chemical Assembly Line
  Salles, A. G.; Zarra, S.; Turner, R. M.; Nitschke, J. R. *J. Am. Chem. Soc.* **2013**, *135*, 19143–19146.
  Abstract:



Chemical syntheses generally involve a series of discrete transformations whereby a simple set of starting materials are progressively rendered more complex. In contrast, living systems accomplish their syntheses within complex chemical mixtures, wherein the self-organization of biomolecules allows them to form “assembly lines” that transform simple starting materials into more complex products. Here we demonstrate the functioning of an abiological chemical system whose simple parts self-organize into a complex system capable of directing the multistep transformation of the small molecules furan, dioxygen, and nitromethane into a more complex and information-rich product. The novel use of a self-assembling container molecule to catalytically transform a high-energy intermediate is central to the system's functioning.

- Self-Assembling Organic Nanotubes with Precisely Defined, Sub-nanometer Pores: Formation and Mass Transport Characteristics
  Gong, B.; Shao, Z. *Acc. Chem. Res.* **2013**, *46*, 2856–2866.
  Abstract:



The transport of molecules and ions across nanometer-scaled pores, created by natural or artificial molecules, is a phenomenon of both fundamental and practical significance. Biological channels are the most remarkable examples of mass transport across membranes and demonstrate nearly exclusive selectivity and high efficiency with a diverse collection of molecules. These channels are critical for many basic biological functions, such as membrane potential, signal transduction, and osmotic homeostasis.

If such highly specific and efficient mass transport or separa tion could be achieved with artificial nanostructures under controlled conditions, they could create revolutionary technologies in a variety of areas. For this reason, investigators from diverse disciplines have vigorously studied small nondeformable nanopores. The most exciting studies have focused on carbon nanotubes (CNTs), which have exhibited fast mass transport and high ion selectivity despite their very simple structure. However, the limitations of CNTs and the dearth of other small (≤2 nm) nanopores have severely hampered the systematic investigation of nanopore-mediated mass transport, which will be essential for designing artificial nanopores with desired functions en masse.

Researchers can overcome the difficulties associated with CNT and other artificial pores by stacking macrocyclic building blocks with persistent shapes to construct tunable, self-assembling organic pores. This effort started when we discovered a highly efficient, one-pot macrocyclization process to efficiently prepare several classes of macrocycles with rigid backbones containing nondeformable cavities. Such macrocycles, if stacked atop one another, should lead to nanotubular assemblies with defined inner pores determined by their constituent macrocycles. One class of macrocycles with aromatic oligoamide backbones had a very high propensity for directional assembly, forming nanotubular structures containing nanometer and sub-nanometer hydrophilic pores. These self-assembling hydrophilic pores can form ion channels in lipid membranes with very large ion conductances.

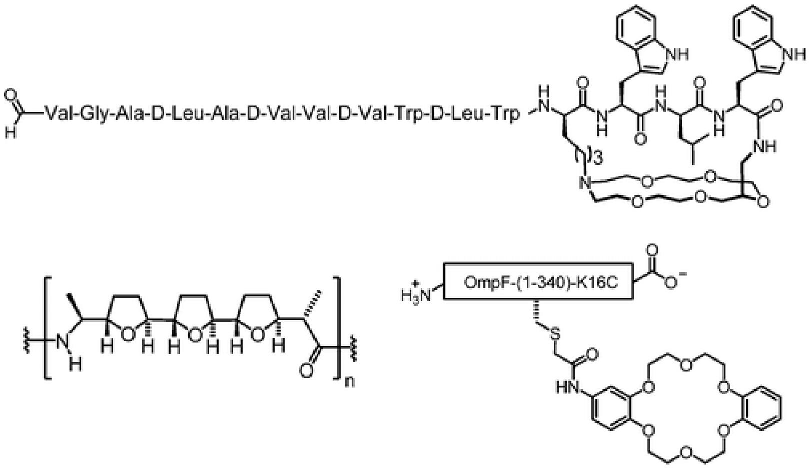
To control the assembly, we have further introduced multiple hydrogen-bonding side chains to enforce the stacking of rigid macrocycles into self-assembling nanotubes. This strategy has produced a self-assembling, sub-nanometer hydrophobic pore that not only acted as a

transmembrane channel with surprisingly high ion selectivity, but also mediated a significant transmembrane water flux.

The stacking of rigid macrocycles that can be chemically modified in either the lumen or the exterior surface can produce self-assembling organic nanotubes with inner pores of defined sizes.

The combination of our approach with the availability and synthetic tunability of various rigid macrocycles should produce a variety of organic nanopores. Such structures would allow researchers to systematically explore mass transport in the sub-nanometer regime. Further advances should lead to novel applications such as biosensing, materials separation, and molecular purifications.

- Ion-Channels: Goals for Function-Oriented Synthesis
  Reiß, P.; Koert, U. *Acc. Chem. Res.* **2013**, *46*, 2773–2780.
  Abstract:



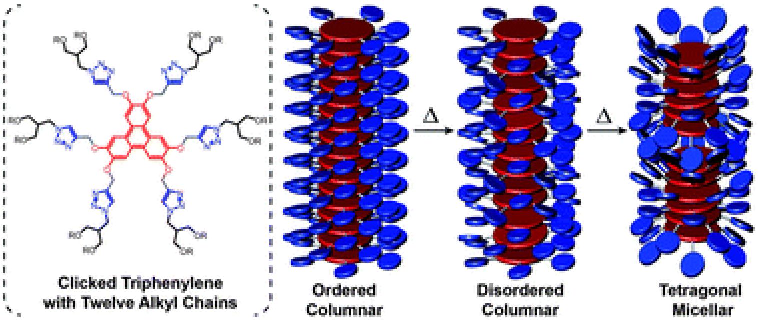
Ion channels provide a conductance pathway for the passive transport of ions across membranes. These functional molecules perform key tasks in biological systems such as neuronal signaling, muscular control, and sensing. Recently, function-oriented synthesis researchers began to focus on ion channels with the goal of modifying the function of existing ion channels (ion selectivity, gating) or creating new channels with novel functions. Both approaches, ion channel engineering and de novo design, have involved synthetic chemists, biochemists, structural biologists, and neurochemists.

Researchers characterize the function of ion channels by measuring their conductance in samples of biological membranes (patch clamp) or artificial membranes (planar lipid bilayers). At the single molecule level, these measurements require special attention to the purity of the sample, a challenge that synthetic chemists should be aware of. Ideally, researchers study the function of channels while also acquiring structural data (X-ray, NMR) to understand and predict how synthetic modifications alter channel function.

Long-term oriented researchers would like to apply synthetic ion channels to single molecule sensing and to implantat these synthetic systems in living organisms as tools or for the treatment of channelopathies. In this Account, we discuss our own work on synthetic ion channels and explain the shift of our research focus from a de novo design of oligo-THFs and oligo-THF-amino acids to ion channel engineering. We introduce details about two biological lead structures for ion channel engineering: the gramicidin $\beta^{6,3}$ helix as an example of a channel with a narrow ion conductance pathway and the outer membrane porins (OmpF, OmpG) with their open β-barrel structure. The increase and the reversal of ion selectivity of these systems and the hydrophobic match/mismatch

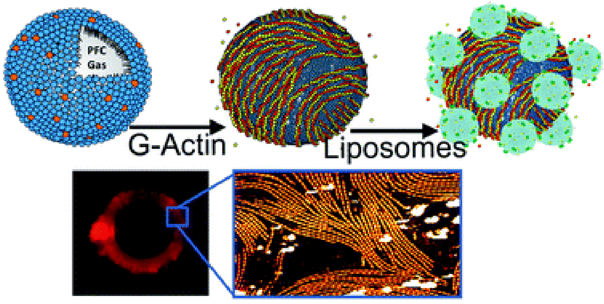
of the channel with the phospholipid bilayer are of particular interest. For engineering ion channels, we need to supplement the single-point attachment of a synthetic modulator with the synthesis of a more challenging two-point attachment.
The successful function-oriented synthesis of ion channels will require interdisciplinary efforts that include new electrophysiology techniques, efficient synthesis (peptide/protein/organic), and good structural analysis.

- Supramolecular transformation from ordered columnar to disordered columnar to tetragonal micellar structures in clicked dodeca-alkylated discotic triphenylene liquid crystals
  Cho, B.-K.; Kim, S.-H. *Soft Matter* **2014**, *10,* 553-559.
  Abstract:



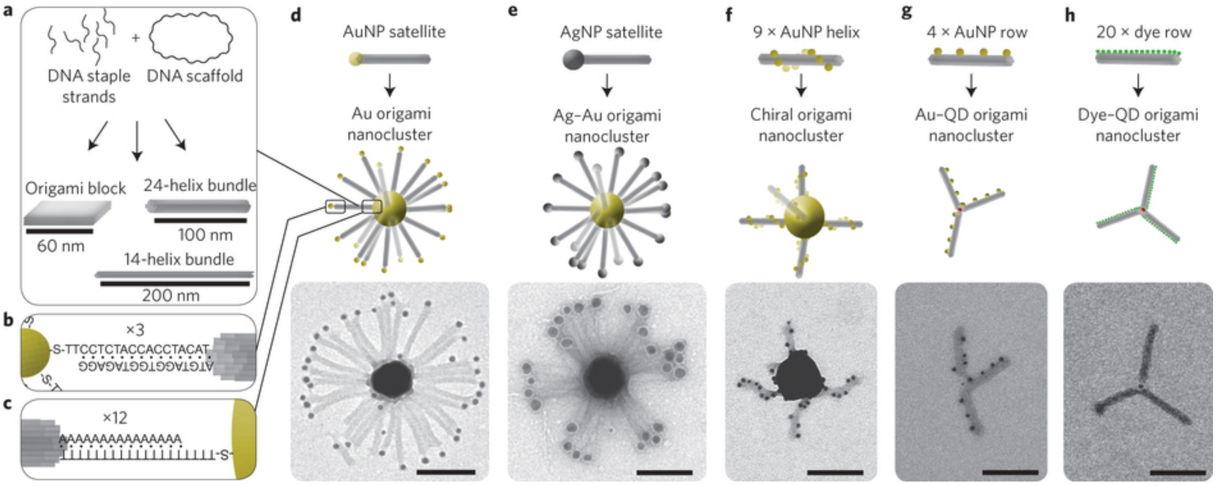
We prepared three discotic liquid crystals (DLCs) based on a triphenylene (TP) disc functionalized with twelve alkyl peripheries. The synthesis of the discogens was performed by a click reaction using $Cu(OAc)_2$ as the catalyst, with six triazolyl groups connecting the TP core with twelve alkyl chains. According to thermal data from differential scanning calorimetry (DSC), discogen **1**, which has the shortest hexyl peripheries, exhibited two LC phases, and **2** and **3**, with decyl and tetradecyl peripheries, respectively, displayed three LC phases as a function of the temperature. Structural analyses using small- and wide-angle X-ray scattering (SAXS and WAXS) techniques revealed ordered and disordered hexagonal columnar LC phases in all the discogens. On the other hand, an unconventional micellar phase with $P4_2/mnm$ symmetry consisting of thirty micelles was found only in **2** and **3**, when the temperature increased. The thermally induced transformation from the columnar to the micellar phase can be explained by increased chain entropy at higher temperatures. The complex micellar packing in the noncubic phase is attributed to the softness of the DLC micelles because the micellar corona consists of flexible alkyl chains. The discogen design concept in this study (*i.e.*, the introduction of multibranched alkyl peripheries to the discotic mesogens via click chemistry) resulted in unconventional columnar-to-micellar transformation in conventional TP DLCs.

- Self-assembly of actin scaffolds on lipid microbubbles
  Heath, G. R.; Abou-Saleh, R. H.; Peyman, S. A.; Johnson, B. R.; Connell, S. D.; Evans, S. D. *Soft Matter* **2014**, *10,* 694-700.
  Abstract:



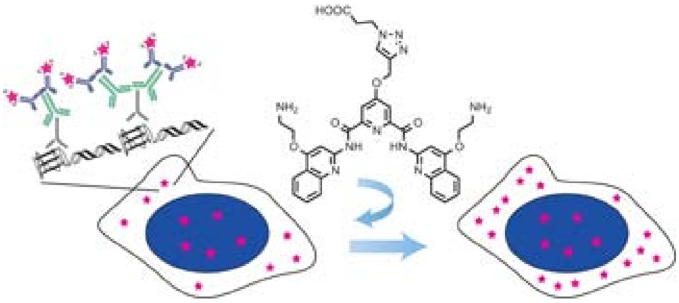
Microbubbles offer unique properties as combined carriers of therapeutic payloads and diagnostic agents. Here we report on the development of novel microbubble architectures that in addition to the usual lipid shell have an actin cytoskeletal cortex assembled on their exterior. We show, using atomic force microscopy that this biomimetic coating creates a thin mesh that allows tuning of the mechanical properties of microbubbles and that the nature of actin assembly is determined by the fluidity of the lipid layer. Further, we show that it is possible to attach payloads and targeting-ligands to the actin scaffold. Resistance to gas permeation showed that the additional actin layer reduces gas diffusion across the shell and thus increases bubble lifetime. This study demonstrates a one step method to creating more complex microbubble architectures, which would be capable of further modification and tuning through the inclusion of actin binding proteins.

- Hierarchical assembly of metal nanoparticles, quantum dots and organic dyes using DNA origami scaffolds
  Schreiber, R.; Do, J.; Roller, E. M.; Zhang, T.; Schüller, V. J.; Nickels, P.C.; Feldmann, J.; Liedl, T.
  Nature Nanotechnol. **2014**, *9,* 74-78.
  Abstract:



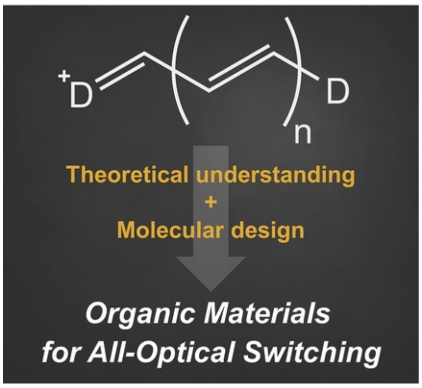
The self-assembly of nanoscale elements into three-dimensional structures with precise shapes and sizes is important in fields such as nanophotonics, metamaterials and biotechnology. Short molecular linkers have previously been used to create assemblies of nanoparticles, but the approach is limited to small interparticle distances, typically less than 10 nm. Alternatively, DNA origami can precisely organize nanoscale objects over much larger length scales. Here we show that rigid DNA origami scaffolds can be used to assemble metal nanoparticles, quantum dots and organic dyes into hierarchical nanoclusters that have a planet-satellite-type structure. The nanoclusters have a tunable stoichiometry, defined distances of 5-200 nm between components, and controllable overall sizes of up to 500 nm. We also show that the nanoscale components can be positioned along the radial DNA spacers of the nanostructures, which allows short- and long-range interactions between nanoparticles and dyes to be studied in solution. The approach could, in the future, be used to construct efficient energy funnels, complex plasmonic architectures, and porous, nanoengineered scaffolds for catalysis.

- Visualization and selective chemical targeting of RNA G-quadruplex structures in the cytoplasm of human cells
  Biffi, G.; Di Antonio, M.; Tannahill, D.; Balasubramanian, S. *Nature Chem.* **2014**, *6,* 75-80.
  Abstract:



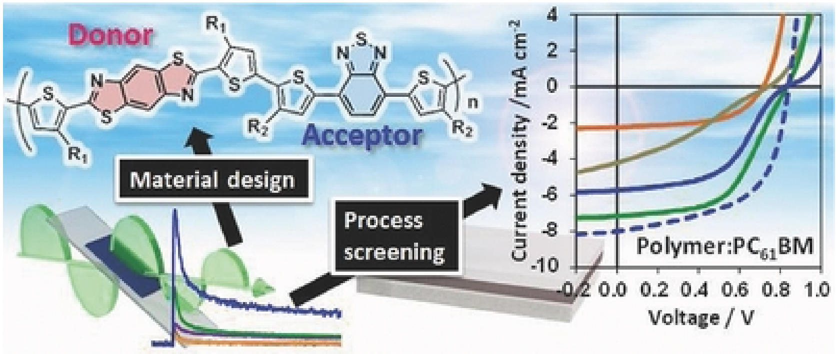
Following extensive evidence for the formation of four-stranded DNA G-quadruplex structures in vitro, DNA G-quadruplexes have been observed within human cells. Although chemically distinct, RNA can also fold in vitro into G-quadruplex structures that are highly stable because of the 2'-hydroxyl group. However, RNA G-quadruplexes have not yet been reported in cells. Here, we demonstrate the visualization of RNA G-quadruplex structures within the cytoplasm of human cells using a G-quadruplex structure-specific antibody. We also demonstrate that small molecules that bind to G-quadruplexes in vitro can trap endogenous RNA G-quadruplexes when applied to cells. Furthermore, a small molecule that exhibits a preference for RNA G-quadruplexes rather than DNA G-quadruplexes in biophysical experiments also shows the same selectivity within a cellular context. Our findings provide substantive evidence for RNA G-quadruplex formation in the human transcriptome, and corroborate the selectivity and application of stabilizing ligands that target G-quadruplexes within a cellular context.

- 25th Anniversary Article: Design of Polymethine Dyes for All-Optical Switching Applications: Guidance from Theoretical and Computational Studies
  Gieseking, R. L.; Mukhopadhyay, S.; Risko, C.; Marder, S. R.; Brédas, J.–L. *Adv. Mater.* **2014**, *26*, 68-84.
  Abstract:



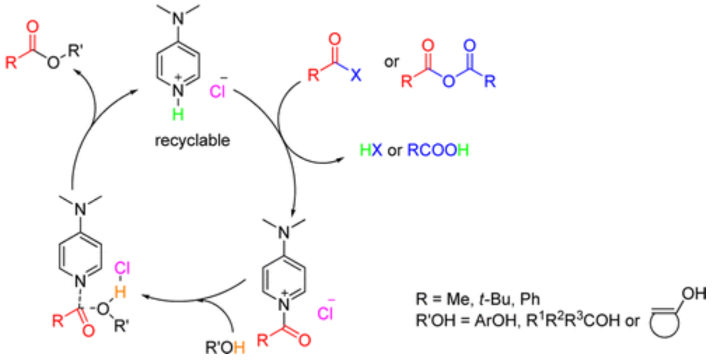
All-optical switching—controlling light with light—has the potential to meet the ever-increasing demand for data transmission bandwidth. The development of organic π-conjugated molecular materials with the requisite properties for all-optical switching applications has long proven to be a significant challenge. However, recent advances demonstrate that polymethine dyes have the potential to meet the necessary requirements. In this review, we explore the theoretical underpinnings that guide the design of π-conjugated materials for all-optical switching applications. We underline, from a computational chemistry standpoint, the relationships among chemical structure, electronic structure, and optical properties that make polymethines such promising materials.

- Benzobisthiazole as Weak Donor for Improved Photovoltaic Performance: Microwave Conductivity Technique Assisted Molecular Engineering
  Tsuji, M.; Saeki, A.; Koizumi, Y.; Matsuyama, N.; Vijayakumar, C.; Seki, S. *Adv. Funct. Mater*. **2014**, *24*, 28-36.
  Abstract:



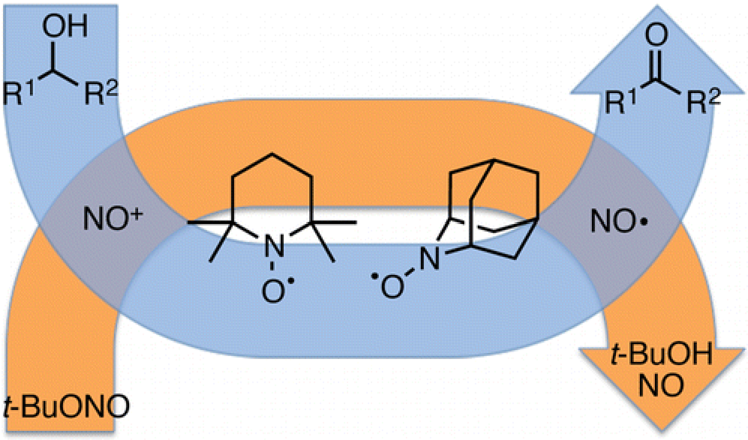
Benzobisthiazole (BBTz), commonly an acceptor unit in low-bandgap polymers of organic photovoltaics, is used as weak donor and polymerized with benzothiadiazole (BT). The BBTz-BT copolymers exhibit deep HOMO (–5.7 eV) and 3.8% power conversion efficiency in an inverted cell. Xe-flash time-resolved microwave conductivity is shown to be a versatile tool for decision-making on the molecular design strategy.

- 4-(*N*,*N*-Dimethylamino)pyridine Hydrochloride as a Recyclable Catalyst for Acylation of Inert Alcohols: Substrate Scope and Reaction Mechanism.
  Liu, Z.; Ma, Q.; Liu, Y.; Wang, Q. *Org. Lett.* **2014,** *16*, 236-239.
  Abstract:



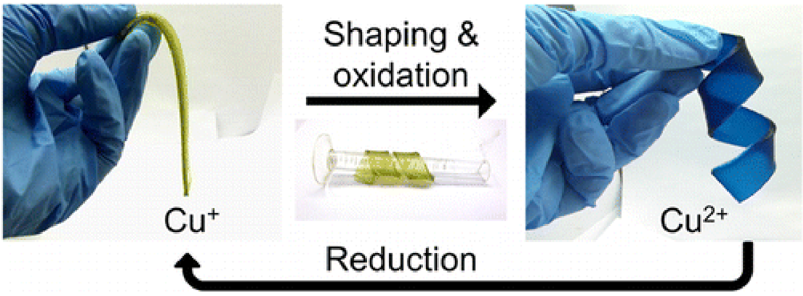
4-(*N,N*-Dimethylamino)pyridine hydrochloride (DMAP·HCl), a DMAP salt with the simplest structure, was used as a recyclable catalyst for the acylation of inert alcohols and phenols under base-free conditions. The reaction mechanism was investigated in detail for the first time; DMAP·HCl and the acylating reagent directly formed *N*-acyl-4-(*N′*,*N′*-dimethylamino)pyridine chloride, which was attacked by the nucleophilic substrate to form a transient intermediate that released the acylation product and regenerated the DMAP·HCl catalyst.

- Anaerobic Nitroxide-Catalyzed Oxidation of Alcohols Using the $NO^+/NO^·$ Redox Pair
  Holan, M.; Jahn, U. *Org. Lett.* **2014,** *16*, 58-61.
  Abstract:



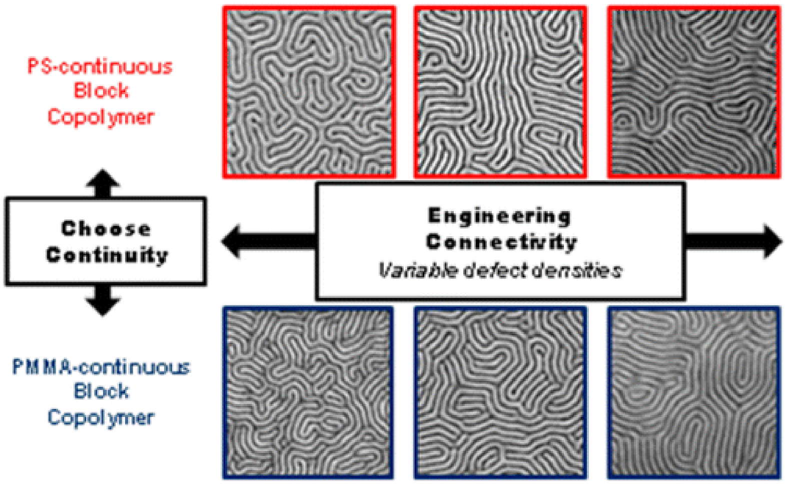
A new method for alcohol oxidation using TEMPO or AZADO in conjunction with $BF_3·OEt_2$ or $LiBF_4$ as precatalysts and *tert*-butyl nitrite as a stoichiometric oxidant has been developed. The system is based on a $NO^+/NO·$ pair for nitroxide reoxidation under anaerobic conditions. This allows the simple, high-yielding conversion of various achiral and chiral alcohols to carbonyl compounds without epimerization and no formation of nonvolatile byproducts.

- Chemical and Electrochemical Manipulation of Mechanical Properties in Stimuli-Responsive Copper-Cross-Linked Hydrogels
  Harris, R.D.; Auletta, J. T.; Mohaghegh Motlagh, S. A.; Lawless, M. J.; Perri, N. M.; Saxena, S.; Weiland, L. M.; Waldeck, D. H.; Clark, W. W.; Meyer, T. Y. *ACS Macro Lett.* **2013**, *2*, 1095–1099.
  Abstract:



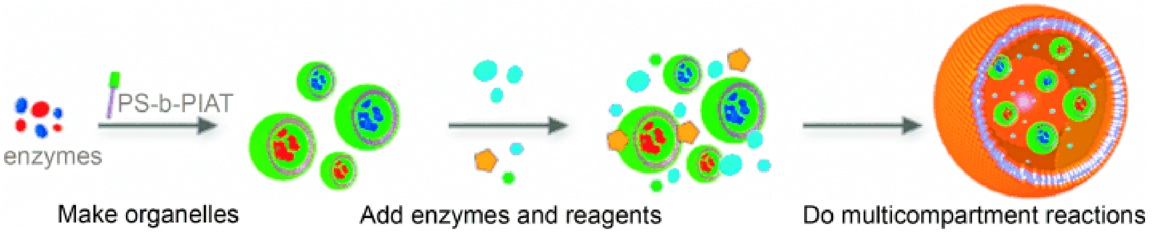
Inspiration for the design of new synthetic polymers can be found in the natural world, where materials often exhibit complex properties that change depending on external stimuli. A new synthetic electroplastic elastomer hydrogel (EPEH) that undergoes changes in mechanical properties in response to both chemical and electrochemical stimuli has been prepared based on these precedents. In addition to having the capability to switch between hard and soft states, the presence of both permanent covalent and dynamic copper-based cross links also allows this stimuli-responsive material to exhibit a striking shape memory capability. The density of temporary cross links and the mechanical properties are controlled by reversible switching between the +1 and +2 oxidation states.

- Processing Approaches for the Defect Engineering of Lamellar-Forming Block Copolymers in Thin Films
  Campbell, I. P.; Hirokawa, S.; Stoykovich, M. P. *Macromolecules* **2013**, *46*, 9599–9608.
  Abstract:



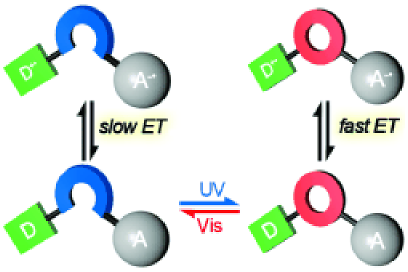
The in-plane connectivity and continuity of lamellar-forming polystyrene-block-poly(methyl methacrylate) copolymer domains in thin films depend on the density and relative population of defects in the self-assembled morphology. Here we varied film thickness, degree of polymerization, thermal annealing time, and annealing temperature in order to engineer the defect densities and topology of the lamellar morphology. Assembly in thicker films leads to lower defect densities and thus reduced connectivity of the lamellar domains, which is considered in the context of the activation energies and driving forces for defect annihilation. Systems with smaller degrees of polymerization were also found to achieve lower defect densities and reduced domain connectivity. Most importantly, the relative populations of each type of defect were unaffected by the defect density, and these morphologies had similar long-range continuities. Controlling processing conditions such as thermal annealing time and temperature, in comparison, was ineffective at tuning the defect density of block copolymer lamellae because quasi-equilibrium morphologies were rapidly achieved and subsequently remained quasi-static. These results provide a framework for selecting the composition, degree of polymerization, and processing parameters for lamellar-forming block copolymers in thin films for applications that either require low defect densities (e.g., in the directed assembly of microelectronic architectures) or benefit from high defect densities (e.g., in network structures for transport).

- Cascade Reactions in Multicompartmentalized Polymersomes
  Peters, R. J. R. W.; Marguet, M.; Marais, S.; Fraaije, M. W.; van Hest, J. C. M.; Lecommandoux, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 146–150.
  Abstract:



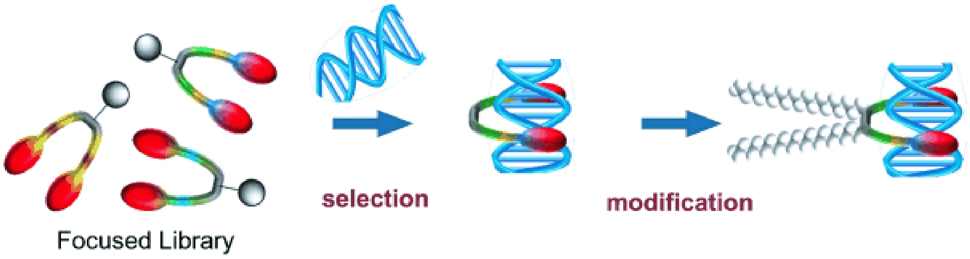
Mimicking cells: Enzyme-filled polystyrene-*b*-poly(3-(isocyano-L-alanyl-aminoethyl)thiophene) (PS-*b*-PIAT) nanoreactors are encapsulated together with free enzymes and substrates in a larger polybutadiene-*b*-poly(ethylene oxide) (PB-*b*-PEO) polymersome, forming a multicompartmentalized structure, which shows structural resemblance to the cell and its organelles. An original cofactor-dependent three-enzyme cascade reaction is performed, using either compatible or incompatible enzymes, which takes place across multiple compartments.

- Gating Charge Recombination Rates through Dynamic Bridges in Tetrathiafulvalene–Fullerene Architectures
  Castellanos, S.; Vieira, A. A.; Illescas, B. M.; Sacchetti, V.; Schubert, C.; Moreno, J.; Guldi, D. M.; Hecht, S.; Martín, N. *Angew. Chem. Int. Ed.* **2013**, *52*, 13985–13990.
  <u>Abstract:</u>



An open and shut case: The competition between charge separation and recombination in artificial photosynthetic systems can be controlled by using photochromic dynamic bridge. The photoinduced opening and closing of the bridge mediates the electronic coupling between donor (D) and acceptor (A).

- Utilizing Combinatorial Chemistry and Rational Design: Peptidic Tweezers with Nanomolar Affinity to DNA Can Be Transformed into Efficient Vectors for Gene Delivery by Addition of a Lipophilic Tail
  Kuchelmeister, H. Y.; Karczewski, S.; Gutschmidt, A.; Knauer, S.; Schmuck, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 14016–14020.
  <u>Abstract:</u>

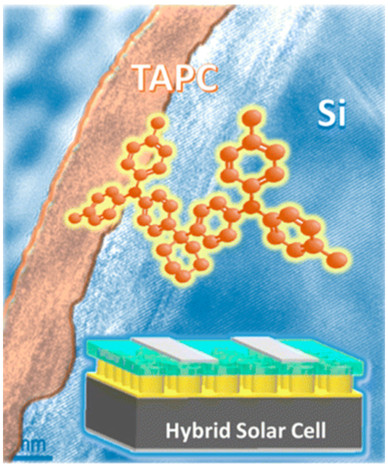


Into the library: Screening a focused library of 259 peptide tweezers, composed of two identical arms with zero to three amino acids and an artificial anion recognition site, yielded DNA binders with nanomolar affinity. These ligands are only modest gene carriers (transfection efficiency <10 %); however, excellent transfection efficiencies (up to 90 %) were achieved after the covalent attachment of long aliphatic chains.

- 13% Efficiency Hybrid Organic/Silicon-Nanowire Heterojunction Solar Cell via Interface Engineering

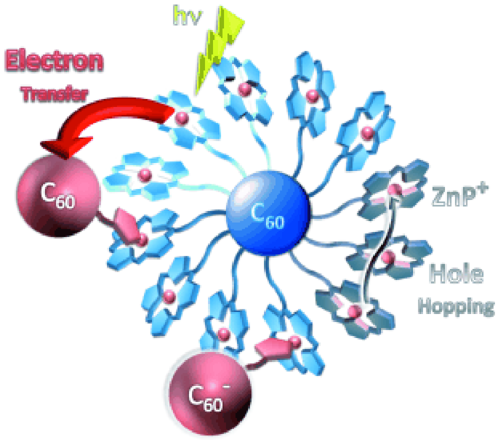
Yu, P.; Tsai, C.-Y.; Chang, J.-K.; Lai, C.-C.; Chen, P.-H.; Lai, Y.-C.; Tsai, P.-T.; Li, M.-C.; Pan, H.-T.; Huang, Y.-Y.; Wu, C.-I.; Chueh, Y.-L.; Chen, S.-W.; Du, C.-H;; Horng, S.-F.; Meng, H.-F. *ACS Nano* **2013**, *7*, 10780-10787.

Abstract:



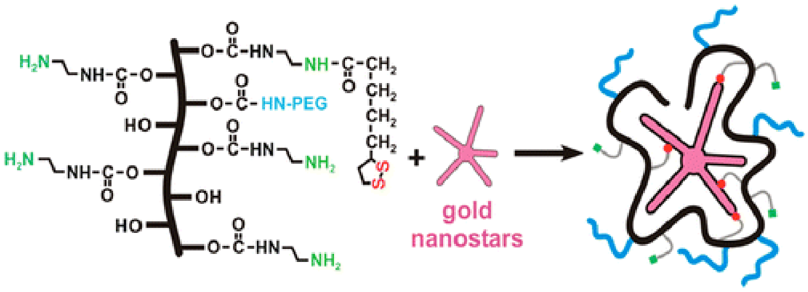
Interface carrier recombination currently hinders the performance of hybrid organic–silicon heterojunction solar cells for high-efficiency low-cost photovoltaics. Here, we introduce an intermediate 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) layer into hybrid heterojunction solar cells based on silicon nanowires (SiNWs) and conjugate polymer poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS). The highest power conversion efficiency reaches a record 13.01%, which is largely ascribed to the modified organic surface morphology and suppressed saturation current that boost the open-circuit voltage and fill factor. We show that the insertion of TAPC increases the minority carrier lifetime because of an energy offset at the heterojunction interface. Furthermore, X-ray photoemission spectroscopy reveals that TAPC can effectively block the strong oxidation reaction occurring between PEDOT:PSS and silicon, which improves the device characteristics and assurances for reliability. These learnings point toward future directions for versatile interface engineering techniques for the attainment of highly efficient hybrid photovoltaics.

- A Supramolecular Photosynthetic Model Made of a Multiporphyrinic Array Constructed around a C_{60} Core and a C_{60}–Imidazole Derivative
  Yoosaf, K.; Iehl, J.; Nierengarten, I.; Hmadeh, M.; Albrecht-Gary, A.-M.; Nierengarten, J.-F.; Armaroli, N. *Chem. Eur. J.* **2014**, *20*, 223–231.
  Abstract:



The photophysical properties of a supramolecular fullerene–porphyrin ensemble resulting from the self-assembly of a pyrrolidinofullerene–imidazole derivative (**F1**) with a multimetalloporphyrin array constructed around a hexasubstituted fullerene core (**F(ZnP)$_{12}$**) have been investigated. The fullerene hexa-adduct core of the host system does not play any active role in the cascade of photoinduced events of the supramolecular ensemble, indeed no intercomponent photoinduced processes could be observed in host **F(ZnP)$_{12}$**. In contrast, upon axial coordination with the monosubstituted fullerene guest **F1**, a quantitative quenching of the fluorescence signal of the metalloporphyrins was observed for the supramolecular complex **[F(ZnP)$_{12}$(F1)$_n$]** both in polar and nonpolar solvents. In toluene, the supramolecular ensemble exhibits a charge transfer emission centered around 930 nm, suggesting the occurrence of intramolecular face-to-face interactions of **F1** with neighboring metalloporphyrin moieties within the self-assembled photoactive array. This mechanism is supported by the fact that a one order of magnitude increase in the binding constant was observed for the supramolecular complex **[F(ZnP)$_{12}$(F1)$_n$]** when compared with a reference system lacking the pyrrolidinofullerene unit. In benzonitrile, a long-lived charge-separated state (τ=0.3 µs) has been detected for the supramolecular adduct.

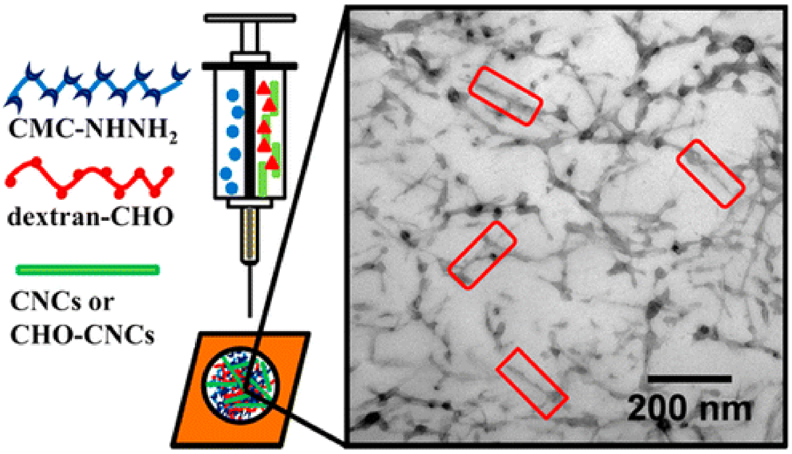
- Amphiphilic Copolymers Based on Poly[(hydroxyethyl)-D,L-aspartamide]: A Suitable Functional Coating for Biocompatible Gold Nanostars
  Cavallaro, G.; Triolo, D.; Licciardi, M.; Giammona, G.; Chirico, G.; Sironi, L.; Dacarro, G.; Donà, A.; Milanese, C.; Pallavicini, P. *Biomacromolecules* **2013**, *14*, 4260–4270.
  Abstract:



Novel amphiphilic copolymers have been synthesized based on a biocompatible poly(hydroxyethylaspartamide) (PHEA) backbone, bearing both anchoring groups for gold nanoparticles, such as thiols and disulfide, and conjugable moieties, such as amino groups, the latter as points suitable for appending further functional agents. The strategy was to functionalize α,β-poly[(*N*-2-hydroxyethyl)-d,l-aspartamide] (PHEA) with PEG$_{2000}$-NH$_2$ and with ethylenediamine (EDA) obtaining a partially pegylated copolymer with a large number of pendant primary amino groups. A fraction of the latter was conjugated with molecules bearing terminal thiol moieties such as 12-mercaptododecanoic acid (MDA) and disulfide groups such as lipoic acid (LA), obtaining the two amphiphilic derivatives PHEA–PEG$_{2000}$–EDA–MDA (PPE–MDA) and PHEA–PEG$_{2000}$–EDA–LA (PPE–LA), which also proved intrinsically able to self-assemble in polymeric micelles. The two copolymers efficiently coated gold nanostars (GNSs, size ~40 nm), wrapping around the surface increasing only slightly the hydrodynamic diameter (reaching ~45 nm), imparting them stability and a pH-switchable surface charge, due to the unreacted amino groups. Remarkably, the poor solvation and the huge steric hindrance experienced by the amino groups lowers the observed logarithmic protonation constants to 5.6–5.7. *In vitro* experiments demonstrated that PPE–MDA and PPE–LA copolymers have an intrinsic excellent biocompatibility in both the human brain neuroblastoma (SH-SY5Y) and human bronchial epithelial (16-HBE) cell lines. Interaction of the same cell lines with "nude" GNS and

GNS coated with PPE–LA was also studied, disclosing a completely satisfactory biocompatibility of the latter.

- Injectable Polysaccharide Hydrogels Reinforced with Cellulose Nanocrystals: Morphology, Rheology, Degradation, and Cytotoxicity
  Yang, X.; Bakaic, E.; Hoare, T.; Cranston, E. D. *Biomacromolecules* **2013**, *14*, 4447–4455.
  Abstract:



Injectable hydrogels based on carboxymethyl cellulose and dextran, reinforced with rigid rod-like cellulose nanocrystals (CNCs) and aldehyde-functionalized CNCs (CHO–CNCs), were prepared and characterized. The mechanical properties, internal morphology, and swelling of injectable hydrogels with unmodified and modified CNCs at various loadings were examined. In all cases, gelation occurred within seconds as the hydrogel components were extruded from a double-barrel syringe, and the CNCs were evenly distributed throughout the composite, as observed by scanning and transmission electron microscopy. When immersed in purified water or 10 mM PBS, all CNC-reinforced hydrogels maintained their original shape for more than 60 days. The maximum storage modulus was observed in hydrogels with 0.250 wt % of unmodified CNCs and 0.375 wt % of CHO–CNCs. CHO–CNCs acted as both a filler and a chemical cross-linker, making the CHO–CNC-reinforced hydrogels more elastic, more dimensionally stable, and capable of facilitating higher nanoparticle loadings compared to hydrogels with unmodified CNCs, without sacrificing mechanical strength. No significant cytotoxicity to NIH 3T3 fibroblast cells was observed for the hydrogels or their individual components. These properties make CNC-reinforced injectable hydrogels of potential interest for various biomedical applications such as drug delivery vehicles or tissue engineering matrices.