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Novel hyperbranched organofunctional polyalkoxysiloxanes: versatile precursors for molecular-level design of advanced colloidal materials

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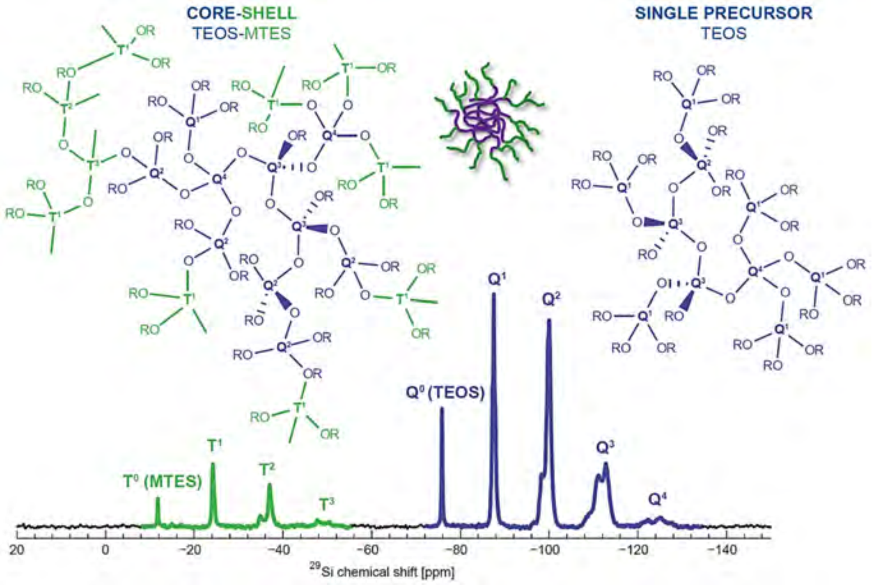
Organic-inorganic hybrid materials combine the robustness of inorganic materials with the multiplicity to design specific function and chemical interactions of organic chemistry [1]. Despite tremendous progress in preparative techniques, many synthetic protocols either offer only limited control over the colloidal material substructure, are not industrially scalable or both. Particularly in the field of organosilica hybrids, the controlled "substructuring" at the nanoparticle or colloid level is hampered by poor molecular-level control over its building blocks, particularly when using hydrolytic chemistry protocols.

Inspired by the works of the Möller group [2], we present a new class of core-shell-type organofunctional polyalkoxysiloxane molecular building blocks. These compounds are liquids at room temperature in neat form and can be thought of as star-polymers made of Q-type siloxane moieties in the core and T-type organofunctional moieties grafted at the extremities of its dendritic arms. In this presentation, we will address the non-hydrolytic synthesis and characterization of these novel building blocks as well as give an outlook into applications in colloidal materials synthesis.



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Mass transport studies in porous silica as a function of core-shell architecture

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The study of molecular transport within the pores of silica is of great importance to many research areas; drug delivery, sensing, catalysis, filtration, encapsulation and gas sorption. Theoretical models describing transport behaviour have already been reported; however, few have presented a physical system for observing the accessibility of guest species in mesoporous silica. Here we report fluorescent core-shell particles as a platform to study molecular transport within a porous silica system with tuneable characteristics such as pore lengths, pore diameters and surface chemistry. The core particles were synthesised from non-porous silica spheres with post-synthetically grafted fluorescein moieties, Figure 1a. A silica shell was subsequently deposited around the functionalised cores. A variety of shell thicknesses were achievable through careful control of the addition rate of silane (tetraethyl orthosilicate (TEOS)) and hydrolysis solution. A primary shell (s1, approx. 800 nm, Figure 1b) demonstrated a very narrow particle size distribution which broadened on additional shell growth (s2, approx. 1300 nm, Figure 1c). The exterior of the core-shell particle was functionalised with rhodamine for convenient visualisation by CLSM, Figure 1d. The shell is inherently macroporous but well-defined mesopores can be introduced into the silica network through pseudomorphic transformation (PT), while retaining the original morphology. PT in addition to postsynthetic functionalisation generated a variety of pore sizes and pore surface chemistries. Core accessibility and surface wettability can then be determined by investigating the quenching of the fluorescent core.

The large variety of core-shell particles available through customisation enabled the testing of core accessibility as a function of the shell architecture.

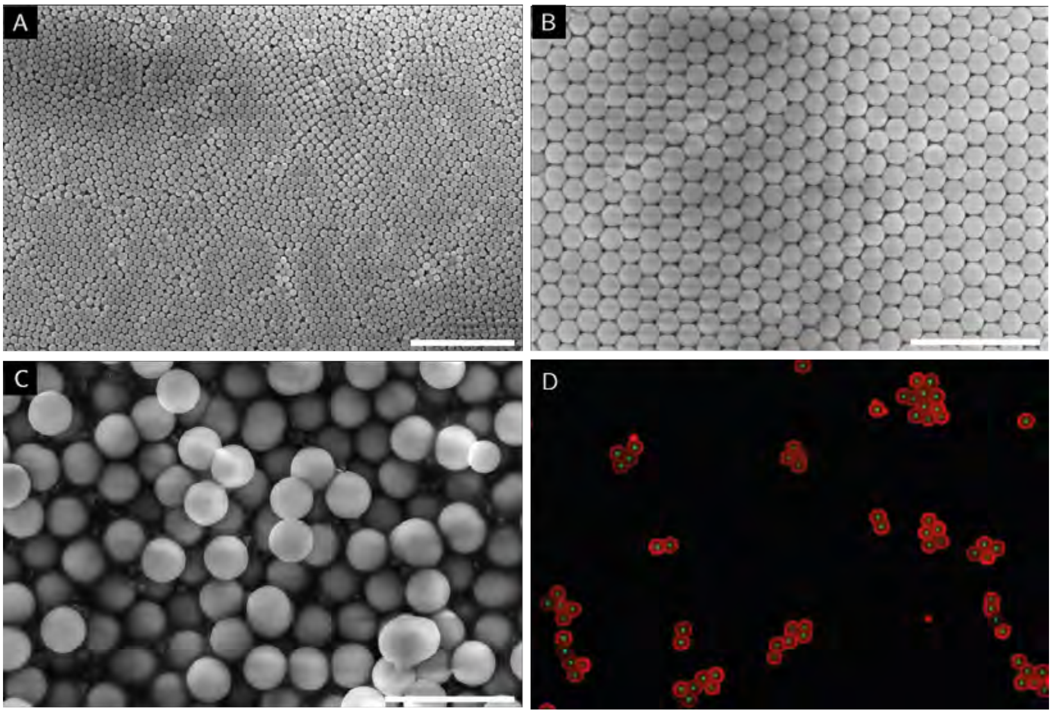

Figure 1) SEM images of the different stages of the functionalised core-shell particles. (A) Stöber particles, (B) core-shell (s1) particles, (C) core-shell (s2) particles and (D) a CLSM image of s2 particles functionalised with two dyes. Fluorescein on the core (green) and rhodamine B on the exterior (red). All scale bars are equal to 5 µm.

Functionalization of Chitosan for Non-viral Gene Delivery to the Liver

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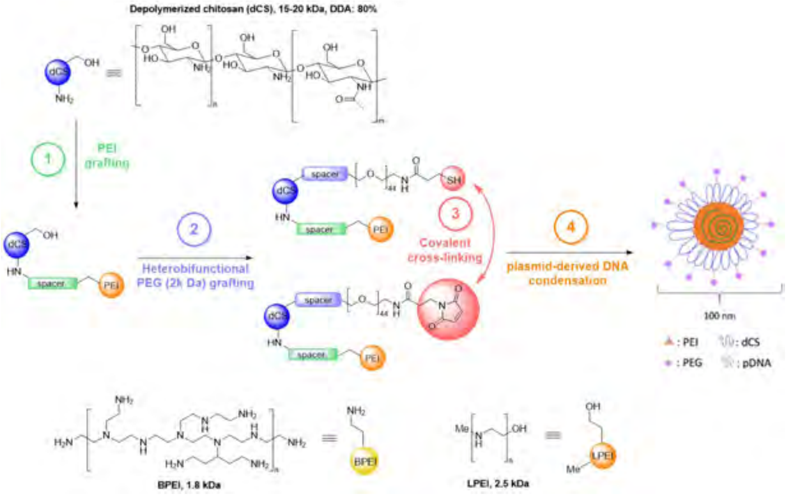
Liver inherited monogenetic disorders like phenylketonuria (PKU) or ornithine transcarbamylase (OTC) deficiency greatly suffer from a lack of available treatments. For most patients, liver transplantation currently remains the only option, leading them to deal with life-long side effects. Gene therapy is nowadays emerging as a powerful alternative for the treatment of such disorders by making profit of viral and non-viral vectors to deliver RNA or plasmid DNA (pDNA).[1] Whereas the former offers better transfection efficiencies, non-viral vectors provide safer profiles with no or low immunogenicity and ease of production and administration to the patient.[2] Such biocompatible delivery systems are based on biodegradable polymers such as chitosan (CS) or polyethylene glycol (PEG).

We herein describe the development of a pDNA polymeric-based nanocarrier designed for liver-targeted gene therapy. This delivery system is composed of a chitosan backbone of 15-20 kDa on average, obtained by depolymerization of commercial chitosan (≈ 90 kDa). This depolymerized CS (dCS) backbone was conjugated to branched or linear polyethyleneimine (BPEI or LPEI) chains, allowing efficient condensation of pDNA through electrostatic interactions. In order to lower cytotoxicity and increase solubility and bioavailability, this copolymeric structure was grafted with heterobifunctional PEG using two different linkers. PEG was linked to the dCS backbone either *via* an ester or a carbamate bond, eventually leading to different pathways of degradability for the copolymer. In order to compare the efficiency of a covalent system versus a non-covalent one, we also designed dCS-PEG systems to be mixed with dCS-BPEI (or dCS-LPEI) ones. The cross-reactive PEG chains allow for further covalent conjugation of PEG-dCS-BPEI systems to enhance the stability of the copolymeric assemblies.

The chemical composition (e.g grafting degrees of PEG and PEI on dCS) and the covalency of the various synthesized systems was determined by ^{1}H and DOSY (Diffusion Ordered SpectroscopY) NMR. *In vitro* assays were performed on the most relevant conjugates, in order to determine the condensation ability, transfection efficiency, physical properties and cytotoxicity of the systems. Promising candidates were compared to commercial jetPEI, a PEI aqueous formulation designed for gene delivery with high transfection efficiencies. Lastly, the first *in vivo* evaluation of LPEI-based system, so far the most promising combination, is disclosed.



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Supramolecular Assembly of Amphiphilic DNA into Vesicular Architectures

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Aggregation-induced emission (AIE) type chromophores are non-emissive in the molecularly dissolved state but become highly fluorescent in their aggregated state. In this emerging field, implementations of the AIE phenomenon include biomolecular sensing or optoelectronic devices, to name a few. DNA conjugates describe the fusion of natural DNA single strands with artificial nucleotide surrogates and thus, expand the scope of DNA. Supramolecular assembly of such DNA conjugates lead to functional constructs, with applications in materials science and DNA nanotechnology. In this contribution, we present our recent findings of a combination of the two previously described concepts.

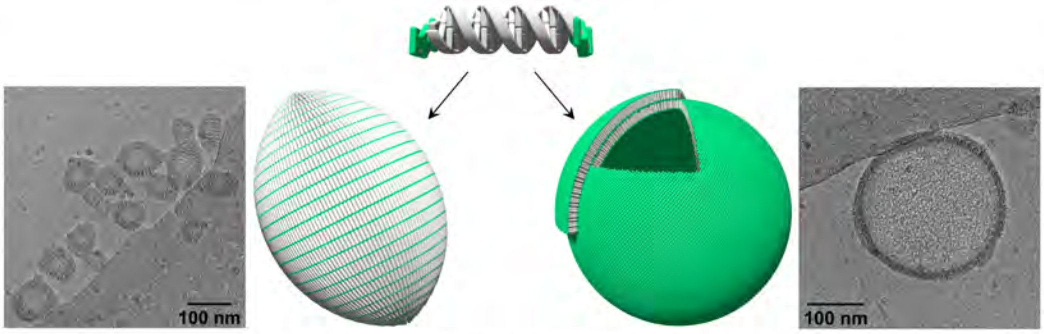

Figure. Illustration of the TPE-DNA hybrid and the two different vesicular constructs, as well as cryo-EM images of these supramolecular assemblies. TPE is represented in green and DNA in gray.

DNA conjugates, terminally functionalized with AIE-active tetraphenylethylene (TPE) units, have been prepared. As visualized by cryo-electron microscopy (cryo-EM), these TPE-DNA conjugates self-assemble into two different vesicular constructs, varying in the alignment of the DNA hybrids. The accessibility of the two DNA architectures is demonstrated by ethidium bromide intercalation experiments and the incorporation of a Cy3-labelled DNA *via* strand exchange, leading to DNA-addressable, light-harvesting constructs. This dynamic behavior of these DNA-constructed vesicles renders them versatile intermediates for nanotechnology applications, such as DNA-triggered delivery devices.

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Quantitative mechanochromism of polydiacetylenes at the nanoscale

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Polydiacetylenes (PDA) are mechanochromic polymers, that show a colour change (e.g. blue to red) upon external stimuli such as heat, stress or changes in the chemical environment [1]. However, how these stimuli change their structure and how that relates to their optical properties is still not completely clear to this day. The overwhelming part of the research hitherto has focused on activation of the colour change of PDA by heat[2] or solvents[3], and little attention has been devoted to the mechanosensitivity of PDA in its true sense, i.e. activation of the blue-to-red colour change by forces. Furthermore, these studies were either only qualitative[4] or macroscopic[5]. The only study on the mechanosensitivity of polydiacetylenes at the nanoscale has been the work of Polacchi et al.[6], however, they correlated the applied vertical force to the fluorescence increase of polydiacetylenes. In contrast, it has been established that lateral forces are needed to trigger the movement of the side chains of PDA and thus trigger the colour change.[4a] Due to experimental difficulties, no quantitative study has been published on the fluorescence response of polydiacetylenes against locally exerted lateral forces.

To address this question, we deposited 10,12-tricosadiynoic acid and 10,12-pentacosadiynoic acid onto plasma-activated glass substrates with Langmuir-Blodgett technique, exposed them to UV for polymerisation, and applied forces to the polymerised film by an atomic force microscope (AFM), while simultaneously measuring the emitted fluorescence. The standard AFM is not able to measure lateral forces directly, thus we needed a calibration method to convert the registered lateral deflection to lateral force.[7] The registered fluorescence is characteristic of the transformed red phase of polydiacetylenes, thus enabling us to follow the phase transition, while the atomic force microscope registers the forces exerted to the polydiacetylene chains. Combining the two techniques could open a path to the fluorescence – lateral force calibration of the colour change, contributing to a deeper understanding of polydiacetylenes and pointing towards potential force sensing applications.

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Patience is a Virtue: Self-Assembly and Physico-Chemical Properties of Cellulose Nanocrystal Allomorphs

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Cellulose nanocrystals (CNCs) are bio-based rod-like nanoparticles with a quickly expanding market. Depending on their origin and chemical treatment, a variety of cellulose crystal allomorphs can be prepared. Industrially produced CNCs are isolated from the native crystalline allomorph cellulose I, giving cellulose I nanocrystals (CNC-I). An interesting feature of CNC-I is that they self-assemble into chiral nematic liquid crystalline phases upon sample concentration as a result of the increase in translational entropy due to the alignment of the CNC-rods. To date, the liquid crystalline properties have only been investigated for the native allomorph, CNC-I. To fill this void, we compare the physico-chemical properties and liquid crystalline behavior of CNC-I to those produced from a different crystal allomorph, known as cellulose II (CNC-II). First, cellulose II is obtained by treating macroscopic cellulose I fibers with a strong aqueous sodium hydroxide solution. Then, the allomorphs are isolated in a top-down manner from macroscopic cellulose I and cellulose II fibers, by sulfuric acid hydrolysis, resulting in colloidally stable sulfated CNC-I and CNC-II, respectively. The two allomorphs show similar surface charge densities and z-potential. Both CNC-types are determined to have a right-handed twist by induced circular dichroism. CNC-II are shorter in length and therefore have a slightly lower aspect ratio compared to CNC-I (Figure 1). Despite having very similar physico-chemical properties, the self-assembly of the two CNC allomorphs in water was distinctive. Whilst CNC-I equilibrate into a chiral nematic phase in under two weeks, CNC-II first phase separate into an upper isotropic and lower nematic phase, after which the CNC-II slowly reorganize into a long-pitch chiral nematic liquid crystal over a period of forty weeks. Here, we propose a number of hypotheses that could contribute to these observations. First, the different self-assembly behavior of the allomorphs may be caused by their faster diffusion, which is most likely related to their shorter lengths. The slow assembly could also be a result of the different crystal structures of the allomorphs, which presumably have distinct dipole moments. Finally, the CNC twist frequency and surface sulfate group distribution may likewise play a role.

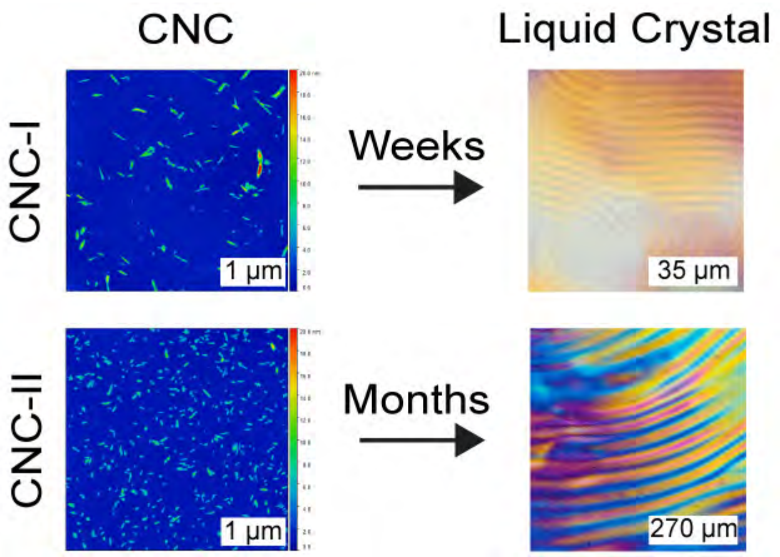

Figure 1. AFM images of CNC-I (top) and CNC-II (down), and their self-assembly to a chiral nematic liquid crystalline phase.

Functionalized Polyolefins for Recycling & Dow's Sustainability Commitments

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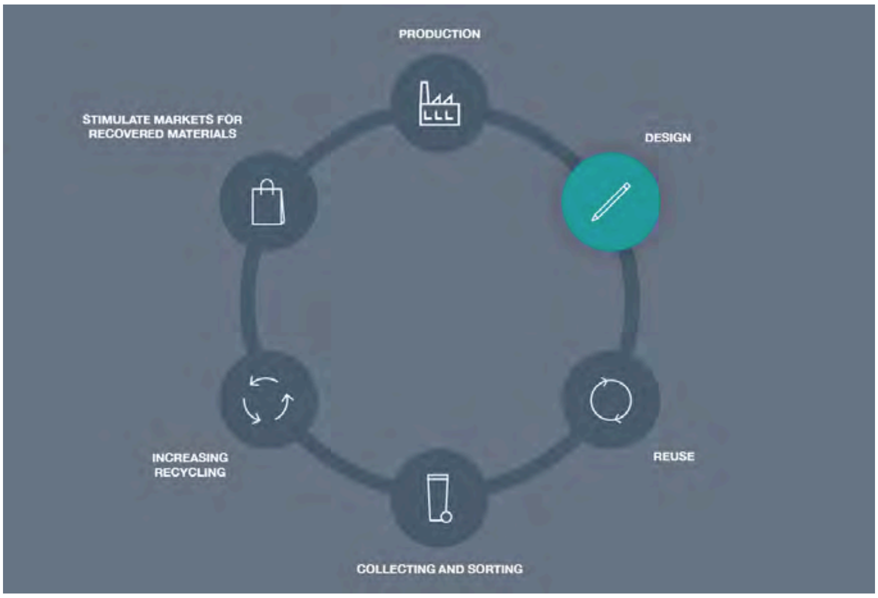
At Dow we believe that plastic should only be used when it offers the lowest environmental impact. Plastic waste should never end up in the environment. That's why we're committed to accelerating the transition to a circular economy and to making plastic part of a circular world – a world where its value is retained, and the environmental impact is minimized. The European Commission has made a political commitment that all plastic packaging must be reusable or economically recyclable by 2030. Major brands and retailers are targeting 2025 to be 100% recyclable. In line with our sustainability goals, we are committed to ensuring that all packaging made from our resins is designed to be recyclable by 2025.



Solutions for recyclable packaging right from the design phase are offered to the value chain. Mono-material concepts, such as the all-polyethylene and all-polyolefin packages with and without barrier are at the forefront of the discussion with first commercial successes available. They are complemented by a unique product portfolio for plastics recycling. Following the integration of DuPont´s ethylene copolymer business Dow can support the polymer and recycling industry with one of the broadest offerings of performance modifiers and compatibilizers. We offer solutions for post-industrial and post-consumer flexible and rigid plastics waste.

The modifier chemistry behind our non-polar and polar products will be presented, illustrated by application examples. Renowned product brands include non-polar polyolefins ENGAGE™, INTUNE™, INFUSE™, and polar offerings like RETAIN™, ELVALOYTM and FUSABONDTM.

With the combined range we can help manage diverse post-industrial and post-consumer recycling streams for a huge variety of polymers, including polyethylene (PE), polypropylene (PP), polyesters (PET), polyamide (PA) and EVOH, and up-cycling opportunities for recyclers and brand owners. Application fields are in the areas of transportation, infrastructure and consumer products, with performance targets similar to virgin materials.

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Polymersome clusters for advanced nanotheranostics

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Nanotheranostics is an emerging field that brings together nanoscale-engineered materials with biological systems providing a combination of therapeutic and diagnostic strategies. However, current theranostic nanoplatforms have serious limitations, mainly due to a mismatch between the physical properties of the selected nanomaterials and their functionalization ease, loading ability or overall compatibility with bioactive molecules. Herein we propose a new nanotheranostic system based on nanocompartment clusters composed of two different polymersomes linked together by DNA. Careful design and procedure optimization resulted in clusters segregating the therapeutic enzyme human Dopa decarboxylase (DDC) and fluorescent probes for the detection unit in distinct but colocalized nanocompartments. The diagnostic compartment provides a twofold function: trackability via dye-loading as the imaging component and the ability to attach the cluster construct to the surface of cells. The therapeutic compartment, loaded with active DDC, triggers the cellular expression of a secreted reporter enzyme via production of dopamine and activation of dopaminergic receptors implicated in atherosclerosis. This novel two-compartment nanotheranostic platform is expected to provide the basis of a new treatment strategy for atherosclerosis, to expand versatility and diversify the types of utilizable active molecules, and thus by extension expand the breadth of attainable applications.

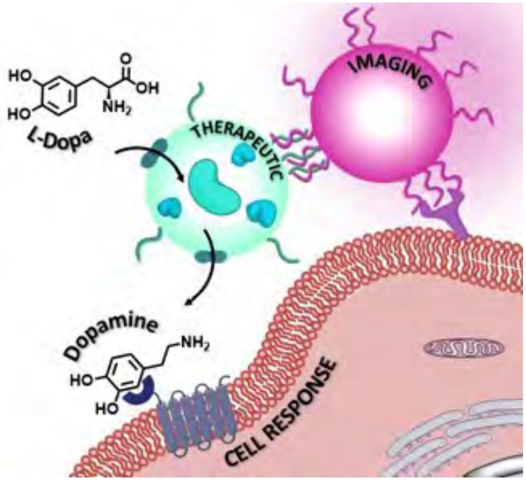

Fig. 1: Schematic illustration of cell attachment of DNA-zipped theranostic polymersome clusters composed of two distinct compartments: the therapeutic DDC-Ncomp and the imaging Dye-Ncomp. While Dye-Ncomps contain fluorescent DY-633 dyes, the DDC-Ncomp contain biologically relevant DDC enzymes that convert L-Dopa into Dopamine. This latter bioactive compound is received by cells and triggers gene expression resulting in the production of a detectable SEAP reporter enzyme.

Signaling Deformation in Polymeric Materials *via* Supramolecular Interactions

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Polymers that change their fluorescence color in response to mechanical deformation provide an easy way to directly assess stresses in a material.[1,2] Such mechanochromic responses could be extremely useful in load-bearing parts that directly signal the location and extent of damage and would crucially allow for a timely repair or replacement. The simple blending of aggregachromic dyes has shown to be a convenient, industrially scalable technique for fabricating mechanochromic materials.[2] However, the approach has largely been limited to semi-crystalline polymer matrices,[3-5] as the dissociation of dye aggregates is thought to require the relatively high shear forces that occur upon disruption of the crystalline domains.

To overcome this challenge, our group has recently focused on the development of mechanophores that feature relatively weak, non-covalent interactions. Expanding beyond the use of simple aggregachromic dyes, we developed a telechelic poly(ethylene-*co*-butylene) with oligo(phenylene-vinylene) (OPV) dyes at the termini (tOPV) and have shown that blending of this tOPV additive with different thermoplastic elastomers renders the latter mechanochromic.[6] We now demonstrate the versatility of this tOPV additive as a sensitive, reversible strain sensor in commerical thermoplastic polyurethanes (TPUs) with varying degrees of crystallinity. Using a simple, *in situ* opto-mechanical testing apparatus, we detect a decisive change in the fluorescence of the TPU-tOPV blend materials at tensile strains as low as 5% and use this visual response to elucidate different processes in the samples.

Moreover, we have developed a derivative of the well-known complementary H-bonding ureido pyrimidinone (UPy) motif that signals dissociation of the non-covalent interaction through a distinct fluorescence signal. The integration of UPy motifs can strengthen a polymer material *via* non-covalent reinforcement and endow it with self-healing properties.[7,8] Using this motif as the core, we have developed a modular synthetic strategy to introduce excimer-forming pyrene units *via* short carbon linkers. When two of these UPy-bispyrene (UPB) molecules interact to form a dimer, the pyrene emission shifts to longer wavelengths, thus directly connecting a visual signal to UPy bonding and breakage events without interfering with the material enhancement properties of the latter. When integrated into polymeric materials, this non-covalent binding motif acts both as a supramolecular crosslinker and as a mechanophore. The investigation of the mechanical as well as mechanochromic properties of polymers that feature this motif is currently ongoing.

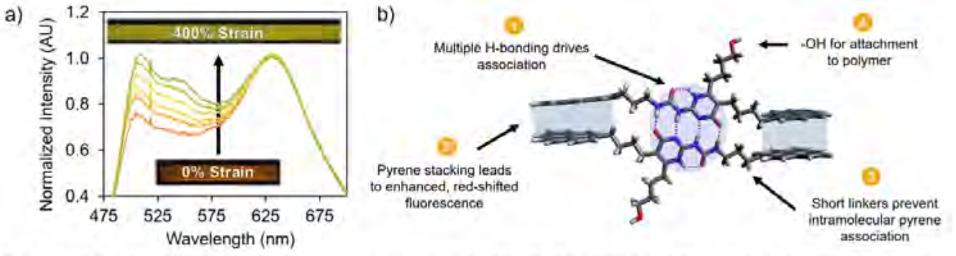

Figure 1. a) Spectroscopic and visual change in emission color of a 0.2 wt% TPU-tOPV blend film stretched at 50% strain intervals. b) Energy-minimized model of the dimer formed between two UPB molecules.

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Simultaneous extraction and controlled chemical modification of polymeric lignin from hardwood

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Lignin, together with cellulose and hemicellulose, is one of the main components of lignocellulosic biomass and the most abundant source of renewable aromatic molecules on earth. Because of this, lignin is a promising candidate for replacing fossil-based materials such as resins, carbon fibers and plastic materials[1]. Despite the many attempts of using lignin in such materials, industrial applications remain limited. This is mainly due to the degradation of lignin's structure during isolation, where the harsh pH and temperature pH conditions favour condensation and repolymerization reactions. This yields to isolated lignins with uncontrolled chemical structures and that are thermodynamically difficult to blend with existing materials or to further functionalize[2]. We have developed a process for the fractionation of biomass and isolation of lignin that uses aldehydes to form stable acetals with the diol present within the beta-O-4 bonds of lignin during extraction from lignocellulosic biomass. This functionalization prevents the condensation of the aromatic biopolymer[3]. Here, we developed a method to extract a chemically modified lignin from hardwood by using a multifunctional aldehyde, which allowed us to both isolate an uncondensed lignin and, at the same time, precisely control the degree of functionalization of the biopolymer for further incorporation into new materials.

In this work we used terephthalic aldehyde (TALD) to stabilize lignin during extraction and at the same time functionalize the biopolymer with residual aldehyde groups. Several TALD functionalized lignins were isolated from birch wood by using different concentrations of terephthalic aldehyde in the reaction system. TALD-Lignins were first characterized through HSQC NMR, and quantitative ^{1}H NMR to determine the molar amount of free aldehydes on the lignin backbone. The quantification showed a linear correlation between the amount of TALD used in the extraction process and the moles of free aldehyde groups bound to the lignin scaffold, demonstrating the possibility of isolating lignins with a controlled quantity of functional groups. Furthermore, to investigate the ability of TALD to efficiently stabilize the aromatic biopolymer, we performed catalytic hydrogenolysis, comparing the results to the reductive catalytic fractionation of birch wood. The high monomer yields obtained in the hydrogenolysis of lignin showed that the terephthalic aldehyde protection strategy is particularly effective at preserving lignin's native structure. Interestingly, the yield of monomers didn't decrease rapidly with a reduction in the amount of bound aldehyde, suggesting that TALD stabilized the lignin not only through the formation of acetals, but potentially also through steric hinderance.

Overall, we demonstrated that lignin could be chemically modified with unprecedent control by introducing on its scaffold a free and non-native aldehyde functional group. Given the ease with which aldehydes can be transformed into a variety of other functional groups under mild conditions, this process could help overcome the challenges that limit lignin's use in new materials such as resins or plastics.

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Ligand-Assisted Solid Phase Synthesis of Mixed-Halide Perovskite Nanocrystals for Highly Electroluminescent Light-Emitting Diodes

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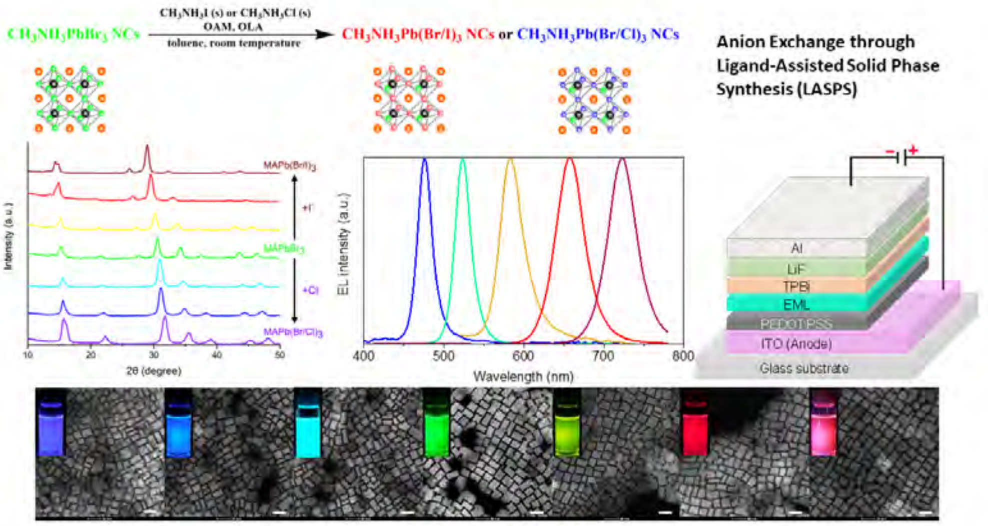
Colloidal organic-inorganic hybrid perovskites (OIHPs) with the general structure ABX_3 (A stands for methylammonium (MA) or formamidinium (FA), B stands for Pb or Sn, and X are halides (Cl, Br, I)) belong to an interesting class of semiconductor materials for optoelectronic applications, including solar cells, lasers, photodiodes, and light-emitting diodes (LEDs). [1-2] Great advantages over other competing semiconductor systems such as cadmium chalcogenides are the simple synthetic routes, high photoluminescence quantum yields (η_{PL}), and especially the color tunability over the whole visible spectra of these materials, which can be easily achieved by varying the halide composition of the OIHPs. In this work, we present a facile solid-state post-synthetic anion exchange method, ligand-assisted solid phase synthesis (LASPS), to prepare highly luminescent methylammonium lead halide ($MAPbX_3$) nanocrystals (NCs), which exhibit a strong PL emission in the entire visible region between 415 and 724 nm with high η_{PL} up to 90%. We report partial substitution processes of the anions at the solid-liquid interface yielding halide mixtures of $MAPb(Br/I)_3$ and $MAPb(Br/Cl)_3$ NCs, respectively. Furthermore, we demonstrate LEDs using LASPS based OIHP NCs with the maximum external quantum efficiency (η_{ext}) of 0.005% to 4.7% at 476 (blue) and 656 nm (red), respectively, whereas parent $MAPbBr_3$ NCs showed an η_{ext} of 3.5% at 524 nm.



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Alginate-based hydrogels as multifunctional materials for cell transplantation, and production of microspheres with a microfluidic technique

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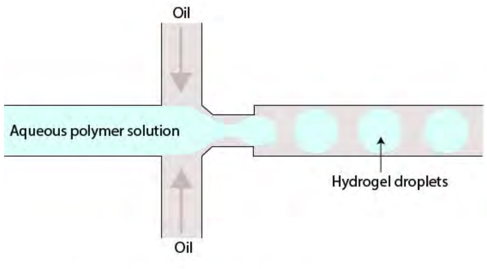
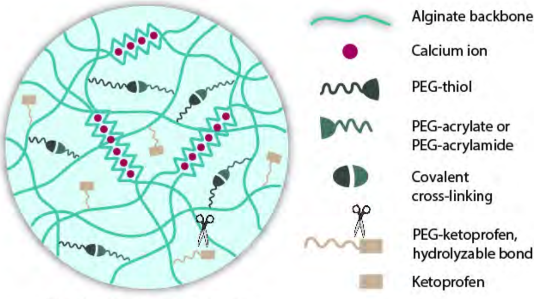
Transplantation of encapsulated xenogeneic cells is a promising treatment alternative for several diseases, where shortage of human donors and the invasive nature of surgery puts the lives of patients at risk. The main field of application is Type I diabetes treatment, where encapsulation of islet producing cells provides protection to the cells while allowing an insulin release to control blood glucose levels.[1] The main shortcomings of the encapsulation materials include instability and poor durability, and the fibrotic cellular overgrowth around the transplanted microspheres. In addition, the field would benefit from new technologies, such as microfluidics, that produce monodisperse microspheres of desired sizes with a high throughput.

We developed a hydrogel matrix that targets the two main issues related to encapsulation materials; enhances stability and elutes anti-inflammatory drugs to mitigate fibrosis. PEGylated alginate hydrogels were prepared by a robust, straightforward grafting process, that resulted in hydrogels with either a reactive functionality to provide a strong covalent cross-linking,[2] or with an anti-inflammatory compound that is released via a hydrolytic reaction.[3] Combination of these PEGylated alginate derivatives led to multifunctional microspheres presenting improved stability, resistance and shape recovery performance compared to unmodified Ca-alginate microspheres, and eluted ketoprofen anti-inflammatory drug for over two weeks in a sustained, controlled manner.

In addition, cross-linked PEGylated alginate and ketoprofen drug eluting hydrogel microspheres were produced with a microfluidic system. Encapsulation of neonatal pig islets within these materials resulted in good cell viability and homogeneous microcapsules of around 400 µm diameter.



Microfluidic microsphere production



Multifunctional microspheres

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Conjugated Polymers via Cyclopentannulation Reaction: Promising Materials for Iodine Adsorption

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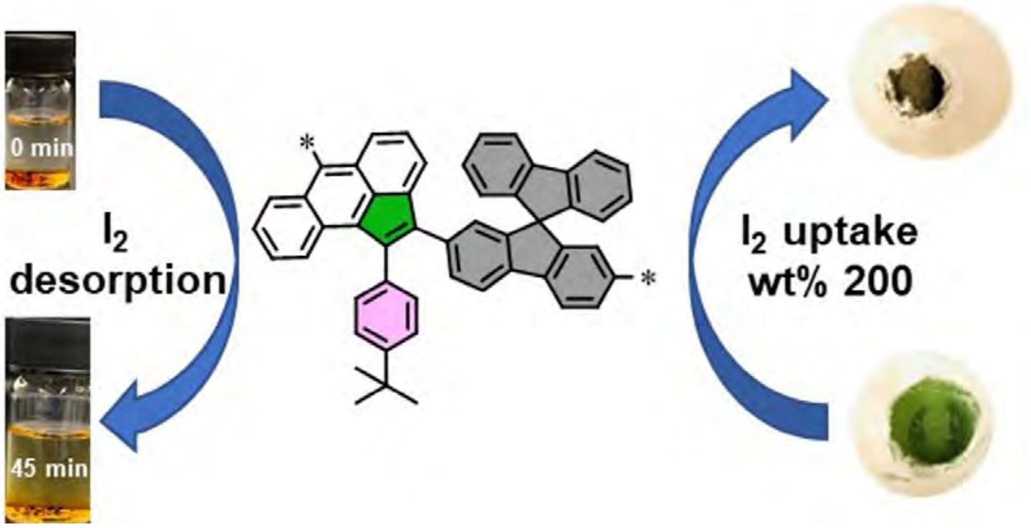
A new class of conjugated polymers is prepared by means of a versatile palladium-catalyzed cyclopentannulation reaction using a series of specially designed diethynyl aryl synthons with the commercially available 9,10-dibromoanthracene **DBA** monomer. The target polymers, **CPP1-3** display high solubility and excellent chemical stability, which allow for their structural and photophysical characterization by various instrumental analysis techniques such as, gel permeation chromatography (GPC), 1H- and 13C-nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), UV-vis absorption, and emission spectroscopies. GPC chromatograms of **CPP1-3** display a high relative weight-average (Mw) molecular weight in the range of 15.8 to 34.3 KDa with a polydispersity index (Đ=Mw/Mn) of ~2.5. Investigation of the iodine adsorption properties of **CPP1-3** reveals their high uptake, namely for **CPP2** ~200 wt%, whose sorption property was sustained even after its reuse several times.[1]



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Conjugated Copolymers Bearing 2,7-Dithienylphenanthrene-9,10-dialkoxy Units: Highly Soluble and Stable Deep-Blue Emissive Materials

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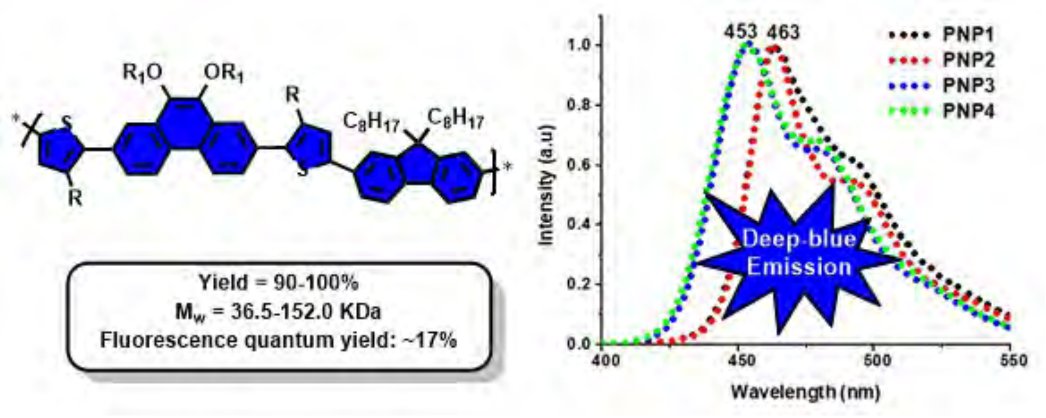
Conjugated copolymers **PNP1-4** were prepared from the palladium catalyzed Suzuki-Miyaura cross-coupling reaction of 2,7-dithienylphenanthrene units - bearing various alkoxy groups - **PNM1-4** and 9,9-dioctylfluorene-2,7-diboronic acid FBA. The formation of copolymers PNP1-4 was confirmed by different analytical techniques, such as, gel permeation chromatography (GPC), thermogravimetry analysis (TGA), 1H- and 13C-nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), UV-vis absorption and emission spectroscopies. The target copolymers were found to have a relatively high thermal and chemical stability as well as an excellent solubility in common organic solvents. GPC traces of copolymers **PNP1-4** display noticeably large weight-average (Mw) molecular weights in the range of 36.5-152.0 KDa and a polydispersity index (Đ = M_w/M_n) of 2.5-3.0. Photophysical analysis of **PNP1-4** divulges their luminescence in the deep blue region, namely, in the range of 453-463 nm with an emission quantum yield up to 17%. In addition, copolymers **PNP1-4** were explored as field-effect transistors revealing a hole mobility up to ~6.4x10–6 $cm^2\ V^{-1}s^{-1}$.[1]



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Tuning Solid-State Emission from a Single Fluorophore by Controlled Radical Polymerization

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Manipulation of molecular fluorescence is of fundamental interest. Owing to the complex interplay between the charge-transfer and singlet excitons, it is highly challenging to manipulate the emission color and quantum yield of single fluorophores, especially for that in solid or aggregated state.[1,2] In this work, we report a systematic yet simple methodology for tuning solid-state emission from a single fluorophore by controlled radical polymerization-mediated charge transfer. Using a library of well-defined donor-type polymers grown from an acceptor-type fluorophore by atom transfer radical polymerization, we reveal their solid-state emission color as well as quantum yield can be efficiently tuned by precision macromolecular engineering, that includes (i) selection of monomers with different electron-donating groups, (ii) end group transformations, and (iii) polymer chain length variation. The emission tunability originates from the structurally dependent through-space charge transfer (TSCT) process that regulates the CT energy. Both experiments and multiscale modeling were performed to support the proposed mechanism. Thanks to the simple chemical composition, we further demonstrate that such polymer systems can be processed into thin films enabling versatile photolithography.

Acknowledgements

The financial support from Fondation Claude et Giuliana (Research project, No. 190313) and Swiss National Science Foundation (Spark grant, No. 1-005137) is acknowledged.

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Energy Transfer in DNA-Organized, Multi-Segmental Chromophore Stacks

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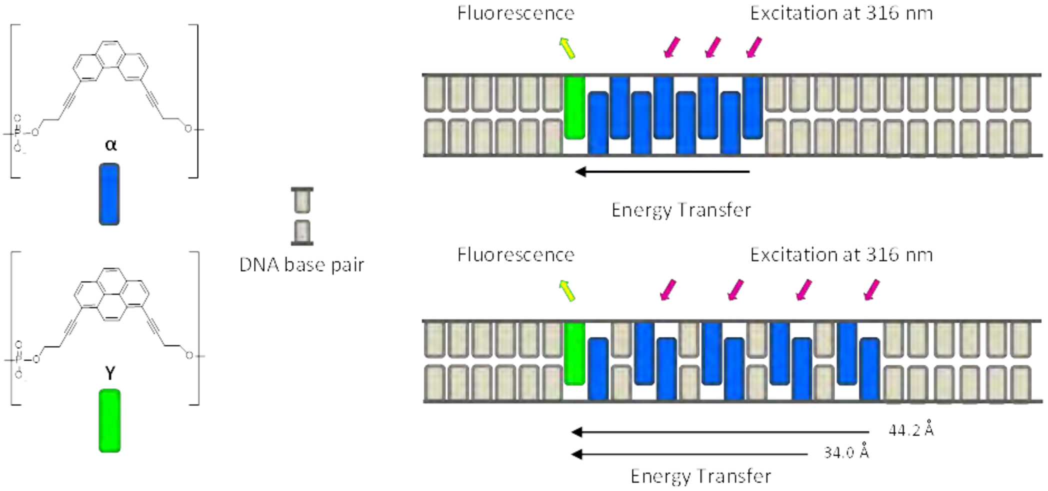
In previous work, our research group showed that the incorporation of 1,8-dicarboxamide pyrene and 3,6-dicarboxamide phenanthrene into a DNA duplex result in an efficient light harvesting antenna, where the phenanthrenes act as donors and the pyrene as an acceptor.[1] In further investigations the carboxamide derivatives were replaced by alkynyl substituted ones and the light collecting antenna was interrupted by base pairs. It was shown that the antenna also transmitted energy when interrupted by up to three base pairs. [2] In this work we show a system where the antenna is always interrupted after two phenanthrenes with one base pair. So that in addition to the energy transfer we have again the specificity of the nucleobases. This new Watson Crick specific light harvesting antenna was studied by thermal UV-vis and fluorescence spectroscopy experiments.



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Efficient Synthesis and Complex Self-Assembly of the Amphiphilic PEO-*b*-PEHOx polymers into Multicompartment Micelles, Pseudo-Vesicles and Yolk/Shell Nanoparticles

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Preparing well-defined amphiphilic block copolymers has become a focus of modern research thanks to their ability to self-organize into various complex structures.[1] However, little attention was given to AB diblock copolymers with a long and branched side chain in the hydrophobic block, potentially leading to novel interactions during the self-assembly. The aim of this work is to design such an AB diblock copolymer and study its self-assembly. We used the hydrophobic poly(2-(3-ethylheptyl)-2-oxazoline (PEHOx) as our hydrophobic block. This polymer shows a low glass transition temperature (T_g) of -6°C and benefits from a purely hydrocarbon side chain of nine carbon atoms providing sufficient hydrophobicity and an ethyl branch that supress crystallinity. PEHOx is thus perfectly suitable as a hydrophobic block in an amphiphilic block copolymer to form new self-assembly structures. By using a new nosylated poly(ethylene oxide) (PEO) macroinitiator, we synthetized a whole library of PEO-*b*-PEHOx amphiphilic AB diblock-copolymers via a microwave-assisted polymerization (Fig 1).[2] Kinetics of the polymerization in different solvents were performed and proved a perfectly controlled polymerization in chlorobenzene but not in acetonitrile or sulfolane.

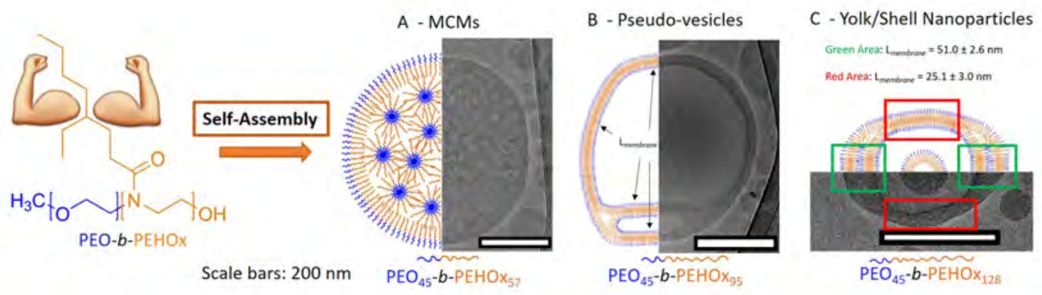

Fig. 1: Amphiphilic diblock copolymer PEO-b-PEHOx and representative cartoons with the corresponding model Cryo-TEM image of the various self-assemblies. Scale bars: 200nm. A - Multi-compartment micelles (MCMs). B - Pseudo-vesicles. C - Yolk/Shell nanoparticles.

Self-assembly of PEO-*b*-PEHOx was performed using film rehydration and solvent switch. Apart from micelles and worms, we were able to prove the formation of multiple complex structures by light scattering, TEM and Cryo-TEM: multi-compartment micelles (MCMs), Pseudo-Vesicles and Yolk-Shell nanoparticles. To the best of our knowledge, this is the first time such complex materials are formed from a single AB diblock copolymer. The side chain of PEHOx with its ethyl branch and long length generated additional hydrophobic-hydrophobic interactions while preventing a compact order or strong entangling of the AB diblock copolymers in a membrane. This shows the unique properties of PEO-*b*-PEHOx and the potential of hydrophobic block with a long and branched side chain to obtain complex nanoparticles. Altogether, our results show that PEO-PEHOx is a meaningful addition to the canon of self-assembling block copolymers. Combined with its backbone structure close to a peptide make PEHOx a compelling hydrophobic block to lead to new complex self-assembly structures and insights into self-assembled nanoparticles.

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Spatiotemporal imaging of water in operating voltage-gated ion channels reveals the slow motion of interfacial ions

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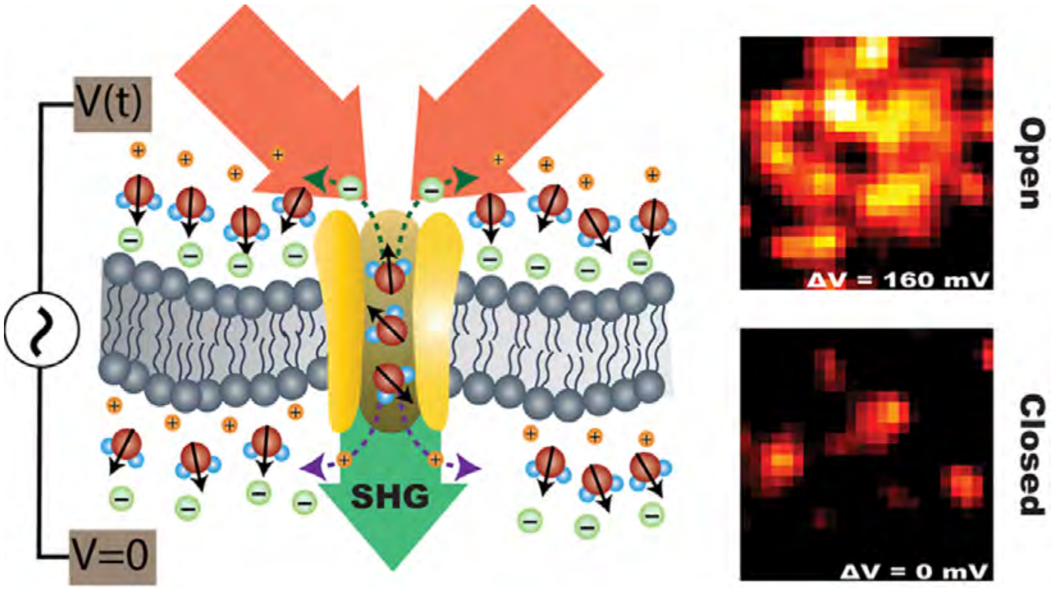
Ion channels are responsible for numerous physiological functions ranging from transport to chemical and electrical signaling. Although static ion channel structure has been studied following a structural biology approach, spatiotemporal investigation of the dynamic molecular mechanisms of operational ion channels has not been achieved experimentally. In particular, the role of water remains elusive. Here, we perform label-free spatiotemporal second harmonic (SH) imaging and capacitance measurements of operational voltage-gated alamethicin ion channels in freestanding lipid membranes surrounded by aqueous solution on either side. We observe changes in SH intensity upon channel activation that is traced back to changes in the orientational distribution of water molecules that reorient along the field lines of transported ions. Of the transported ions, a fraction of 10^{-4} arrives at the hydrated membrane interface, leading to interfacial electrostatic changes on the time scale of a second. The time scale of these interfacial changes is influenced by the density of ion channels and is subject to a crowding mechanism. Ion transport along cell membranes is often associated with the propagation of electrical signals in neurons. As our study shows that this process is taking place over seconds, a more complex mechanism is likely responsible for the propagation of neuronal electrical signals than just the millisecond movement of ions.



Light-Harvesting Antenna: Detection of Polyaromatic Molecules by Supramolecular Fibers

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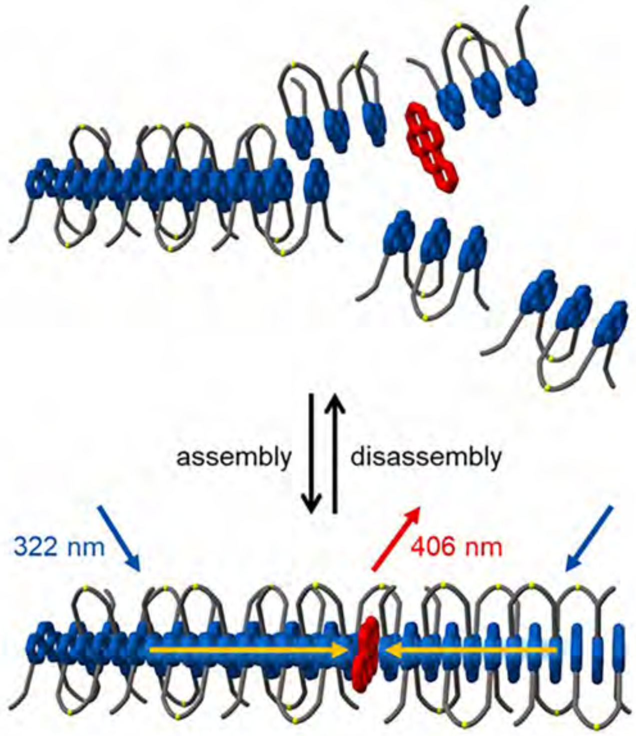
The self-assembly of 3,6-disubstituted phenanthrene trimers with phosphodiester-bridges leads to the formation of supramolecular fibers. Previously, it was shown that these fibers act as an efficient light-harvesting antenna. So far, the acceptor was incorporated into an oligomer and added as such. Our new approach enables us to use various monomeric chromophores: the polyaromatic acceptor is added during the self-assembly process of the forming supramolecular polymer. Upon excitation of the phenanthrene units, the energy is transferred to the acceptor, which emits the light in increased intensity. Benzo(a)pyrene reached as one of the highest fluorescence quantum yields of 31% at an acceptor/phenanthrene ratio of 12 mol-%. The fibers were analyzed by microscopy (AFM, UV-vis, fluorescence). This allows us to detect small amounts of chromophores in an aqueous medium.



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Phase-Separated Metallosupramolecular Polymer Blends with Tunable Mechanical Properties

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Metallosupramolecular polymers (MSPs) are obtained upon formation of coordination complexes between (macro)monomeric building blocks that carry at least two ligands and suitable metal ions. The dynamic nature of the metal-ligand complexes in MSPs offers a way to create stimuli-responsive materials.[1] For example, MSPs that heal upon exposure to light or heat were obtained from poly(ethylene-*co*-butylene) endcapped with tridentate methylbenzimidazolyl pyridine-ligands (BKB) and transition metal salts.[2] The polymer backbone, ligand, metal ion, and counter ion all influence the properties of MSPs,[1] and it is the interplay of these components that determines the polymers' microstructure and dynamics.[3] Due to the low glass transition temperature of most of the employed macromonomers, typical MSPs show mechanical properties that are comparable to those of classical (thermoplastic) elastomers.

Here we report that blending of different MSPs, in this case one based on the trifunctional component THM and one made by BKB, allows to tune the materials properties.[4] The co-assembly of the two components, which individually assemble into semicrystalline, rigid and rubbery materials, respectively, relies on the use of the same type of ligand. The variation of the weight fraction of the two components allows one to adjust the strength and toughness of the blends beyond the properties of either component alone, and MSPs with properties comparable to commodity plastics are obtained. We further show that the addition of a plasticizer allows further expanding the accessible property regime and the introduction of new ligands further improves processability.

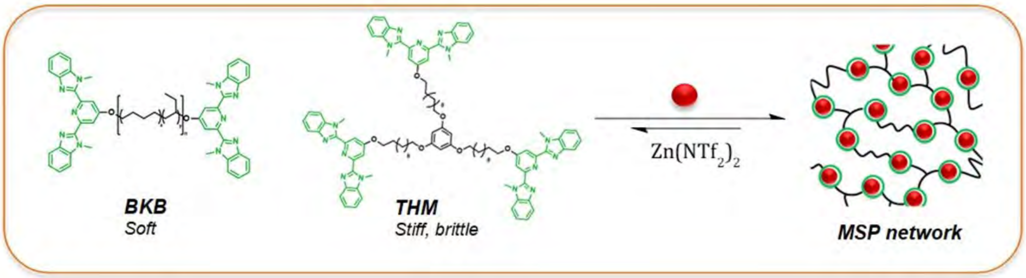

Figure 1. Blending of two metallosupramolecular polymers in different ratios affords materials whose mechanical behavior can be tuned from soft to stiff.

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Functional insertion and characterization of hexameric resorcinarene capsules into solid-supported, synthetic membranes for use as biomimicking surface and ion carrier

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When synthetic polymer membranes on a solid support are decorated with different biomolecules including proteins and DNA, smart active surfaces are formed which can be used in many applications such as biosensing, antimicrobial surfaces and catalysis.[1, 2] Calix[4]arenes, also called resorcinarenes, are polyaromatic macrocyclic molecules, possessing the ability to form capsules with a large volume of around 1400 Å^3, which can be exploited amongst others for the stabilization of carbocationic intermediate and transition states.[3] Insertion of resorcinarenes into synthetic membranes allows us to monitor functional properties of resorcinarenes as enzyme-like catalysist or to cation host. Therefore, in this study, we aim to insert resorcinarenes into synthetic membranes assembled from amphiphilic polymers, lipids and hybrid membranes combining both. Since the resorcinarenes are soluble only in apolar solvents such as chloroform, we first investigated changes in polymer membrane behavior in the presence of resorcinarenes at the air-water interface by recording Langmuir isotherms. Then, well-characterized polymer-resorcinarene films were deposited on different solid supports by Langmuir-Blodgett deposition. Resulting membranes with resorcinarenes were characterized to monitor the changes in membrane homogeneity and integrity by atomic force microscopy (AFM). Finally, electrochemical impedance spectroscopy is undertaken to measure the ion carrying capacity of the membranes. Taken together, we wish to create a new kind of biomimicking membranes which are endowed with orthogonal function, thereby opening doors to multiple imaginable applications.

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Polyphenylene Networks Containing Triptycene Units: Promising Porous Materials for CO_2, CH_4, and H_2 Adsorption

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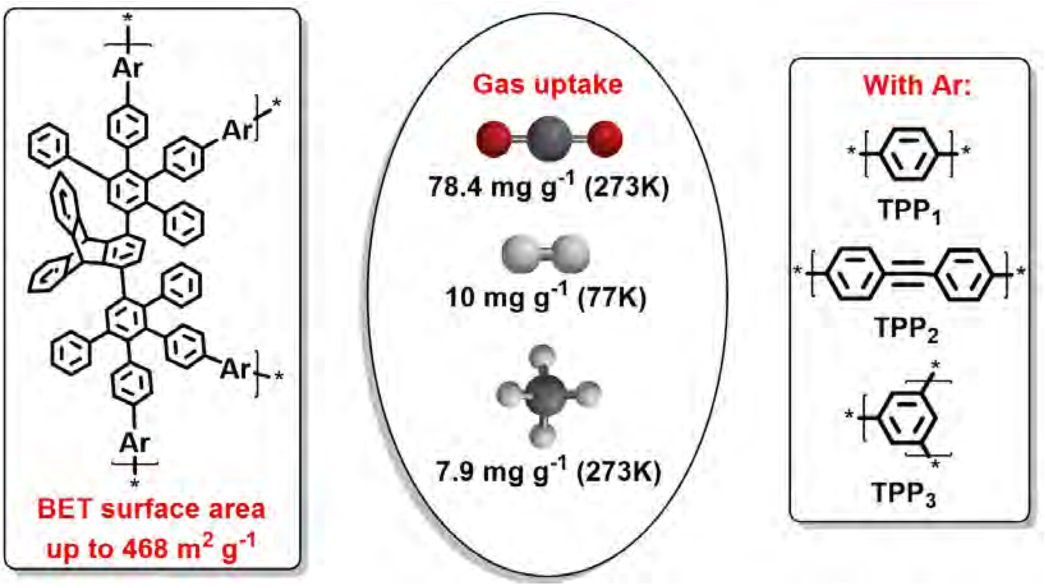
The synthesis of triptycene-based three-dimensional networks and their uptake towards various gases are described. The target polymers **TPP1-3** were synthesized by employing a convenient palladium-catalyzed Suzuki-Miyaura cross-coupling reaction between a triptycene synthon bearing two peripheral dibromotetraphenyl benzene (**TBT**) units and various arylboronic acid/ester moieties. Polymers **TPP1-3** were characterized by several instrumental analysis techniques, namely, solid-state ^{13}C-nuclear magnetic resonance (SSNMR), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), and emission spectrophotometry. Brunauer-Emmett-Teller (BET) nitrogen adsorption investigation of **TPP1-3** revealed surface areas up to 468 m^2 g^{-1} and an average pore volume of ~0.25 cm^3 g^{-1}. Interestingly, low-pressure gas adsorption studies of **TPP1-3** disclosed a CO_2 uptake for **TPP1** of 78.4 mg g^{-1} (273 K) and a gas adsorption capacity for **TPP2** towards H_2 and CH_4 of 10 mg g^{-1} (77 K) and 7.9 mg g^{-1} (273 K), respectively.[1]



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PBO-*b*-PG Self-assemblies: a Straightforward Path towards Biomedically Relevant Nanoparticles

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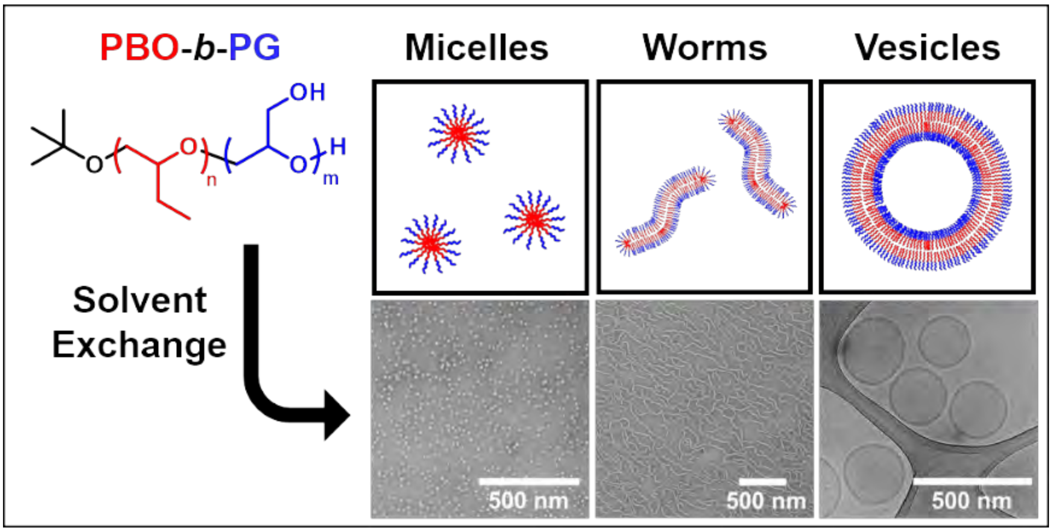
Aqueous self-assembly of amphiphilic block copolymers is studied extensively for biomedical applications like drug delivery and nanoreactors.[1] The commonly used hydrophilic block poly(ethylene oxide) (PEO), however, suffers from several drawbacks. As potent alternative, poly(glycidol) (PG) has gained increasing interest, benefiting from its easy synthesis, high biocompatibility and flexibility as well as enhanced functionality compared to PEO.[2] Here, we present a quick and well-controlled synthesis of poly(butylene oxide)-*block*-poly(glycidol) (PBO-*b*-PG) amphiphilic diblock copolymers together with a straight-forward self-assembly protocol.[3] Depending on the hydrophilic mass fraction of the copolymer, nanoscopic micelles, worms and polymersomes were formed as well as microscopic giant unilamellar vesicles. The particles were analysed regarding their size and shape, using dynamic and static light scattering, TEM and Cryo-TEM imaging as well as confocal laser scanning microscopy. We have discovered a strong dependence of the formed morphology on the self-assembly method and show that only solvent exchange leads to the formation of homogenous phases. Thus, a variety of different structures can be obtained from a highly flexible copolymer, justifying a potential use in biomedical applications.



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Mechanoresponsive Ag@SiO_2 nanorattles-polymer antimicrobial nanocomposites

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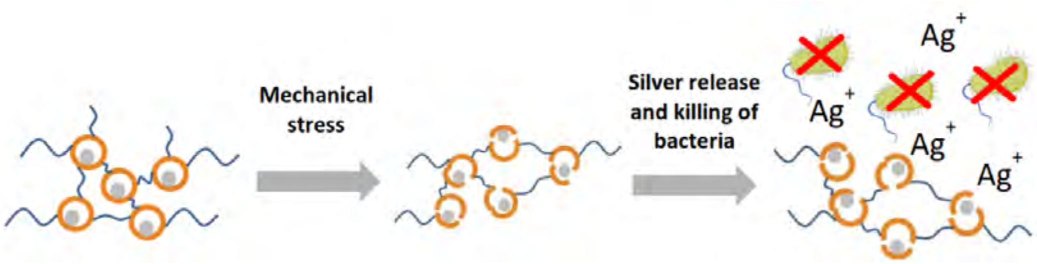
Nanorattles or yolk-shell nanoparticles are similar to core-shell nanoparticles but with a void between the core and the shell. This kind of structure has many applications in different fields such as catalysis, batteries or drug delivery depending on the chemical composition of the core/shell and the void/pore size. [1]

Our group has developed Ag@SiO_2 nanorattles as an antimicrobial agent. [2] The antimicrobial properties of silver are well-known for centuries and gain back interest due to its multimodal antibacterial activities. [3] In addition, the presence of the silica shell around the silver nanoparticles helps to avoid aggregation, controls the release of Ag^+ and enlarges the possibilities of functionalization with different functional groups. The next step of this work is to develop a mechanoresponsive nanocomposite of silver nanorattles embedded into a polymer matrix to trigger the release of silver ions and kill bacterial cells. (Scheme 1)



Scheme 1: Schematic representation of silver ions release trigger by mechanical forces to kill bacteria

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