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Tapered Graphene Cross-Sectional Materials: Synthesis of Various Molecular and Polymer Derivatives

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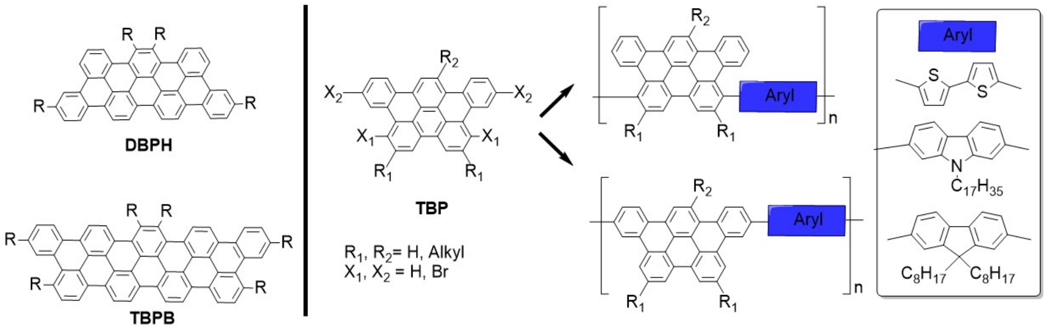
Efficient methods for the synthesis of various derivatives of tribenzopentaphene (TBP), dibenzophenanthroheptaphene (DBPH), and tetrabenzotriphenylenopyranthrene (TBTP) were developed. In addition, three polyaromatic based polymers were synthesized containing co-monomers of the trapezoidal tribenzopentaphene (TBP).[1-4] These new laterally stretched trapezoidal PAH derivatives expand the scope of producing unsymmetrical tapered polycondensed aromatic hydrocarbon derivatives with customizable structural modifications. In addition, the hitherto moieties can be employed as synthons to produce graphene-related materials. The copolymers containing the trapezoidal tribenzopentaphene (TBP) polycyclic aromatic hydrocarbon present a straightforward synthetic method with the possibility to introduce several functional groups into to the polymer backbone, and consequently, enable the synthesis a wide variety of TBP-based polymers for various optoelectronic and sensing applications (figure 1).



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Organogel and Microporous Polymers from a One-pot Synthesis of Iron (II) Clathrochelate Building Blocks

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A series of clathrochelate polymers is reported by reacting iron(II) chloride with various vicinal dioxime units and different aromatic diboronic acids. When this latter is a fluorene unit, the resulting 2D organometallic polymers form oragnogel from 10 wt% concentrations in organic solvents of low and medium polarity. On the other hand, when the aromatic diboronic acid is benzene, the clathrochelate derived polymers become microporous revealing a Brunauer-Emmett-Teller (BET) surface area of 412 m^2/g and average pore volume of 0.36 cm^3/g for the one bearing aromatic side groups.[1,2]

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New Materials For the 3D Printing of Biodegradable Personalized Medical Devices

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3D printing technology (also called additive manufacturing) has attracted great attention due to its powerful ability to create complex 3D geometries with precise microarchitectures. In combination with medical imaging techniques, this might provide enormous opportunities to design customized drug formulations and biomedical devices.[1] Among current 3D printing methods, stereolithography (SLA) exhibits distinguished advantages including high resolution, desktop size, and relatively low cost. The printing is based on a localized light-initiated photopolymerization process, which takes place in a bath containing liquid (macro)monomers and photoinitiators.[1] However, the lack of biocompatible and biodegradable materials suitable for SLA limits their application in the biomedical area, especially for the manufacture of personalized devices. Biodegradable devices prepared by SLA often show poor mechanical properties, in part because the (macro)monomers used need to be small enough to maintain a low viscosity, and obtain good printing properties.[2,3] Up to now, there are still no available biodegradable 3D printing materials reported suitable for producing elastic devices. Herein, we report new 3D printing materials based on copolymers of lactide and caprolactone, with high molecular weight (MW) yet relatively low viscosity, and highly tunable mechanical properties (Figure 1). The printed biomedical device prototypes (i.e. stents) exhibit high flexibility and stretchability, which is comparable to that of commercial silicone products whilst also being bio-resorbable. This work opens new perspectives for developing precise personalized medical devices with biodegradability as well as high mechanical properties by 3D printing.

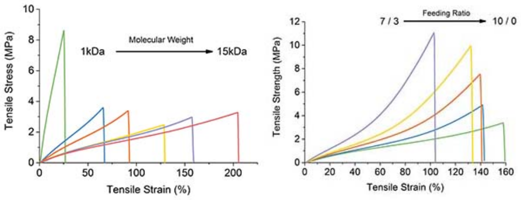

Figure 1. Representative tensile stress-strain curves of 3D printed specimens with highly tunable mechanical properties. Left: by changing polymer MW; right: by changing feeding ratio (w/w) of two polymers with different MW.

Financial support from the OPO Foundation is acknowledged.

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Multilayered polymeric hybrid materials: How to covalently bond silk proteins on polymers for optical materials

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Silk fibroin is nowadays very often used in optical devices. The natural material offers remarkable optical properties[1,2] and various possibilities to chemically modify its structure[3]. The combination of optical silk fibroin layers with polymeric materials allows creating composites with enhanced properties. However, an interface between a modified protein and a polymeric material does not allow strong intermolecular bonding[4]. It is of great interest to us to modify silk fibroin to make it attachable to a polymeric material. Hence, we report the synthesis of a heterogeneous bifunctionalized linker, which binds to tyrosine residues in silk fibroin by performing a diazonium coupling reaction and reacts with any organic polymer by C,H-insertion crosslinking chemistry. Being spin-coated on a polymer layer and crosslinked under UV light, multilayers of silk fibroin and polymers can be made. Furthermore, the effect of mechanical stimuli on the stack will be investigated concerning any possible change its the optical properties.

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Compartments and cascades: a model reaction for complex nanoscale systems

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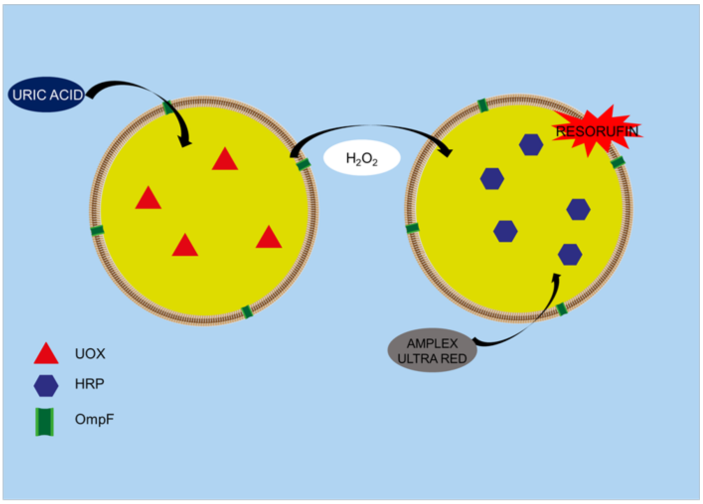
Compartimentalization at the nanoscale is fundamental in nature, where the spatial segregation of biochemical reactions within cells ensures optimal conditions for regulating metabolic pathways. Here, we present a nature inspired approach to engineer enzymatic cascade reactions taking place between separate vesicular nanocompartments, each containing one enzyme type. We propose by the selected combination of enzymes, an efficient solution to detoxify the harmful effect of uric acid and H_2O_2, associated with various pathologic conditions (e.g. gout and oxidative stress). The two-step enzymatic cascade involves the fungal uricase (UOX) and horseradish peroxidase (HRP) that are separately encapsulated within nanocompartments, equipped with a channel porin to allow passage of substrates and products of each step of the reaction. We established the molecular factors affecting the efficiency of the overall reaction, and the protective role of the compartments. Interestingly, the cascade reaction between two separate nanocompartments was as efficient as for free enzymes in complex media, such as human serum. Addition of the tandem catalytic nanocompartments to cells exposed to uric acid provided simultaneous detoxification of uric acid and H_2O_2 whilst the nanocompartments were non toxic for cells. Such catalytic nanocompartments can be used as a platform for understanding fundamental factors affecting intra- cellular communication and introduce non-native metabolic reactions to living systems for therapeutic applications.



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Enhanced Vibrational Circular Dichroism signal as a result of interaction between water soluble gold nanocluster and $CoCl_2$

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Vibrational circular dichroism (VCD) i.e. the differential absorption of left- and right-circularly polarized light by a chiral sample, is one of the powerful techniques to study the configuration as well as conformational state of molecules in solution. One of the major experimental challenges of VCD spectroscopy is the relatively small signals and hence search for alternative techniques to enhance the VCD signal is demanding. Helbing et.al have used elliptically polarized ultrashort laser pulses to increase the VCD signal (1). Domingos et.al. have shown to enhance the VCD signal of amino acids and oligopeptides by a factor of two by coupling the molecule to a paramagnetic metal ion (2). The same group has also shown the enhancement of VCD signal for open shell organic molecular system compared to closed shell system (3).

Based on the literature study we have tried to enhance the VCD signal for water soluble gold nanoclusters (4, 5) in order to better understand the structure of their surface layer, as such information is very hard to obtain for water soluble nanoclusters. For this study we have used glutathione and captopril as thiol ligand (SR) for synthesizing $Au_{25}(SR)_{18}$ nanocluster. An enhancement of at least one order of magnitude in VCD signal is observed when these nanoclusters were mixed with $CoCl_2$ solution. The increase in VCD signal of gold nanocluster stoichiometrically depends on the $CoCl_2$ added. Interaction of nanocluster and $CoCl_2$ is further studied by UV/vis, fluorescence and circular dichroism spectroscopy. All these study reveals a strong interaction between gold nanoclusters and $CoCl_2$.

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Polarimetric angle-resolved second harmonic scattering on colloidal TiO_2 nanoparticles in aqueous environments

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Titanium dioxide (TiO_2) is a semiconductor material with a high physical and chemical stability. Therefore it is extensively studied for the use in environmental and energy applications, such as for example photocatalytic water splitting. Despite its highly promising characteristics, the underlying performance of TiO_2 is still limited. In order to enhance surface-mediated processes and photochemical reactions, it is crucial to understand the microscopic structure of the TiO_2/electrolyte interface.

Nonlinear optical techniques are powerful tools to study processes at surfaces and interfaces as they are sensitive to surface molecular orientation and interfacial electric fields. In this work we investigate TiO_2 nanoparticles in aqueous environments with nonlinear optical techniques, more specifically polarimetric angle-resolved second harmonic scattering (AR-SHS). We apply AR-SHS in order to extract information on the TiO_2/electrolyte interface and determine parameters such as surface potential and surface molecular orientation, which are difficult to obtain by other techniques.

Degrafting of Zwitterionic Poly(2-Methacryloyloxyethyl Phosphorylcholine) Brushes from Silicon Substrates in Aqueous Media

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Surface-initiated controlled radical polymerization (SI-CRP) is a powerful tool to densely graft chain-end tethered polymers on a surface, usually referred to as polymer brushes. This technique allows to control grafting density and chain conformation. Immersed in a good solvent polymer brushes swell and individual chains are forced into an extended conformation. This extended chain conformation is an important contributor to the non-fouling and low friction properties, which were reported for a number of hydrophilic polymer brushes. While for a long time surface grafted polymer brushes were considered as very stable thin films, an increasing number of papers has been published within the last decade reporting degrafting of hydrophilic brushes in aqueous media. Hence, the stretched chain conformation is not only an important factor for the brush properties, but also influences the chemical reactivity at the substrate-brush interface. A fundamental understanding of this phenomenon, however, is still lacking. In the field of polymer mechanochemistry external force fields are usually applied to alter the polymer reactivity using techniques such as ultrasound sonication, and turbulent or elongational flow fields. Mechanochemical activation by swelling of a polymer brush may offer an alternative tool with the advantage that no external stimulus is needed.

With the objective to investigate the degrafting behavior of hydrophilic polymer brushes systematically, zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) brushes with various grafting densities and chain lengths were prepared and degrafting in aqueous media was monitored. The brushes were grown via surface-initiated atom transfer radical polymerization (ATRP) from silicon substrates modified with a dimethylchlorosilane-based ATRP initiator. For varying the grafting density a mixture of the initiator and a corresponding dummy compound lacking the initiating moiety was used resulting in a lower initiator density and accordingly in a lower grafting density after polymerization. After incubation at 37 °C in water, phosphate buffered saline (PBS) and ethanol-water mixtures, the degrafting process was monitored by ellipsometry and apparent initial rate constants were determined from the degrafting profiles assuming pseudo-first-order kinetics. We will describe and discuss the analysis of these apparent rate constants and our attempts to correlate these with the swelling behavior of polymer brush films of different polymer molecular weights and grafting densities in different media.

Oscillatory structural forces of confined silica particles in solution

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Molecules and particles in confinement tend to form well ordered layers close to surfaces.[1] These layers exhibit a higher density than the lower density bulk solution that they are bordering. While the interfacial region is densely packed the degree of ordering decreases exponentially with the distances from the surface.[2] To understand the behavior of particles in confinement is important in order to better understand the behavior of foams, paints and other colloidal solutions and also to better understand microfluidics. Hence, knowledge of the behavior and forces governing such mixtures is crucial for industrial and scientific purposes.[3] Therefore we chose colloidal probe AFM (CP-AFM) to measures the forces particles in solution experience when put in confinement. Due their nature these forces are commonly referred to as oscillatory structural forces.[4] The dense surface bordering layer is compressed and ordered when put under external stress therefore long range attractive and repulsive forces can be detected that govern the DLVO forces in long ranges. Attraction and repulsion are a result of the higher order of particles in the boundry layers and the final expulsion of a particle layer due to high forces.[3]

In order to better understand these forces we investigated solutions of varying concentration of positive and negative charged silica particles of different sizes. For the experiments silica particles with a size of 7, 12 and 22 nm have been chosen in order to investigate the dependency of the site of the particles in solution on the oscillatory structural forces. Particle concentrations ranging from 3.0 vol% up to 12 vol% are studied to also investigate possible correlations between the particle size and the concentration of the particles in solution. This study aims at exceeding research already done in this field by also investigating systems beyond silica nanoparticles and expanding the research effort towards metallic e.g. gold nanoparticles and soft latex nanoparticle systems of different size and charge. By broadening the types of systems investigated we aim at presenting a more complete picture of these oscillatory structural forces that play such a crucial role in a number of research fields and commercial applications.

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Micro-heterogeneous Catalysis of the N-Nitrosation of Secondary Amines by Micelles Forming Surfactants

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According of the classification of the International Agency for Research on Cancer for carcinogenic compounds, most of *N*-nitrosamines belong to the group 2A, 2B and 3, which means that these compounds are probable and possible human carcinogens.[1] *N*-nitrosamines can be present in consumer and industrial products, biological fluids, sediments and water.[2–4] These *N*-nitroso compounds can be formed under acidic condition by reaction of nitrosating agents such as NO^+ or N_2O_3 with secondary amines.[5] This study investigated the catalytic effect of cationic and anionic micelles forming surfactants on the nitrosation of dialkylamines in presence of nitrite at pH 3.5, 5 and 7. The results of this study show that the nitrosation of aliphatic secondary amines with a high octanol/water partition coefficient (e.g. dipropylamine, dibutylamine) is catalysed in the presence of cetyltrimethylammonium chloride (CTAC), a cationic micelle-forming surfactant, whereas anionic micelles formed by sodium dodecylsulfate (SDS) did not significantly catalyse the formation of *N* -nitrosamines. CTAC micelles enhanced the formation of *N*-nitrosodibutylamine up to 100-fold. The magnitude of the catalytic effect of cationic micelles on the nitrosation depended mainly of the alkyl chain length (i.e., hydrophobicity) of the amine precursors, the stability and the charge of the micelles and the pH. One important enhancement factor is the pK_a depression of the precursor dialkylamine due to the electrical potential at the micelle-water interface by up to ~1.7 pH units. These results suggest that cationic micelles-forming surfactants might play a role in the formation of *N*-nitrosamines in wastewater, consumer products and in industrial processes using high concentration of cationic surfactants.

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DNA-Functionalized amphiphilic Spheres

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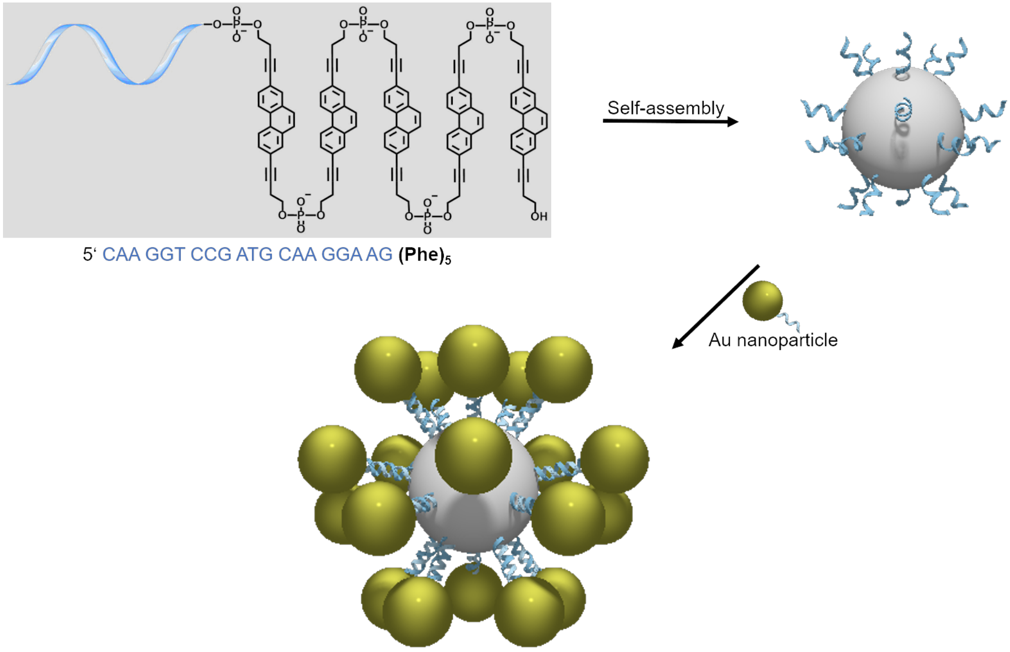
We previously showed that the 2,7-disubstituted phosphodiester-linked phenanthrene trimers **Phe$_3$** self-assembles in to tubular structures in aqueous medium.[1] Further it was shown that phenanthrene oligomers conjugated to DNA assemble into vesicles.[2] In this work, the DNA-phenanthrene conjugates were found to form sphere-like structures. The morphology depends on the salt concentration and annealing conditions.

The amphiphilic spheres were hybridized with Au nanoparticles linked to DNA strands complementary to the DNA-phenanthrene conjugates. The spheres were characterized by UV-vis spectroscopy, fluorescence spectroscopy and atomic-force microscopy (AFM). The results will be presented.



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Elasticity in physically cross-linked amyloid fibril networks

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Amyloid fibrils are β-sheet rich supramolecular polymers resulting from the self-assembly of proteins or peptides [1]. These structures initially identified in nature, in the context of pathological protein-prone neurodegenerative diseases, but now artificial variants of these systems are also emerging as functional materials for the design of ultralight aerogels, drug delivery platforms, cell scaffolds, artificial bones, degradable films, solar energy conversion, and water purification [2]. Many of these applications depend strongly on the structural and mechanical properties of the amyloid fibril networks. Yet, compared to other biological networks, such as elastin for example, the structure-properties relationship in amyloid networks, and how physical properties of the individual fibrils are reflected at larger scales, is significantly less established [3].

We provide a constitutive model of semiflexible and rigid amyloid fibril networks by combining the affine thermal model of network elasticity with the Derjaguin-Landau-Vervey-Overbeek (DLVO) theory of electrostatically charged colloids. When compared to rheological experiments on β-lactoglobulin and lysozyme amyloid networks, this approach provides the correct scaling of elasticity versus both concentration ($G \sim c^{2.2}$ and $G \sim c^{2.5}$ for semiflexible and rigid fibrils, respectively) and ionic strength ($G \sim I^{4.4}$ and $G \sim I^{3.8}$ for β-lactoglobulin and lysozyme, independent from fibril flexibility). The pivotal role played by the screening salt is to reduce the electrostatic barrier among amyloid fibrils, converting labile physical entanglements into long-lived cross-links. This gives a power-law behavior of G with I having exponents significantly larger than in other semiflexible polymer networks (e.g., actin) and carrying DLVO traits specific to the individual amyloid fibrils.

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Silicone elastomers with thioether side groups as dielectric for electromechanical transducers

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Electromechanical transducers (ETs) are stretchable capacitors that show muscle like motion when charged. ETs require materials with excellent elastic properties and high dielectric permittivity. Commercially available silicone elastomers (*e.g.* PDMS) show excellent elastic and dielectric properties but suffer from a low permittivity. We synthesized high permittivity silicone elastomers as a promising alternative to PDMS. They are prepared *via* post-polymerization modification of a high molecular weight polymethylvinylsiloxane using thiol-ene click chemistry leading to thioether functionalized polymers. Thin elastic films were prepared by tin catalyzed condensation reactions with alkoxysilanes as cross-linker. This approach allowed preparation of silicones with well-balanced dielectric and mechanical properties. The thickness of the silicone films was tuned from 200 up to 100 microm using doctor blade techniques. Test devices showed lateral actuation strains of more than 25% at an electric field of 24 V/microm and reached lifetimes of over 50.000 cycles. The impact of thioether side groups and the functional cross-linker on the elastic modulus, viscoelastic behaviour, permittivity, conductivity, dielectric breakdown and actuation strain of the silicone films will be presented in detail.

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Stiff and tough bio-inspired hydrogels

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Hydrogels with well controlled and engineered properties are often used in biomedicine, for example for wound healing, or tissue engineering. Moreover, hydrogels with a very high toughness, that are well suited as soft dampers, can be fabricated if they are composed of polymer networks containing mixtures of covalent and non-covalent bonds. However, these hydrogels are typically elastic such that they cannot be used for load-bearing applications. Nature can produce hydrogels that are tough and yet sufficiently strong, that they can bear load. Inspired by the marine mussel, we investigate the influence of hydrogel networks containing transient and covalent bonds on their mechanical properties, as a function of their spatial distribution within the hydrogels. In this talk, I will present our approach to correlate the structure and local composition of hydrogels to their mechanical properties.

Patchy Modification of Cellulose Nanocrystals towards Symmetric and Asymmetric Twisted Nanorods

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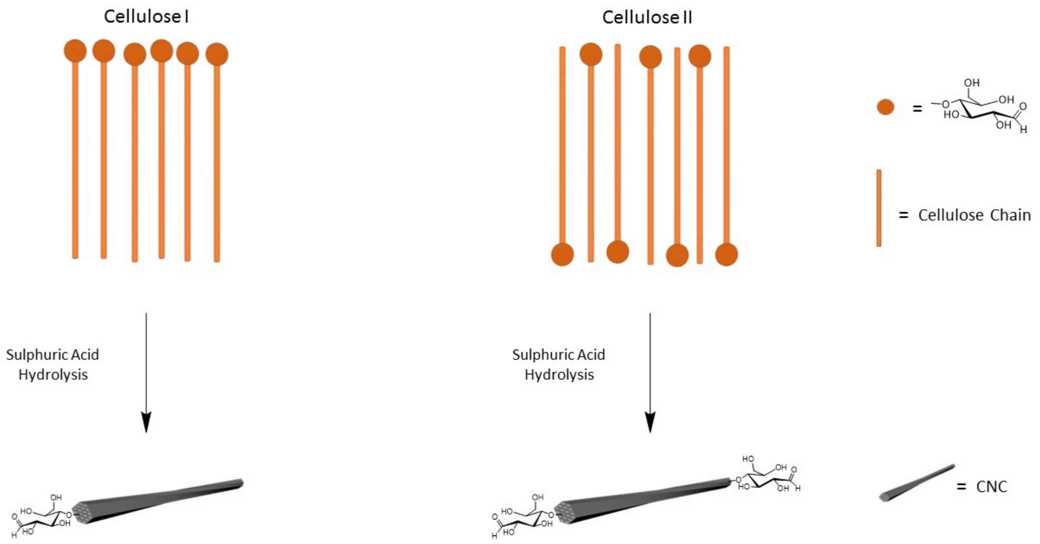
Cellulose fibers contain reducing and non-reducing ends as a result of their biosynthetic pathway. Depending on the treatment of the cellulose fibers, different cellulose polymorphs can be obtained. Mercerisation consists of treating cellulose-I fibers with a concentrated NaOH solution which transforms the parallel cellulose chains into an anti-parallel cellulose-II conformation. When the cellulose fibers are subjected to sulphuric acid hydrolysis, the amorphous regions of the fibers degrade and the crystalline parts remain, which are known as cellulose nanocrystals (CNCs).[1] The obtained CNCs are negatively charged due to anionic sulphate half-ester groups on their surface and thus are colloidally stable in water. Hydrolysis of different polymorphs yields their respective asymmetric cellulose I nanocrystals (CNC-I) and symmetric cellulose II nanocrystals (CNC-II) (Figure 1). Here, site-selective modification, e.g. reducing end groups, of these CNC polymorphs was investigated in order to attach atom transfer radical polymerization (ATRP) initiators for polymer chain growth from the CNC reducing ends.[2] Quantification of the reducing end groups and subsequent reaction yields were obtained using colorimetric methods.[3] Finally, the self-assembly of CNC hybrids into lyotropic liquid crystal phases was investigated.



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Diffusion of polymers through periodic networks of lipid-based nanochannels

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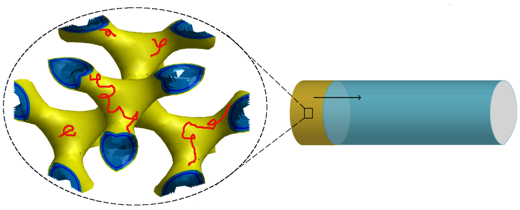
We present an experimental investigation on the diffusion of unfolded polymers in the triply-periodic water-channel network of inverse bicontinuous cubic phases. Depending on the chain size, our results indicate the presence of two different dynamical regimes corresponding to Zimm and Rouse diffusion. We support our findings by scaling arguments based on a combination of blob and effective-medium theories, and suggest the presence of a third regime where dynamics is driven by reptation. Our experimental results also show an increasing behavior of the partition coefficient as a function of polymer molecular weight, indicative of a reduction of the conformational degrees of freedom induced by the confinement.



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Enzyme immobilization on different solid silicate surfaces with the help of a dendronized polymer

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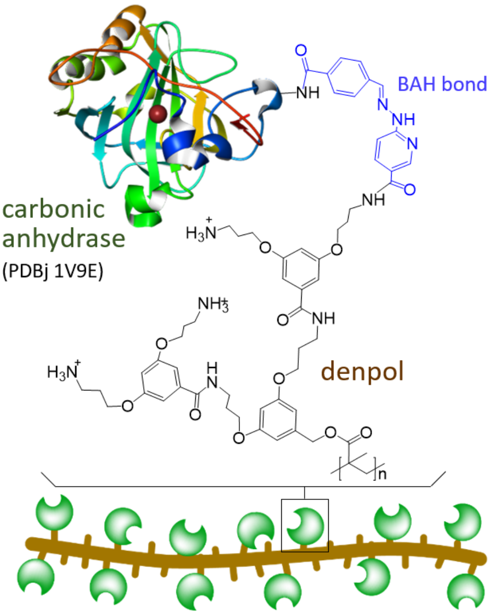
Water soluble, polycationic, dendronized polymers (denpols) allow for the covalent attachment of a large number of enzyme molecules on the same polymer chain through stable bis-arylhydrazone bonds (BAH) [1]. These denpol-enzyme conjugates can easily be immobilized on different types of silicate surfaces without any subsequent desorption and under retention of enzymatic activity [2, 3]. Using bovine erythrocytes carbonic anhydrase and a second-generation denpol, reactive and storable carbonic anhydrase-denpol conjugates could be prepared according to the method reported for other enzymes [1-3] with only minor optimization. With those conjugates, successful enzyme immobilization was demonstrated in glass micropipettes and for the first time in porous glass fiber filters as simple flow-through reactor systems.



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A Nanoparticle Platform for Heterogeneous Nucleation Events in Amyloid Formation and Protein Aggregation

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Heterogeneous nucleation processes and surface-induced aggregation in protein solution are observed in a variety of fundamental and practical problems in biological and biomedical sciences. Here we develop a platform based on polymeric nanoparticles which provides a highly controlled surface-mediated driving force for aggregation under both stagnant and shaking conditions. The high surface-to-volume ratio of the nanoparticles and the flexibility of polymer chemistry allow to accurately control both the total area and the chemistry of the surface exposed to the proteins. This high-throughput assay represents a convenient system to perform kinetic assays and investigate the fundamental physics underlying surface-induced protein aggregation. In particular, in this work we demonstrate the potential of this strategy by unraveling the combined effect of surfaces and hydrodynamic flow on protein aggregation. We show that under physiological conditions hydrophobic surfaces remarkably promote the formation of amyloid fibrils from soluble human insulin. We further show that this effect is due specifically to a dramatic increase in primary heterogeneous nucleation events. In contrast, mechanical forces accelerate the formation of amyloid fibrils by favoring mass transport and further amplify the number of fibrils by promoting fragmentation events. Thus, surfaces and agitation have a combined effect on the kinetics of protein aggregation observed at the macroscopic level but, individually, they each affect distinct microscopic reaction steps: the presence of interfaces generates primary nucleation events of fibril formation, which is then amplified by mechanical forces. These results suggest that the inhibition of surface-induced heterogeneous nucleation should be considered a primary target to suppress aggregation and explain why in many systems the simultaneous presence of surfaces and hydrodynamic flow enhances protein aggregation.

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Polyhydroxyalkanoate blockcopolymers – A comparison of different approaches

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Our work aims at the enzymatically catalyzed modification of biorenewable and biodegradable polyhydroxyalkanoates (PHA) to form well-defined blockcopolyesters. Such materials are recognized to increase available PHA properties (i.e. viscosity, crystallinity, Young's modulus, yield strength, and tensile strength) [1] and have gained increased attention due to their potential for high-value added applications (e.g. bio-implants, tissue engineering, drug delivery and smart materials) [2]. While current chemical synthesis strategies encumber economically realistic access due to reaction complexity, a distinct need for new methods of their preparation has been identified. We investigate two methods with a different range of combinations of PHA block segments.

The first method employs genetically engineered bacteria and diligent substrate feed techniques to synthesize in vivo chiral, block-copolymeric PHAs. The second method utilizes polymeric material from fermentative biotransformation as substrates for the enzymatically catalysed conversion into novel blockcopolymeric PHAs and thus omitting the use of bio-incompatible reagents, reactants or catalysts [3].

Combining fermentation expertise with the molecular design of the biogenic polymers by chemical modification, we create an integrated approach to provide advanced materials to a variety of highly demanding applications (e.g. medical devices and implants, drug carriers and coatings). Covering fermentation optimization and chemical modification, allows to lower the barrier to create new tailor-made materials for highly demanding applications.

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Stimuli-responsive supramolecular polymer adhesives exhibiting high toughness and stiffness

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Supramolecular polymers (SPs) are macromolecular assemblies composed of monomeric units that are associated via highly directional, secondary interactions such as hydrogen-bonding, π-π stacking or metal-ligand coordination. As a consequence of the reversible, non-covalent nature of the binding moieties, the dynamics of a SP can be tuned by shifting the equilibrium of the assembled and disassembled state with external triggers such as heat, light or pH. Thus, the mechanical properties of SP materials can be tailored by external stimulation, a feature which is valuable in the context of healable surface coatings or debonding-on-demand adhesives.[1] Yet, the design of SP materials exhibiting mechanical properties comparable to their covalently linked counterparts remains difficult.

Here, we report the synthesis and characterization of a platform of trifunctional supramolecular macromonomers based on a polypropylene oxide (PPO) core containing three quadruple hydrogen-bonding ureido-4-pyrimidinone (UPy) end groups, as well as the solid-state assembly of these monomeric entities into supramolecular networks. Three PPO backbones of different molecular weights (M_n = 440, 3000 and 5000 g/mol) were used. The SP based on 440-PPO-UPy3 formed a disordered glass with a glass transition temperature (T_g) at 84 °C, while phase separated morphologies were obtained for both 3000-PPO-UPy3 and 5000-PPO-UPy3, with the UPy-dimers forming a crystalline phase displaying a complex melting pattern around 95 - 113 ºC and a rubbery phase with T_g = -60 ºC. Compression-molded films (T = 130° C, 4 min at 5 tons) of the latter two materials exhibited Young’s moduli of 28 and 14 MPa, a strain at break of 9 and 6%, and a tensile strength of 1.6 and 0.7 MPa at room temperature. In addition, we show that by mixing the different building blocks, *i.e.* tuning the UPy hard phase content, considerable increase in both toughness (≤112 kJ/m3) and stiffness (≤ 250 MPa at 25 °C) was achieved, creating blends with attractive property combinations. These characteristics in combination with the low melt viscosity induced through the supramolecular motif afford materials offering promising mechanical performance, adhesive properties and (de)bonding-on-demand features that may be useful for a wide range of industrial applications.

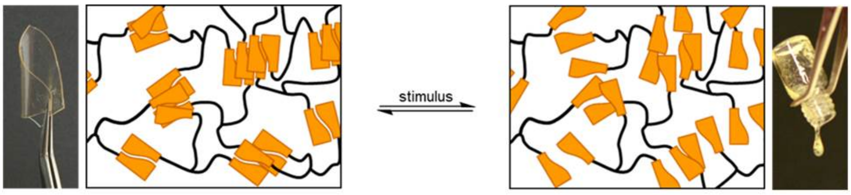

Fig. 1: Pictures and schematic representation of the trifunctional supramolecular network and its disassembly upon external stimulation.

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Aggregation-Induced Emission in Lamellar Solids of Colloidal Perovskite Quantum Wells

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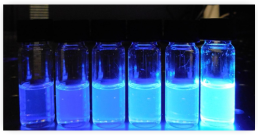
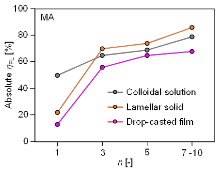
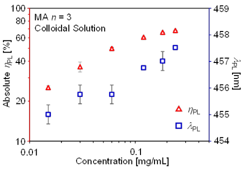
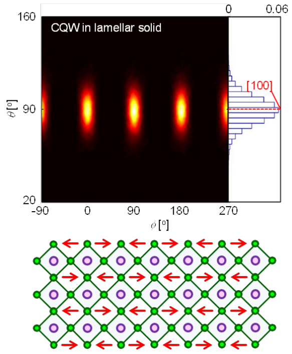
The outstanding excitonic properties, including photoluminescence quantum yield (η_{PL}), of individual, quantum-confined semiconductor nanoparticles are often significantly quenched upon aggregation, representing the main obstacle toward scalable photonic devices. We report aggregation-induced emission phenomena in lamellar solids containing layer-controlled colloidal quantum wells (QWs) of hybrid organic-inorganic lead bromide perovskites, resulting in anomalously high solid-state η_{PL} of up to 94%. Upon forming the QW solids, we observe an inverse correlation between exciton lifetime and η_{PL}, distinct from that in typical quantum dot solid systems.

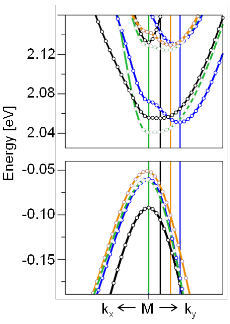






Our multiscale theoretical analysis reveals that, in a lamellar solid, the collective motion of the surface organic cations is more restricted to orient along the [100] direction, thereby inducing a more direct bandgap that facilitates radiative recombination. Using the QW solids, we demonstrate ultrapure green emission by completely downconverting a blue gallium nitride light-emitting diode at room temperature, with a luminous efficacy higher than 90 lumen W^{-1} at 5000 cd m^{-2}, which has never been reached in any nanomaterial assemblies by far.





Alternating Layers of Cationic and Anionic Supramolecular Polymers on Mica

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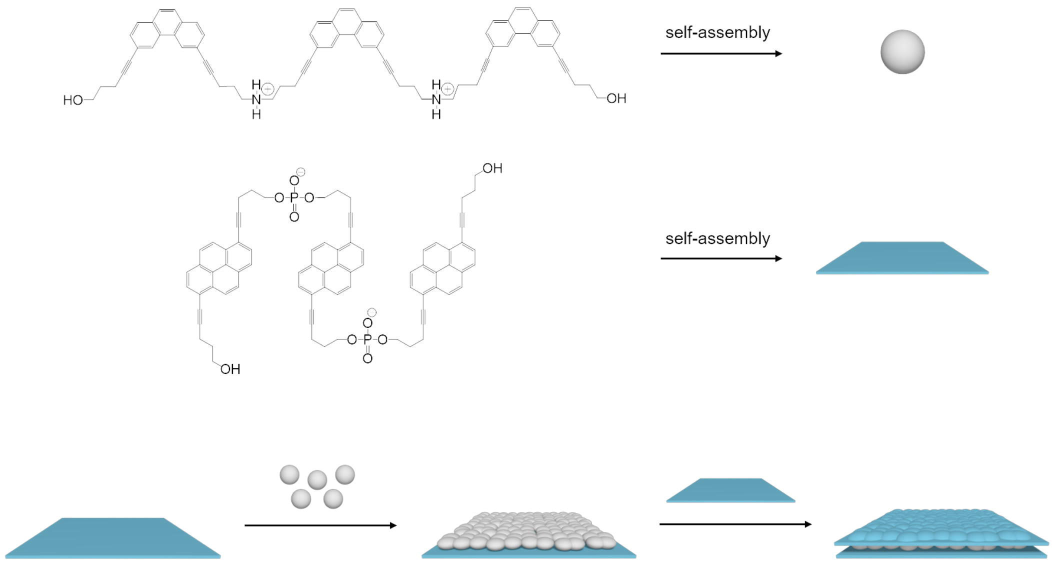
The self-assembly of 3,6-disubstituted amine-linked phenanthrene trimers, with a positive charged backbone in aqueous medium, form vesicles. In contrast, it was shown that 1,6-disubstituted phosphodiester-linked pyrene trimers, with a negative charged backbone, assemble to sheets. By preforming the supramolecular assemblies in its specific conditions, a buffer dependency can be avoided. Further it is possible to layer the cationic and anionic structures on top of each other. The different charged supramolecular assemblies were alternately layered on top of mica and analyzed by atomic-force microscopy.



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Multi-functional hydrogel systems based on PU and PAAA hydrogels

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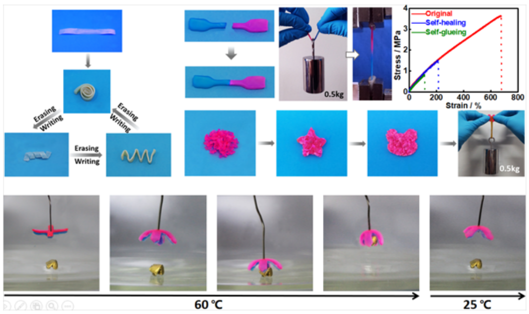
Hydrogels can be used as scaffolds for tissue engineering and actuators for optofluidic devices. Smart hydrogels that can withstand consecutive and high-level load-unload cycles are ideal candidates for load-bearing applications. However, combining stimuli responsiveness with toughness and self-healing properties has been challenging. To address these requirements, we integrated robust polyurethane (PU) hydrogels with hydrogels reinforced by dipole-dipole and H-bonding interactions (PAAA) to form double network (DN) gels and bilayered actuators. The DN gels show rubber-like behaviour while exhibiting self-healing and shape-memory properties, which together make these structures promising candidates for building artificial cartilage or muscle. As an alternative approach, we developed thermally-responsive PAAA-PU bilayered actuators for building soft manipulators. In this configuration, the PAAA gel with thermo-sensitive volume change property acts as responsive swelling layer while PU gel serves as a non-swelling support layer. The actuators are programmed to specific shapes by mismatch of swelling ratios between two layers. The proposed materials expand the scope of hydrogel applications in robotics and medicine.



Growth Nano-/Micro- Architectures by ATRP

C. Kang[1], A. Honciuc[1]

[1]Zurich University of Applied Sciences

Atomic transfer radical polymerization (ATRP) is widely used for synthesizing narrowly polydispersed polymer chains, but thus far it has not been employed in fabricating colloidal particles. We show that nano-/micro-architectures with various geometries and tunable surface nanostructures can be “grown” from nanoparticle seeds by ATRP technique. Our strategy is based on concentrating ATRP initiators in bulk of solid seed nanoparticles (NPs), after initiating the polymerization, these solid “nano-initiators” could be grown into nano-/micro- architectures. In the present study, we show that by attaching several different ATRP-initiator containing lobes on seed nanoparticle, the shape and the surface structures of the grown nano-/micro-architectures can be controlled. This method provides a new approach for synthesizing anisotropic colloids with complex geometries and tunable surface morphologies, enriching the family of colloidal particles.

$CdSe/CdSe_xTe_{1-x}$ Core/Alloyed Crown Nanoplatelets with Highly Tunable Excitonic Properties

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Colloidal semiconductor nanoplatelets (NPLs) also known as colloidal quantum wells have recently emerged as a promising class of chemically synthesized semiconductor nanocrystals.[1] With their quasi two-dimensional electronic structure resembling epitaxially-grown quantum wells, these free-standing NPLs exhibit strongly thickness-dependent and unique excitonic features including narrow emission linewidths, large linear and nonlinear absorption cross-sections, giant oscillator strength and ultrafast fluorescence lifetimes. Also, assorted heterostructures of colloidal NPLs including core/crown (laterally grown shell) and core/shell (vertically grown shell) have been synthesized to further engineer their excitonic properties. However, owing to pure vertical confinement along their magic-sized vertical thicknesses, the resulting excitonic properties of colloidal NPLs have suffered from the limited spectral tunability. Here, to overcome these limitations and further tailor their electronic structure, we designed and synthesized $CdSe/CdSe_xTe_{1-x}$ core/alloyed crown NPLs.[2] By precisely tuning the composition of the $CdSe_xTe_{1-x}$ crown layer, we have shown highly tunable emission within the range of 570 – 660 nm without changing the thickness of NPLs. Also, with the formation of alloyed crown region, we achieved substantially improved photoluminescence quantum yield (up to ~90%), which is attributed to suppression of non-radiative hole trap sites. Furthermore, we observed significantly increased fluorescence lifetime (from ~49 up to ~326 ns) by increasing the amount of Te in the crown region, suggesting the transition from the quasi-type-II to type-II electronic structure. We believe that these core/alloyed crown NPLs with their highly tunable excitonic features will enable us the development of high performance solution-processed optoelectronic devices.

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Controlling the Local Composition of Hydrogels

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Many natural materials have optimized structures on different length-scales and locally varying compositions, imparting them unique mechanical properties. Inspired by nature, we are developing tools that enable the production of structured hydrogels whose conformation changes over short length scales. This is achieved using drops with well-defined sizes and compositions that are produced with microfluidics. I will present microfluidic devices that allow control over the arrangement of the drops. These assembled drops are subsequently converted into macroscopic structured hydrogels with locally varying compositions. I will report different tools to control local conformations and show how it influences the macroscopic mechanical properties of hydrogels.

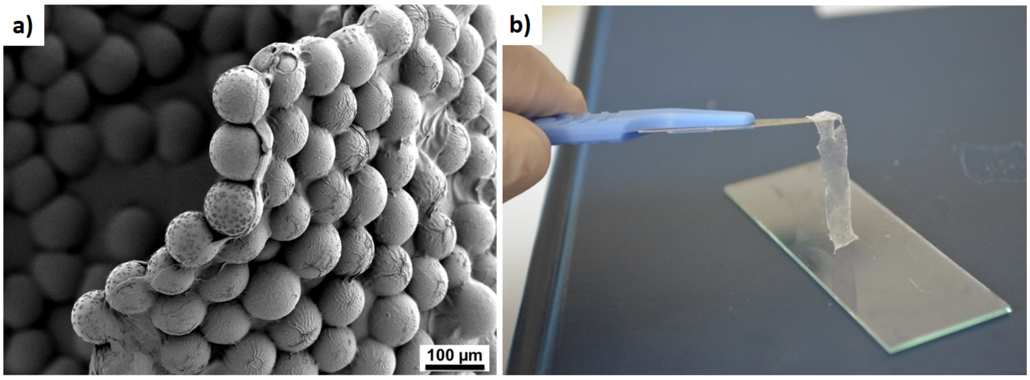

Figure: a) Structured composite hydrogel sheet. PEG particles, which were fabricated using a special microfluidic setup, form a monolayer. The particles are embedded into an alginate matrix, holding the sheet together. b) Macroscopic image of a structured composite hydrogel sheet, stable enough to be mechanically tested.

Merging of DNA-Photonic Wires with Light-Harvesting Supramolecular Polymers

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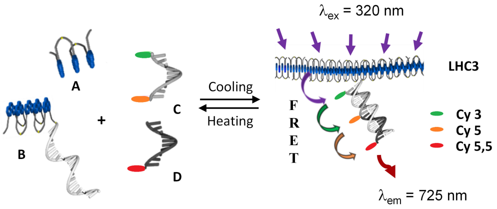
An approach combining DNA nanoscaffolds [1,2] with supramolecular polymers [3] for the efficient and directional propagation of light-harvesting cascades has been developed. A series of photonic wires with different arrangements of fluorophores in DNA-organized nanostructures were linked to light-harvesting supramolecular phenanthrene polymers (SPs) in a self-assembled fashion. Among them, a light harvesting complex composed of SPs and a photonic wire of phenanthrene, Cy3, Cy5 and Cy5,5 chromophores reveals a remarkable efficiency of 66%. Stepwise transfer of the excitation energy collected by the light-harvesting SPs *via* the intermediate Cy3 and Cy5 chromophores to the final Cy5,5 acceptor proceeds by a Förster resonance energy transfer mechanism. In addition, the light-harvesting ability is documented by antenna effects ranging from 1.4 up to 16 for the different LHCs.



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Depletion forces present between silica particles in solutions of polyelectrolytes

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Various industrial applications including papermaking and water treatment require knowledge of the properties of particle suspensions, such as their stability and rheology. These parameters can be modified by the addition of polyelectrolytes.

Our research concentrated on the interaction forces between silica particles measured in aqueous solutions of poly(2-vinylpyridine) (P2VP), poly(L-lysine hydrobromide) and polyamidoamine (PAMAM) dendrimers using the colloidal probe technique based on an atomic force microscope (AFM). The observed forces were described by a superposition of damped oscillatory forces and double layer forces quantitatively. The double layer forces were modeled using Poisson–Boltzmann (PB) theory for a mixture of a monovalent symmetric electrolyte and a highly asymmetric electrolyte, whereby the multivalent coions represent the polyelectrolyte chains.

Results of our investigations show that the polyelectrolyte concentration change has an influence on the parameters characterizing oscillation forces. We also proved that the increasing roughness of the silica particles deriving from the adsorbed cationic polyelectrolyte does not influence the presence of the oscillatory forces.

Using dynamic covalent bonds to fabricate high-performance bio-inspired composites

R. Libanori[1], S. T. Roldan Velasquez[1], J. A. Ulbrich[1], M. R. Binelli[1], A. Studart[1]*

[1]Complex Materials, ETH Zurich

Conventional processes commonly used for the fabrication of composites with high volume fraction of reinforcing elements usually require the infiltration of monomers that are subsequently consolidated into a continuous polymer matrix. [1-3] Such infiltration step often leads to long processing times and limits the choices of materials that can be used as soft polymer matrices. In this work, we present a new infiltration-less route in which a co-suspension of organic/inorganic powders is assembled through vacuum-assisted magnetic alignment and the resulting composite consolidated by uniaxial hot pressing at temperatures slightly above the topological transition of the dynamic polymer network. Formation of a strong and stiff continuous phase during hot pressing is enabled by employing polymers that contains dynamic covalent bonds as crosslinking points in their molecular network. We demonstrate that the fabrication process of highly-loaded composites can be significantly simplified using such infiltration-less approach. Incorporation of 50% in volume of reinforcing platelets within dynamic polymer matrices enhances the flexural modulus and flexural strength by 14-fold and 3-fold as compared to the pure polymer, reaching values as high as 13 GPa and 90 MPa, respectively. These results demonstrate the potential of using infiltration-less routes to enable the fabrication of high-performance platelet-reinforced composites using high volume fraction of reinforcing ceramic particles and polymer matrices that cannot be infiltrated otherwise by other conventional processing methods.

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Mechanical interlocking in highly-stretchable hydrogel-based composites

R. Libanori[1], S. T. Roldan Velasquez[1], A. Studart[1]*

[1]Complex Materials, ETH Zurich

Nacre exhibits toughening mechanisms operating at multiple length scales that leads to unusual combination of mechanical properties. One important toughening mechanism that provides a significant contribution to the overall energy dissipation during fracture is the platelet-platelet interlocking through nanoasperities that are present on the platelets' surface. Such mechanical interlocking is not commonly observed in artificial platelet-reinforced composites that are fabricated through conventional processing techniques as it requires either a high loading of reinforcing material or high stretchability of the continuous phase to enable the platelets to be in close proximity to each other. In this work, we present a mechanical analysis on the mechanical interlocking of shrinking hydrogel-based composites that contains roughened platelets with tunable sizes of surface nanoasperities as a reinforcing phase. The resulting highly-stretchable composites were characterized through quasi-static and cyclic mechanical testing and exhibit strain at failure as high as 500% for 20 vol% of reinforcing platelets. The results revealed a 2-fold and 6-fold increase in dissipated energy at 150% of applied strain and in the maximum number of cycles before rupture, respectively. The research in this field can offer a new concept in obtaining optimized mechanical properties, high strength and toughness in soft bioinspired composites.

Colloid-electrospinning: polymer properties controlling the release rate of volatiles from microcapsules-in-fibers morphology

N. Luisier[1], C. Toncelli[1], R. Rossi[1], G. Fortunato[1]*

[1]Laboratory for Biomimetic Membranes and Textiles, Swiss Federal Laboratories for Materials Science and Technology

Efficient encapsulation of volatile compounds via polycondensation of multi-functional building blocks at the interface of micro-emulsions is appealing for different markets, e.g. for food and cosmetics industries. The release rate of entrapped volatiles is highly influenced by the chemical nature of the core compounds and the shell polymer, as well as the chemical and physical interactions between each other. Other parameters such as shell porosity, microcapsules size and size distribution also affect this release kinetics. Encapsulation by electrospinning is an alternative to classical techniques, but the use of standard emulsion electrospinning for the entrapment of volatiles compromises the ratio between the different compounds: The most volatile compounds will partially evaporate together with the solvent, lowering the encapsulation efficiency.[1]

Colloid electrospinning is a novel technique,[2] which combines microencapsulation and electrospinning. With this tool, it is possible to entrap substances within two layers of polymers serving as release barriers. Using interfacial polycondensation reaction, microcapsules containing a hydrophobic core, e.g. fragrances, can be obtained. These core-shell microcapsules can be resuspended in an aqueous polymer solution and electrospun into nanofibers (Figure 1).

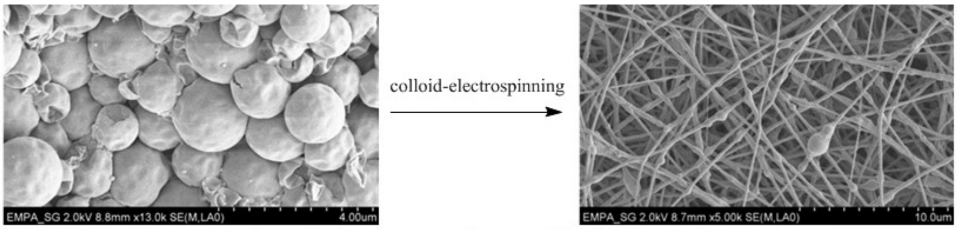

Figure 1: Electrospinning of PEO nanofibers containing liquid core microcapsules.

In this study, we investigated the effects of the polymer physico-chemical properties (crystallinity, hydrophobicity, ...) on the release rate of model volatile mixtures. Each of the polymers (the microcapsule shell and the fiber matrix) can be separately modified. Mainly, we use polyurethanes/polyureas of different chemical compositions for the capsules, and various water soluble polymers for the fibers (PVA, PEO, chitosan, ...). The polymer properties are mainly evaluated by SAXS, DSC and TGA. The release kinetics of the model volatile mixture is deduced from Headspace-GCMS measurements.

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Colloidal Cu_3VS_4 nanocrystals as promising candidates for efficient energy conversion and storage systems

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The use of renewable energy is highly demanded to interrupt the depleting hydrocarbon deposits and the boosting CO_2 levels in the atmosphere. In particular, fundamental progress has been made in developing devices which can allow for the conversion of sunlight into electricity or into storable chemicals[1]. The main scientific challenges involve the identification and synthesis of materials which can perform the aforementioned conversion. Typical required features are high photo and chemical stability, wide band gap (1.7-2eV), good charge transport properties, long term stability and ideally consisting of abundant and no-toxing elements. One such screening study was addressed toward the exploration of more complex "multinary" metal chalcogenides[2]. In this work, a colloidal strategy to access ternary Cu_3VS_4 semiconductor nanocrystals, with different sizes ranging from 3 nm to 23 nm, is developed. In order to achieve control on the crystalline phase, several synthesis parameters were rationally changed (i.e. the reactivity of precursors, ligands, temperature) with the ultimate goal of understanding the mechanistic paths governing the nucleation and growth of such complex metal sulfide. The as-obtained nanocrystals were thoroughly characterized using X-Ray diffraction and Raman techniques, along with Transmission Electron Microscopy to direclty image nanocrystal size and shape at subnanometer scale. The optoelectronic properties, i.e. its intermediate band gap electronic structure were investigated using UV-Vis absorption, along with density functional theory. Obtaining this material in the form of colloidal nanocrystals will lead to obtain a fine control of characteristic nanocrystal effects, such as the variation of the electronic state density, band gap, which systematically evolve with size and jointly impact on the chemical, magnetic and optoelectronic response of nanostructures, relative to those of their bulk material counterparts.

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Aggregation of a squaraine-modified oligonucleotide in aqueous solution

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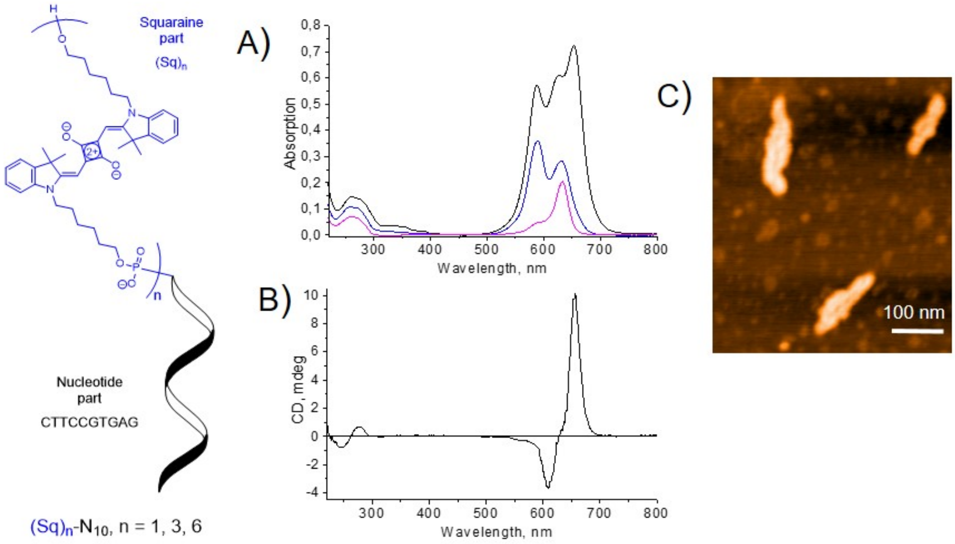
Squaraine-based compounds are promising chromophores for the creation of new materials for biomedical or diagnostic applications through the methods of supramolecular chemistry. Squaraine dyes exhibit a molar absorptivity of up to 260 000 $M^{-1}cm^{-1}$. They absorb and emit light in the long-wavelength region of the visible spectrum. Furthermore, they tend to form well-ordered aggregates in organic and aqueous solutions.

In this work, we study the aggregation properties of oligomers which consist of squaraines (1, 3, or 6 molecules) and nucleotides (10 units). Their aggregation properties are studied by spectroscopic (UV-Vis and CD) and microscopic (AFM and TEM) methods in water/ethanol solutions (see Figure below).



A) UV-Vis spectra of the oligomers: (**Sq)$_1$-N$_{10}$** (magenta, no aggregation), (**Sq)$_3$-N$_{10}$** (blue, H-aggregation), and (**Sq)$_6$-N$_{10}$** (black, oblique aggregation) B) CD spectrum and C) AFM image of the (**Sq)$_6$-N$_{10}$** oblique aggregates

Based on UV/vis spectroscopy, oligomer **(Sq)$_1$-N$_{10}$** with one squaraine molecule shows no well-defined type of aggregation. Oligomer **(Sq)$_3$-N$_{10}$** containing three squaraine units, however, reveals stacking of the chromophores in H-type fashion (blue shifted absorption band). Finally, oligomer (**Sq)$_6$-N$_{10}$** can form both H-type and oblique (splitting of the absorption band) aggregates depending on the conditions of preparation. The oblique aggregates of the (**Sq)$_6$-N$_{10}$** exhibit the signs of the supramolecular polymers, in which the squaraine-nucleotide oligomers are arranged in a helical fashion.

Synthesis of PEDOT Capsules from Pickering Emulsions Stabilized by Janus Nanoparticles

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In the last few years, conductive polymers such as polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), polythiophene and polyphenylene, found use in a plethora of devices, such as OLEDs, functional electrodes, electro chromic devices, optical switching devices, sensors, batteries, conductive textiles, fabrics, etc. [1–4]. Nanostructures of conducting polymers have attracted much attention due to the significant effect of the nanostructuring on the physical properties of the materials. The Janus nanoparticles (JNPs) can offer a promising platform for the synthesis of multifunctional materials with tunable optical and electronic properties[5]. In this work we show that semiconductive and amphiphilic Janus nanoparticles synthesized in surfactant-free conditions can be employed in the stabilization of the emulsion of EDOT in water. Further, from the EDOT/Water emulsions it is formed PEDOT microcapsules. The structure and the electronic properties of the PEDOT capsules can be tuned by the JNPs concentration and the amount of APS. These outstanding properties are attributed to the highly ordered structure in the microcapsule-particle assembly and cooperative doping between two semiconductive polymers.

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Reversibly crosslinked polymer brushes by covalent and hydrogen bonding.

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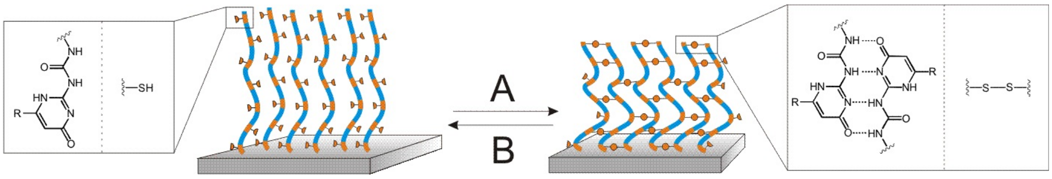
Polymer brushes represent an attractive class of thin layer coatings, in which an organization and close-packing of singly tethered polymer chains lead to, among others, remarkable non-fouling and lubricating properties. Their synthesis by surface-initiated polymerization (SIP) enables precise control over polymer molecular weight (film thickness), grafting density and chemical composition. Polymer brushes can be designed to respond to certain stimuli (smart surfaces) that can be utilized in drug delivery or sensors. Their lubricative coatings can support synovial joints of prosthetics (e.g. in hips or knees). However, application of polymer brushes can be problematic, due to their, sometimes, low stability. They are soft materials that can be easily damaged. Moreover, their high grafting densities often lead to high osmotic pressures that lead to degrafting of the chains (e.g. in PBS aq. solutions). Therefore, many efforts have been made to extend their lifespan under physiological conditions. They include, among other, self-healing assemblies and crosslinking. While covalent crosslinking improves stability of polymer brushes, it also impairs some of the properties; e.g. it generally leads to higher frictions. A compromise can be made by using crosslinks with bonding of a weaker nature, such as ionic instead of covalent bonding. Another possibility is to utilize reversible crosslinks and tune their dissociation kinetics. Both strategies proved to be very effective in maintaining low friction of the surfaces. However, the approaches have not been explored further in detail.



Here, we propose a strategy to systematically investigate these effects. First, we designed a polymer brush platform that can be functionalized with crosslinks by post-polymerization modification. The crosslinks include covalent disulfide linkers and hydrogen-bonding ureidopyrimidinone (UPy) motifs. Both crosslinks can be reversibly opened and restored and their effect on properties will be further investigated (e.g. by tribometry). First, poly((2-(dimethylamino)ethyl methacrylate-co-3-azido-2-hydroxypropyl methacrylate) (PDMAEMA-co-AzHPMA) brushes with azide content of ca. 1-50 mol% were grafted from silicon wafers via surface-initiated atom transfer radical polymerization (SI-ATRP). Then, thiol and UPy linkers were introduced using copper azide-alkyne cycloaddition (CuAAC) reaction. The polymer brushes were characterized by X-ray photoelectron spectroscopy (XPS), ATR-FTIR, ellipsometry (in dry and swollen state). The reversible crosslinking was monitored by ellipsometry, which was marked by changes in swelling of the polymer brushes.

Development of Mechanically-Adaptive, Stimuli-Responsive Polymer Networks

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The need for materials that are capable of changing their properties upon exposure to an external stimulus has led to many developments,[1] notably in the biomedical field.[2] Materials with switchable mechanical properties have been prepared by taking advantage of weak hydrogen-bonding interactions, such as in the case of polymers reinforced with cellulose nanocrystals that, triggered by the presence of water, exhibit a dramatic change of the materials' mechanical properties.[3]

We here report a new family of physiologically responsive polymers based on cross-linked poly(2-hydroxyethyl methacrylate)s. For this purpose, a series of copolymer networks containing 2-hydroxyethyl methacrylate (HEMA), methacrylic acid, and a cross-linker were prepared by bulk photopolymerization. Their aqueous swelling behavior could be tuned by adjusting the monomer feed and the cross-link density. The copolymer networks containing methacrylic acid further exhibited pH-dependent swelling characteristics, which may conceivably be attractive for biomedical applications.[4]

The mechanical properties of the copolymer networks made were studied by dynamic mechanical analysis (DMA), in the dry state and upon exposure to water. The storage modulus of the dry materials was in range of 2-3 GPa, whereas in optimized composition the immersion in artificial cerebrospinal fluid (ACSF) at 37°C caused a drastic modulus decrease to 3-40 MPa upon moderate swelling (30-70% w/w).

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Nonlinear optical imaging of silica-water interface

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The structure of interfacial water molecules at silica-water interface differs from the structure of water molecules in the bulk [1-3]. This interfacial structure is created by surface charges represented by silanol groups interacting with interfacial water molecules. Silica-water interface has been studied in numerous reports [4-6] with emphasis on determining the acid dissociation constant (pK_a) with a wide range of 2.1 - 16.2. However, these results seem to be contradictory and the pK_a values differ significantly from report to report. Here we image the dynamical interfacial changes on a silica-water interface on a sub second time scale acquiring pK_a values spatially ranging from 2.3 to 10.7 with an average of 6.7. It is for the first time, that an experimental work reports a whole spectrum of pK_a values. The measurement is performed by a structurally illuminated wide-field second harmonic microscope on a curved surface of glass micropipette immersed in an aqueous solution. The second harmonic images reporting on the orientational order of interfacial water are converted to surface potential maps. By following the pH changes of aqueous solution we employed Gouy-Chapman-Stern theory to calculate the final pK_a values of individual pixels (400 nm x 400 nm) of the SH image corresponding to the interface. Further we demonstrate that by applying sinusoidally varied electric field across the opening of micropipette we can image the oriented bulk water molecules confined in the tip, with second harmonic signal following the sinusoidal trend. Such observation of surface heterogeneity is important for catalysis, geochemistry or electrochemistry, and devices using electrokinetic phenomena in nanofluidic environments.

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Covalent conjugation of ketoprofen to alginate-based hydrogels reduces fibrosis in the transplantation of insulin producing cells

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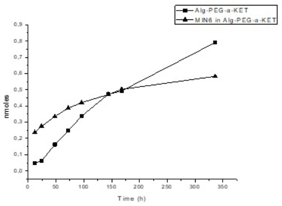
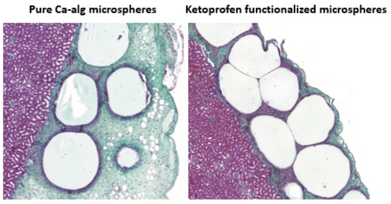
Cell microencapsulation in hydrogels is used to develop cell therapy products.[1] Due to the advantageous gelling properties of sodium alginate (Na-alg) in contact with divalent cations, this biopolymer has been widely studied for the microencapsulation of cells.[2] However, cell transplantation without immunosuppressive treatment have to face adverse host responses such as inflammation and fibrosis, which lead to necrosis of the encapsulated cells and loss of graft function.[3] Using a method developed in our group allowing the functionalization of Na-alg for the formation of hybrid hydrogels,[4] herein the covalent functionalization of Na-alg with ketoprofen and its effect on the reduction of pericapsular fibrotic overgrowth in the transplantation of microencapsulated insulin producing cells (MIN6) is presented.



Controlled release of ketoprofen from MIN6 cells containing microcapsules



Reduction of pericapsular fibrotic overgrowth 30 days post-transplantation

The strategy relies on the conjugation of PEGylated ketoprofen to the hydroxyl groups of Na-alg, involving either ester or amide bond as chemical linkage to the drug. Empty microspheres and microspheres containing MIN6 cells where formed with the resulting alginate derivatives and transplanted into immune competent mice to study both the drug release kinetics and the effect on fibrosis.

Quantification of cumulative release of ketoprofen by LC-MS from MIN6 containing capsules indicated continuous delivery of the active ingredient over two weeks, with faster kinetics in the case of the ester linkage. Following transplantation in mice and retrieval of empty and MIN6 containing microcapsules after 30 days, pericapsular fibrotic overgrowth was significantly reduced in the case of hydrogels functionalized with ketoprofen through an ester linkage.

In conclusion, the derivatization of Na-alg with PEGylated anti-inflammatory agents such as ketoprofen has the potential to reduce adverse fibrotic response and improve cell function in transplantation applications based on microencapsulated effector cells.

Acknowledgment: We thank the Swiss National Science Foundation (grant N° CR23I2_152974 and 310030E-164250), the Enable program and the Foundation Insuleman for financial support. We are grateful to Dr Christine Wandrey for helpful scientific discussions.

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Understanding phase diagrams in organic ternary blend solar cells

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Ternary blends are interesting concepts to broaden the spectral sensitivity in organic solar cells. Typically a binary bulk-heterojunction system with high performance is sensitized by an additional component having a specific sensitivity, e.g. in the near-infrared domain. The resulting morphologies and phase structures indeed are very complicated and have rarely been studied in depth. It is generally assumed that a third phase forms nanometer scale domains that are distributed in one or the other way within the binary blend system. Cascade charge transfer has been invoked to explain improved solar cell performance.

Here, the effect of adding cyanine dyes to a binary blend of $PC_{70}BM$ / PBDTTT-C to form a ternary organic solar cell is presented. Using near-infrared absorbing dyes with two different counterions, we show that next to the composition space where the system separates into three phases, a ternary diagram is characterized by six more composition regions: the stable a, b and g regimes plus three regions where the system separates into two phases. We identify the phases which are favorable for photovoltaic performance and demonstrate how phase compatibility can be introduced via ionic interactions.

Stimuli-responsive Pt$^{(0)}$-containing metallosupramolecular polymers

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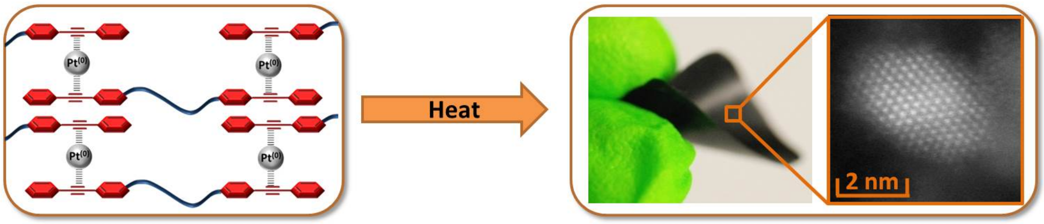
Low-molecular weight telechelics equipped with suitable terminal ligands can be self-assembled in the presence of stochiometric amounts of a metal salt to furnish metallosupramolecular polymers (MSPs). The properties of MSPs can be altered by stimuli such as heat or light, which affect the dynamic non-covalent interactions and shift the equilibrium between the assembled and disassembled states. This intrinsic stimuli-responsive nature of MSPs has been exploited to create functional materials for applications that range from healable surface coatings to shape-memory polymers.[1]



While the majority of MSPs rely on charged metal-ligand complexes, zero-valent metal complexes remain largely unexplored. In previous work, bis(η^2-alkyne)platinum(0) complexes were explored as conjugated cross-links in poly(*p*-phenylene ethynylene)s.[2] Building on this, we prepared a ditopic diphenylacetylene carrying telechelic core and linear chain extension with platinum(0) complexes led to the formation of soluble and stable MSPs. Such polymers permit for a spatially resolved generation of metal nanoparticles (NPs) via decomplexation, nucleation, and growth without requiring a reduction step.[3] Thus, the MSPs were found to be stable under ambient conditions but undergo an irreversible decomplexation above a threshold temperature. A characterization of films before and after annealing by means of differential scanning calorimetry, small angle X-ray scattering, and high-resolution transmission electron microscopy showed that the Pt-complexes dissociate, covalent cross-links of the polymer form, and 1 nm-sized clusters of Pt-atoms are obtained. At temperatures of 200°C, Pt-NPs with diameters between 1 and 3 nm are obtained. The NPs are homogenously distributed throughout the cross-linked polymer matrix, rendering such materials potentially interesting for applications that range from catalysis, to sensing and optoelectronic applications.

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Polyamides Comprising Bithiophene Segments

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Materials often feature varying degrees of structural order, which plays a key role in determining their macroscopic properties. Approaches to control the balance between short-range order and overall disorder are also relevant for developing mechanically durable polymer semiconductors. In this context, we designed polyamides comprising semiconducting segments, with the aim to exploit hydrogen bonding and the nanoscale crystalline features of polyamides (Figure 1) to control short-range order and macroscopic transport properties. To this end, we developed a three-step, gram scale synthesis of a bithiophene dibutyric acid monomer. Seven polyamides with different diamines were synthesized by solution-phase polycondensation using Yamazaki-Higashi conditions. All polymers had distinct melting and crystallization behavior depending on the length of the diamine, showing an odd-even effect. The resulting polyamides can be melt-processed, providing uniform films with instrumented moduli of 1.5 – 2.9 GPa, that are comparable to the industrial-grade polyamides. Furthermore they exhibited promising conductive properties, yielded a mobility of about 0.018 cm^2/Vs, regardless of the diamine length, as studied by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC).

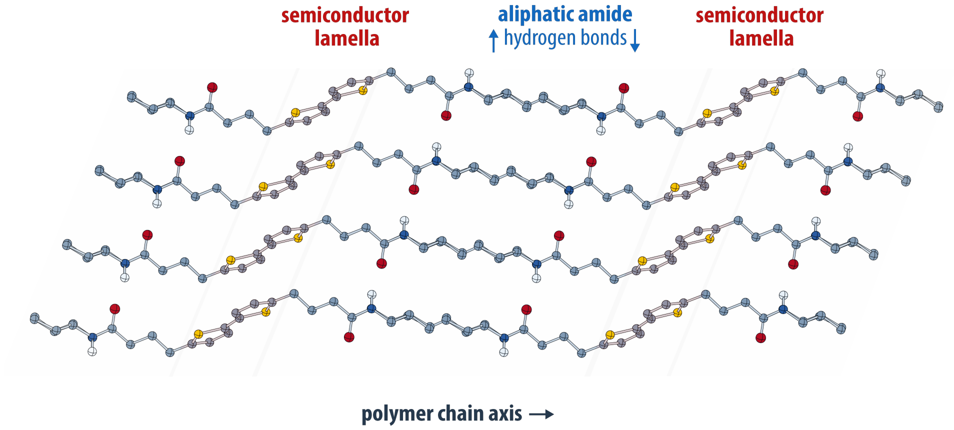

Figure 1: Schematic illustration of the expected lamellar structures in polyamides comprising bithiophene segments in the solid state. Note the molecular design concept, a short exible spacer enables the coexistence of hydrogen-bonded end groups and π–π stacking interactions.

How to transfer electrons across liposomal membranes with light

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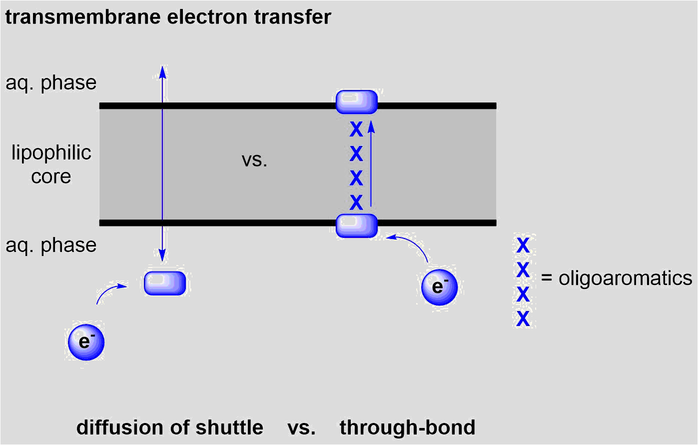
One concept in nature's toolbox for achieving efficient chemical transformations is the spatial separation of individual reactions by means of compartmentalization in vesicles. The best example in the context of light-driven reactions is the combination of photosynthetic water oxidation and $NADP^+$ reduction. These opposing redox reactions are spatially separated by the thylakoid membrane of the chloroplasts. Simultaneously, an electrochemical and pH gradient is built up across the membrane, which stimulates ATP production via a proton motive force. In our efforts to mimic the concept of compartmentalization we are studying the light induced transfer of electrons across the phospholipid bilayer of liposomes, which is important for the reduction of CO_2 or protons on one side of the membrane, while oxidation takes place on the other side. Two concepts for transmembrane charge transfer have been considered in artificial systems, namely diffusion-based transport, mediated by molecular shuttles,[1,2] and electron hopping via redox active stepping stones.[3] Studies in homogeneous solution have shown that oligoaromatic molecular wires are suitable building blocks for mediating long-range charge transfer.[4] We present here the integration of functionalized oligofluorenes as molecular wires in liposomes, and their ability to transfer electrons across phospholipid membranes.



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Synthesis of novel cyclosiloxane monomers containing push-pull moieties and their anionic ring opening polymerization

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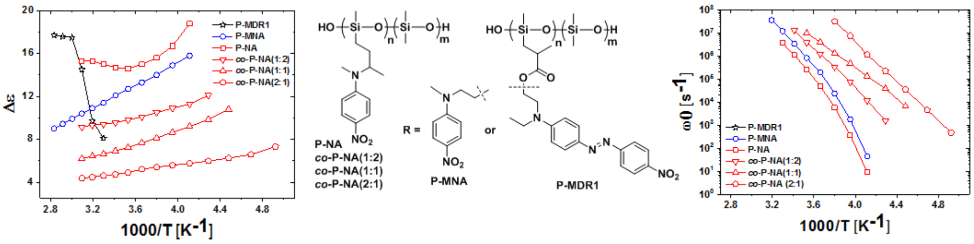
Push-pull molecules such as nitroaniline (NA) and disperse red 1 (DR1) have a large dipole moment and are often used as active components in nonlinear optic (NLO) polymer devices to increase the NLO coefficient as well as in electromechanical transducers to increase the polarizability and thus the dielectric permittivity [1]. The main gold of this work was to develop a synthetic strategy to tetracyclosiloxane monomers that carry push-pull dipoles and to polymerize them by anionic ring opening polymerization reaction to polymers with appreciable molecular masses. The content of NA moieties was tuned by copolymerizing a mixture of octamethyltetracyclosiloxane and push-pull functionalized cyclosiloxane monomers. The prepared monomers and polymers were characterized by different spectral methods and gel permeation chromatography. For the crystalline monomers, the structures were further proven by single crystal X-ray diffraction. Dynamic scanning calorimetry shows that the polymers that carry NA groups have a glass transition temperature (T_g) well below room temperature, while the one that carries DR1 groups melts. The transition temperatures have a strong effect on permittivity as indicated by broadband impedance spectroscopy measurements conducted at different temperatures and frequencies [2]. Due to the high dielectric permittivity and rather low T_g, the polymers modified with NA are attractive as active dielectric materials in actuators, capacitors, and stretchable electronics, whereas the polymer modified with DR1 may be of interest in nonlinear optical devices.



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Immobilisation of Photosensitizers by Electropolymerization

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Our group is investigating photocatalytic water reduction in homogenous solution, using cobalt polypyridyl based water reduction catalysts (WRC) and rhenium or ruthenium based photosensitizers (PS). [1] Homogeneous catalysis suffers from different drawbacks, eg diffusion limited reaction rates, or catalyst decomposition. Different approaches to immobilize both, WRC and PS, are thus followed to address this issues. One approach is the polymerization of the catalysts onto an electrode to form a photo cathode.

The electropolymerization of different ruthenium complexes with 4-vinyl-pyridine and/or 4-vinyl-4'-methyl-2,2'-bipyridine are known and well studied. [2] A di-vinyl-derivative (**1**) of a known rhenium photosensitizer was synthesised and first polymerization experiments were successful as shown in figure 1.

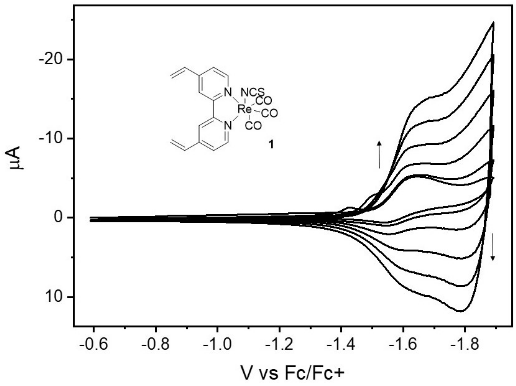

*Figure 1: Photosensitizer (**1**) was polymerized from a 1 mM solution in MeCN containing 0.1 M TBAPF$_6$. The Electropolymerization was achieved by cycling the potential between -0.59 V and -1.89 V vs Fc/Fc$^+$. Representative scans number 1, 10, 20, 30, 40 and 50 are shown.*

Results from the investigation of electropolymerization with (**1**) will be presented. We will focus on the influence of the electrode type (GC, Pt, Au) and preparation, factors governing the uniformity of covering, film thickness and physical properties.

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Self-assembly of a Bolaamphiphilic Cyclopenta[hi]aceanthrylene Derivative in Aqueous Medium

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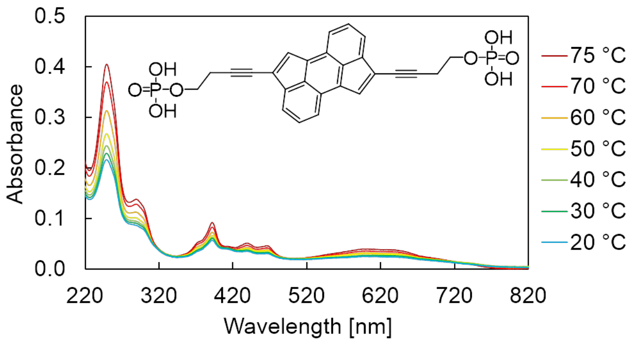
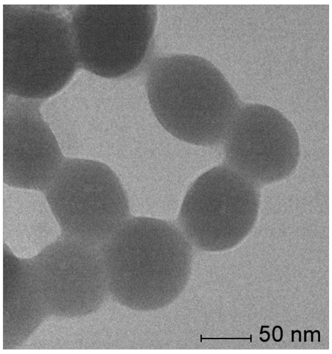
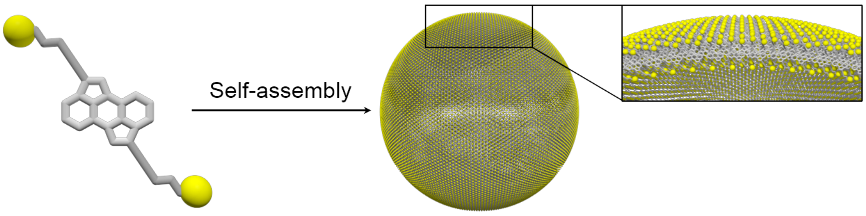
A low optical bandgap and fullerene-like electron affinity of functionalized cyclopenta[*hi*]aceanthrylene (cypac) was reported and potential applications as electron acceptors in organic solar cells are suggested among others.[1] In this work, a bolaamphiphilic cypac derivative was synthesized, which exhibits absorbance over the entire visible spectrum and self-assembles in aqueous medium into a vesicular morphology. The average size distribution of the vesicles can be controlled by the concentration of the monomeric building block cypac-bis-phosphate.







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Low voltage actuators with polar silicones

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Dielectric elastomer actuators (DEA) are promising devices with applications ranging from valves, pumps, braille displays, loud speakers, optical and energy harvesting devices, to artificial muscles. Acrylic and silicone elastomers are the most widely studied materials for DEA applications.[1] They however require high driving voltage (above 1 kV) for actuation due to their rather low dielectric permittivity.

Polar silicones hold promise as dielectrics for DEA.[2] By incorporating polar groups into polysiloxanes, we were able to prepare elastomers with dielectric permittivity above 18.[3-5] Polar nitrile groups were grafted to polymethylvinylsiloxane by a thiol-ene reaction and the formed polymer was processed in thin films and cross-linked. This resulted in an elastomer which exhibits high permittivity values (above 20 at 10 kHz) and excellent elastic properties (tan $\delta<0.05$ at frequencies below 1 Hz). Actuators constructed with 20 µm thick films gave a lateral actuation strain of 2-3% at 250 V. Additionally, cyclic tests show that the actuation is stable over 100.000 cycles. Furthermore, the actuators can withstand a very high electric field of 80 V/mm, where ultra large actuation was observed.

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Engineering of Multifunctional Alginate-based Hydrogels to Enhance Mechanical Properties and Immunoprotection in the Transplantation of Microencapsulated Cells

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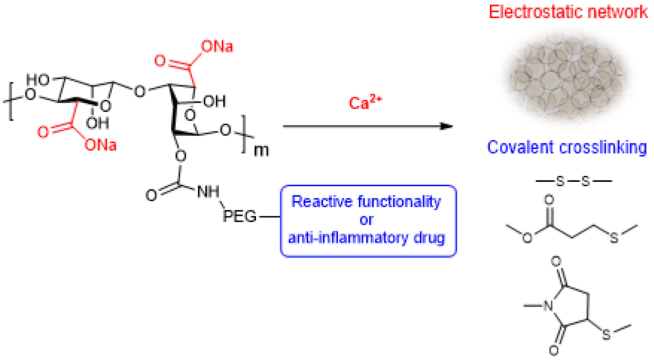
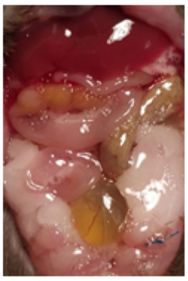
The shortage of human donor materials to replace dysfunctional cells and organs is a concerning worry in the current medical world. From many points of view, cell based therapies, especially allo- or xenotransplantation of microencapsulated cells in a semi-permeable 3D matrix offers a promising alternative solution, in particular by reducing the risks associated with whole organ replacement surgery.[1]Despite the significant progress made in the development of alginate-based cell transplantation so far,[2]the translation to clinical applications is still limited due to several unsolved factors, including the lack of biomaterials with adequate properties supporting cell survival and long-term stability, as well as the formation of pericapsular fibrotic tissue which ultimately results in the loss of graft functionality.

Our group focuses on the development of alginate-based spherical hydrogels for the transplantation of human and porcine effector cells to provide alternative treatment for type I diabetes or acute liver failure. Sodium alginate (Na-alg) is the most widely used biomaterial in cell microencapsulation due to its advantageous gelling properties in the presence of divalent cations and its high cell compatibility. However, hydrogels prepared from pure Na-alg lack *in vivo*mechanical durability and are subject to pericapsular fibrotic overgrowth.

We present herein several strategies to improve the physical/mechanical properties of alginate-based hydrogels. The covalent conjugation of cross-reactive poly(ethylene glycol) PEG derivatives to Na-alg gives access to hybrid hydrogels stabilized by both ionotropic gelation and covalent cross-linking, which demonstrated long-term*in vivo*stability. The synthetic pathway involved direct activation of the hydroxyl groups of the alginate backbone followed by formation of a stable carbamate linkage[3]to graft the PEG oligomers. The resulting complementary polymers were used to form spherical hydrogels, which presented enhanced elasticity and stability towards ion exchange, in comparison with pure Na-alg. Their performance in the microencapsulation of endocrine cells and their potential for cell transplantation were evaluated both *in vitro*and *in vivo*.





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Label-free and charge-sensitive dynamic imaging of lipid membrane hydration on millisecond time scales

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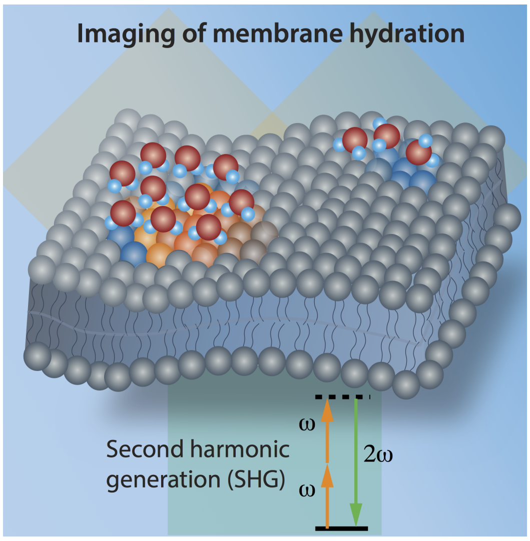
Biological membranes are highly dynamic and complex lipid bilayers, responsible for the fate of living cells. To achieve this function, the hydrating environment is crucial. However, mem- brane imaging typically neglects water, focusing on the insertion of probes, resonant responses of lipids, or the hydrophobic core. Owing to a recent improvement of second-harmonic (SH) imaging throughput by three orders of magnitude, we show here that we can use SH microscopy to follow membrane hydration of free- standing lipid bilayers on millisecond time scales. Instead of using the UV/VIS resonant response of specific membrane-inserted fluo- rophores to record static SH images over time scales of >1,000 s, we SH imaged symmetric and asymmetric lipid membranes, while vary- ing the ionic strength and pH of the adjacent solutions. We show that the nonresonant SH response of water molecules aligned by charge−dipole interactions with charged lipids can be used as a label-free probe of membrane structure and dynamics. Lipid domain diffusion is imaged label-free by means of the hydration of charged domains. The orientational ordering of water is used to construct electrostatic membrane potential maps. The average membrane po- tential depends quadratically on an applied external bias, which is modeled by nonlinear optical theory. Spatiotemporal fluctuations on the order of 100-mV changes in the membrane potential are seen. These changes imply that membranes are very dynamic, not only in their structure but also in their membrane potential land- scape. This may have important consequences for membrane func- tion, mechanical stability, and protein/pore distributions.



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Microwave-Assisted Synthesis of PDMS-PMOXA as Amphiphilic Diblock Copolymer

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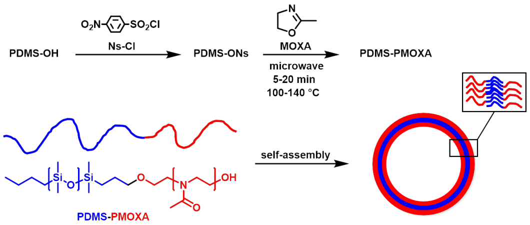
Amphiphilic block copolymers have shown to perform defined self-assembly into distinct morphologies in aqueous dispersions. From those, vesicles are of particular interest for biomedical applications due to their aqueous cavity and ability to encapsulate cargo[1]. A prominent example of a suitable biocompatible block copolymer is poly(dimethyl siloxane)-poly(2-methyl-2-oxazoline) (PDMS-PMOXA). However, its synthesis is time-consuming (reaction times up to three days) and challenging as it contains highly reactive intermediates (e. g. triflates)[2]. Here we present an alternative way of synthesising a PDMS-PMOXA diblock copolymer that shows improvements regarding the reaction time, control and reproducibility.



Starting from a commercially available monocarbinol-functionalised PDMS homopolymer we activated the terminal hydroxy group by deprotonation and addition of nosyl chloride (Ns-Cl). The following cationic ring-opening polymerisation of 2-methyl-2-oxazoline was performed in a microwave-based reaction. Eventually an amphiphilic diblock copolymer was obtained, consisting of a hydrophobic PDMS block and a hydrophilic PMOXA block. This microwave-assisted synthesis benefits from a highly controlled and reproducible polymerization with massively reduced reaction times of only 5 to 20 minutes. The obtained polymers are promising candidates to perform self-assembly and to serve as nanoreactors or drug delivery systems in biomedical applications[3].

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One-component polymer nanocomposites based on hairy cellulose nanocrystals

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One-component nanocomposites (OCNs) are emerging materials resulting from the assembly of hairy nanoparticles (HNPs) in solid state.[1] In contrast to conventional multi-component nanocomposites, OCNs do not suffer from phase separation or de-mixing of their components due to covalent linkages between the polymers and nanoparticles. As a consequence, the composition of OCNs can be tuned over a wide range of filler-to-polymer ratios that would otherwise not be accessible.

The modification of the surface of cellulose nanocrystals (CNCs) has been extensively reported in the context of filler-matrix nanocomposites.[2] Nevertheless, the solid-state properties of OCNs based on such HNPs are virtually unexplored. Here, we present the synthesis of OCNs based on poly(methacrylate)s and block-copoly(methacrylate)s grafted from cotton-derived CNCs though free and controlled radical polymerization, respectively. The resulting OCNs show thermomechanical properties that strongly depend on the nature of the grafted polymers, and in some cases, display properties superior to conventional polymer nanocomposites. For example, the glass transition of OCNs based on poly(methyl methacrylate) (PMMA) was ca. 20-40 °C higher than that of conventional PMMA/CNC nanocomposites, both containing 10 wt% of CNCs. Such materials have great potential for different applications due to the unique combination of high stiffness, strength and toughness.

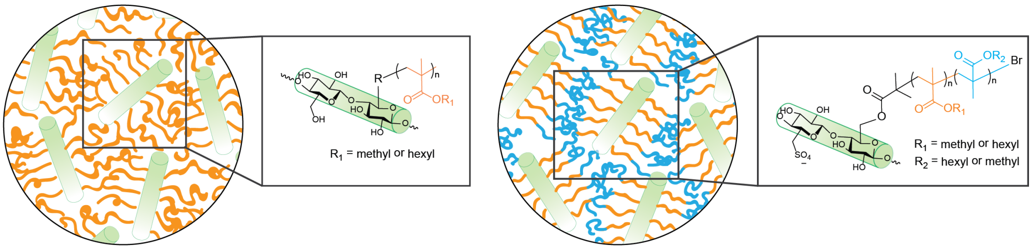

Figure 1. Schematic representation of OCNs based on homo-(left) or block-(right) copoly(methacrylate)s grafted from cotton-derived CNCs.

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Ultralight nanofiber aerogels with dual functionality for oil/water and water/oil separation

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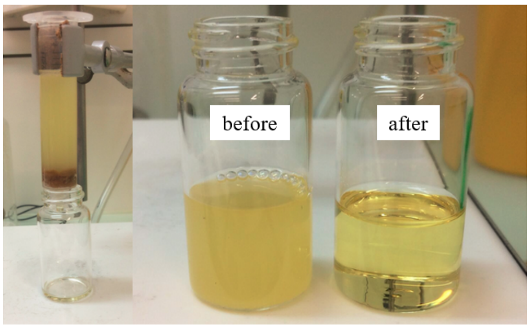
There is a tremendous environmental and technical demand for improved oil/water and water/oil separation technologies, e.g. for the purification of 2.4 billion gallons of produced water associated with the daily oil and gas production. Recently, hydrophobic aerogels based on polymeric nanofibers were successfully applied for water from oil separation [1]. Here, we adopted the concept to biodegradable pullulan/poly(vinyl alcohol) (PUL/PVA) nanofiber aerogels (NFAs) for dual functional separation by switching between hydrophobic and oleophobic surface properties.

NFAs for water/oil separation were prepared from electrospun PUL/PVA nanofibers cutting and dispersing them in 1,4-dioxane (average length of 30 µm), freezing the suspension at -20 °C, followed by freeze-drying and thermally crosslinking at 180 °C. The resulting amphiphilic NFAs (average pore size 50 µm) were hydrophobized with trichloro(octyl)silane by chemical vapour deposition [2-4]. The flexible NFAs exhibited a cellular architecture with porous cell walls generated from the nanofiber building blocks and interconnected pores. They showed ultralow density of 10 mg cm^{-3}, high porosity (99.2 %), a Young's modulus of 36.41 kPa, and a contact angle of 123.6°. The resulting NFAs were able to hold up to 28.16 g diesel/g of NFAs and they were easily recycled by extraction with *n*-hexane. Thanks to their interconnected pores and hydrophobicity, water from oil separation was feasible through simple gravity driven filtration.

NFAs for oil/water separation are prepared by reversing the hydrophobic surface properties with trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane followed by air plasma treatment. These materials are currently successfully applied for oil from water separation.



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Key Properties of Nanoparticles that Control Their Spontaneous Adsorption at Liquid-Liquid Interfaces

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Understanding the mechanisms and finding out the key factors controlling spontaneous adsorption of nanoparticles (NPs) at Liquid-Liquid (L-L) interface is critical for their application as solid emulsifiers and bubble stabilizers.[1] In this work, the mechanism of interfacial adsorption is investigated for two types of NPs, “constituted of” and “grafted with” pH-responsive polymers such as poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) (pKa = 7.0-7.3) and poly(2-dimethylamino)ethyl methacrylate) (PDMAEMA) (pKa = 7.4-7.8)[2]. For this, dynamic interfacial tension (IFT) measurements were carried out to investigate the spontaneous adsorption behavior of the NPs at Toluene-H_2O (Tol-H_2O) interface. For PDMAEMA grafted PS NPs, the IFT results demonstrate that the solubility of PDMAEMA in toluene is the determining factor that controls the NPs’ interfacial spontaneous adsorption. In detailed, in acidic condition pH < 6.0, the PDMAEMA grafted NPs do not adsorb at Tol-H_2O interface, but in basic condition pH > 7.0, PDMAEMA is deprotonated and becomes soluble in toluene, therefore the PDMAEMA grafted NPs can adsorb at Tol-H_2O interface, with a significant decrease in IFT value from 34 mN/m to 5.5 mN/m. Interestingly, when NPs are constituted of PDEAEMA, they can adsorb spontaneously at Tol-H_2O interface in acidic condition (pH < 6.0), but not in basic conditions (pH > 7.0). In this case, the key factor determining the spontaneous adsorption at Tol-H_2O interface is the softness degree of NPs rather than the solubility of PDEAEMA in toluene.

Finally, the synthesized NPs show a high efficiency in stabilizing Pickering emulsion and behave as solid surfactants. The obtained Picking emulsions are very stable, for more than half a year without phase separation. Furthermore, the obtained Pickering emulsions are pH-responsive and the emulsion phase can be changed dynamically by pH adjustment from 2.0 to 10.0.

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Soft Sensitive Matter: Structure, Dynamics, and Function of Supramolecular Polymer Gels

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Supramolecular polymer gels consist of polymer chains connected by non-covalent interactions [1]. These materials are promising for a plethora of applications, ranging from adaptive and self-healing scaffolds [2] to designed extracellular matrixes [3]. To truly exploit the utility of these gels, it is necessary to understand the interplay between their structure, dynamics, and properties [1]. We address this challenge on the basis of macromolecular toolboxes derived from the same precursor polymer but functionalized with different crosslinkable motifs, thereby exhibiting greatly varying strength of association without perceptible alteration of other parameters [4, 5]. We find that a prime factor of impact on the mechanics and responsive performance of the resulting supramolecular gels is their nanometer-scale polymernetwork architecture. To specifically account for this circumstance, we prepare our sample platforms such to either exhibit irregular, heterogeneous distributions of their supramolecular crosslinking nodes [4] or model-type, homogeneous and regular supramolecular chain interconnection [5]. These different gels are then further studied to correlate their macroscopic properties to their supramolecular binding–unbinding equilibria [4–6], nanoscopic polymer-network topologies [4, 5], and chain and junction dynamics [7–11].

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Dynamics and Welding Behavior of Metallosupramolecular Polymer Films

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Supramolecular polymers show intriguing materials' properties such as the healing of scratches and welding of films, all of which are enabled by the reversible and dynamic linkage between individual macromonomers.[1,2] The progression of such processes is typically evaluated by comparison of the macroscopic mechanical properties of healed or welded samples to those of their pristine counterparts.[3] However, an improved understanding of the underlying mechanisms responsible for both healing and welding is required to allow for a precise engineering of such materials. In order to gain a deeper understanding of the rearrangements that restore the original materials' properties of metallosupramolecular polymers (MSPs), we combined bulk mechanical investigations with an analysis of the network relaxation and microscopically explored the reshuffling at the interface. This approach allowed for an elucidation of the role of molecular mixing and interphase generation during the welding process.

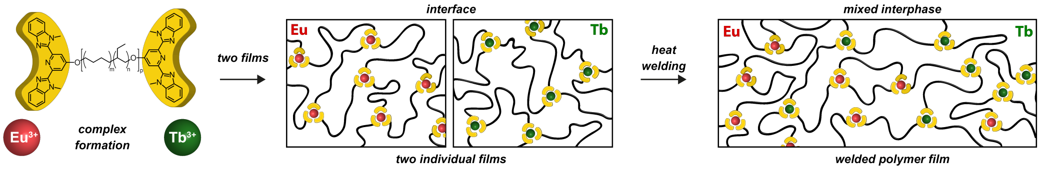

Figure 1: Schematic illustration of the formation of Eu^{3+} and Tb^{3+}-based metallosupramolecular films and heat-induced welding under formation of a mixed interphase. Restoration of the mechanical properties is investigated on a macroscopic and microscopic level with films featuring two different metal ions.

Two MSP networks were prepared by coordination of either Eu^{3+}- or Tb^{3+}-ions to telechelic poly(ethylene-*co*-butylene) end-capped with methylbenzimidazolyl pyridine ligands. The two resulting supramolecular polymers were compression-molded into flexible films, in which defects such as cuts could be readily healed or welded upon exposure to heat or UV-light.[4] To allow for a detailed investigation of such processes, films of MSPs with different metal ions were welded together and the efficiency of the welding process was evaluated by mechanical testing. Moreover, investigations by scanning transmission electron microscopy with energy dispersive X-ray spectroscopy allowed us to follow the diffusion of metal ions and the growth of a mixed interphase. In combination with rheological measurements, the molecular processes were directly correlated with the macroscopic welding efficiency. The results establish an improved understanding of these dynamic processes, which is a prerequisite in developing materials with tailored properties.

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Colloidal shuttles for programmable cargo delivery

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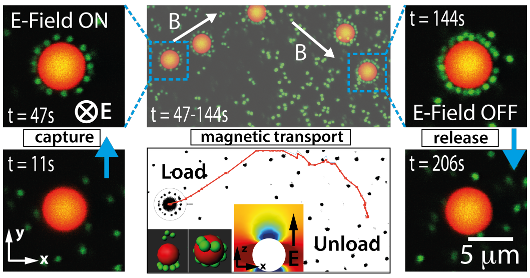
External field gradients are commonly used for separation, contactless manipulation[1] and assembly[2] of nano- and microparticles. Here, we introduced a novel colloidal shuttle by using electric field gradients, so called dielectrophoresis. In a homogenous electric field, a dielectric colloid can act as a field gradient-maker and changes the electric field strength around itself. Such field strength alteration around the dielectric colloid was employed as a trap for other particles. Orthogonally using magnetic fields in addition to electric fields and employing magnetic "shuttle-colloid" allowed for loading, transporting and unloading of the trapped cargo. We further extended this technique to transport bio-cargo and even used anisotropic colloids as carriers[3].



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Colloidal $CsPbX_3$ (X=Cl, Br, I) Nanocrystals 2.0: Zwitterionic Ligands for Improved Durability and Stability

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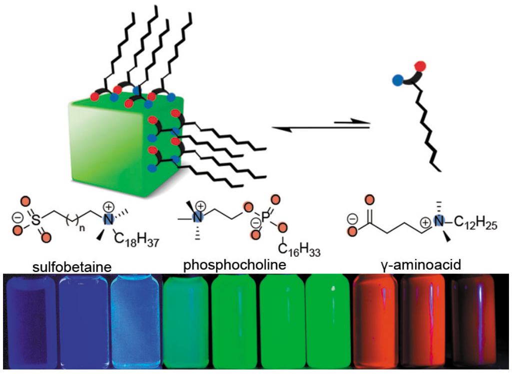
Colloidal $CsPbX_3$ perovskite nanocrystals (NCs) are promising materials for opto-electronic applications such as LEDs, lasers and photo-detectors, owed to their efficient, tunable emission with narrow line width. [1] An important challenge which remained was chemical instability due to loosely bound ligands, standing in rapid equilibrium with the solution. [2] In our recent work we addressed this problem by the use of zwitterionic ligands. These ligands are not subject to Brønsted acid base equilibria and shift the binding equilibrium to the bound state due to chelation. In this way the beneficial optical properties could be retained while the synthesis yield was improved and long term stability after purification was achieved. Such clean colloids can not only be used for device fabrication yielding efficient LEDs, photo-detectors and low-threshold lasers [3] but will also forego the development of novel materials and composites such as core-shell structures or could enable chemical manipulation of the NC's ligand shell post- synthetically.



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Decoding the folded chains and nanostructures inside electrospun nanofibers by SAXS and WAXS

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Over the years, electrospinning has been developed as a technique to produce nano to micron-sized fibers. It is well understood that the internal structure of these fibers highly depends on the polymer type, the spinning solution properties and the spinning parameters [1]. In our recent studies, we have investigated the structure of electrospun Poly(vinylidene fluoride-co-hexafluoropropylene), PVDFhfp, based fiber membranes for non-aligned and aligned (using a high speed rotating drum) samples by SAXS and WAXS techniques. Interpretations of SAXS profiles from such membranes exhibit both densely packed lamellar and fibrillar structures with extended amorphous tie-molecules. Fibrillar surface structure can also be seen in AFM performed on single fibers. In addition, the WAXS profiles revealed the orthorhombic structure of the crystallites in both non-aligned and aligned fiber membranes.

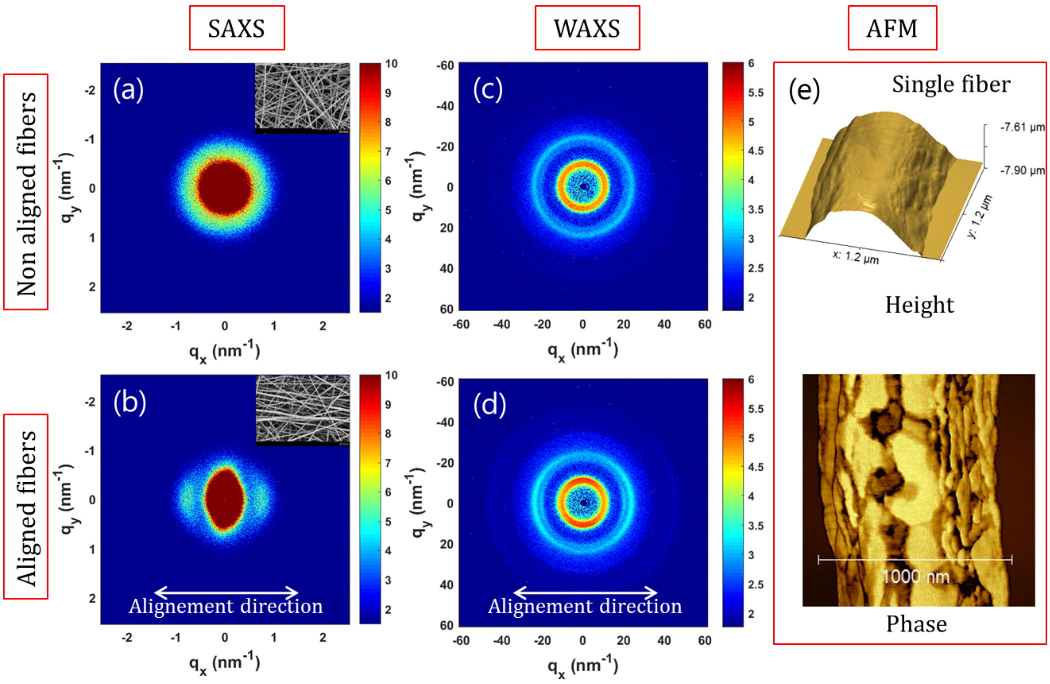

Figure 1. SAXS and WAXS profiles from PVDFhfp fibers; (a,c) non-aligned, (b,d) aligned samples, and their corresponding SEM image in the inset. (e) AFM of single fiber, height (top) and phase image (bottom).

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Radical Ring-Opening Polymerisation for Biodegradable Nanoparticles and Temporary Enzyme Protection

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Amphiphilic block-copolymers are ideal for self-assembly into nanoparticles.[1] While the majority of self-assembly studies are done with non-degradable polymers, we target the formation of biodegradable polymeric self-assemblies.

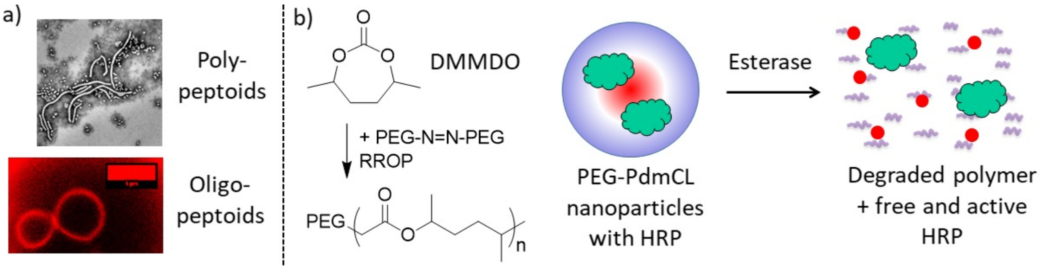

Figure 1: a) Peptoid self-assembly can give worms or giant vesicles. b) Deploying RROP, the monomer is converted to PEG-PdmCL, which self-assembles into nanoparticles, serving as temporary protein shells.

We came to notice that block-copolypeptoids show high value for polymeric self-assembly. Polypeptoids from ring-opening polymerisation enable onion-like self-assemblies and well-defined worms due to their low dispersity.[2] Oligopeptoids from solid-phase synthesis, easily form giant vesicles simply by hydrating them in water (**Fig. 1a**).[3] However, although they are hydrolysable, peptoids are not biodegradable. Aliphatic polyesters are biodegradable and accessible through radical ring-opening polymerisation. We revisited their monomer synthesis and achieved a milder protocol and also developed a new route via a cyclic carbonate. The monomer proved to form homopolymers and block-copolymers using free radical polymerisation (FRP). Our resulting polyesters self-assembled into nanoparticles that were degradable by esterase as well as biocompatible **(Fig. 1b)**.[4] The nanoparticles proved to be an effective protective shell for an entrapped horse radish peroxidase that was released and fully active upon degradation of the nanoparticles by esterase.

Our data shows that polyesters from RROP are already readily available and are especially promising in applications involving biodegradable self-assembled nanoparticles.

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New packaging technologies and industrial perspectives from a material science company

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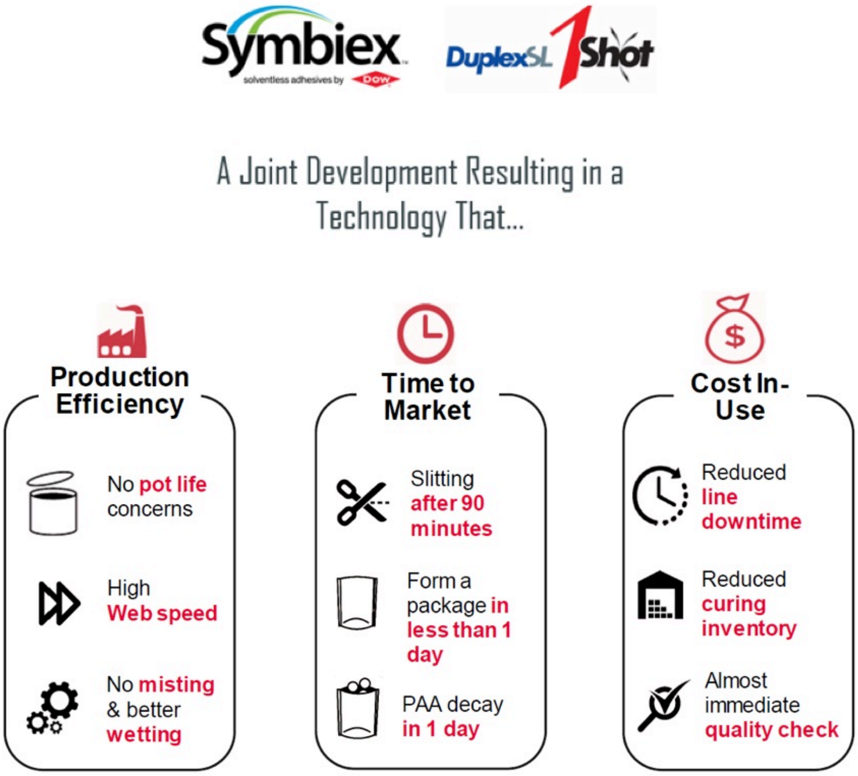
The Dow Chemical company is leading innovations in the packaging industry. A recent example is the launch of SYMBIEX™, solvent-less laminating adhesive for ultra-fast curing.

With SYMBIEX™, Dow offers an innovative adhesive technology for creating multilayer packaging films for food, appliances, etc. These films require layers of different plastics glued together to create a film with desired properties. Current adhesives require long cure times before handling the film to be slit and made into packages and even longer times before food contact. SYMBIEX™ uses a unique reactive cure system that dramatically speeds up processing and reduces the wait time for food contact. The SYMBIEX™ adhesive system applied using Duplex one shot machine save processors time and money while reducing waste and providing superior performance balance.



A Joint Development Resulting in a Technology That...

Production Efficiency

- No **pot life** concerns
- High **Web speed**
- No **misting** & better **wetting**

Time to Market

- Slitting **after 90 minutes**
- Form a package **in less than 1 day**
- PAA decay **in 1 day**

Cost In-Use

- Reduced **line downtime**
- Reduced **curing inventory**
- Almost immediate **quality check**

Confinement-Induced Liquid Crystalline Transitions in Amyloid Fibril Cholesteric Tactoids

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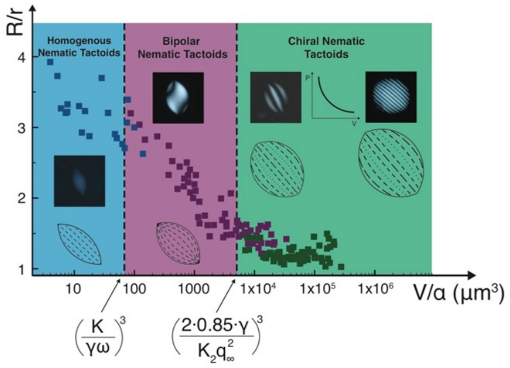
[1]Department of Health Sciences and Technology, ETH

Understanding and controlling chirality is an important research challenge with broad implications. Here we report the discovery of cholesteric phases in amyloids, using b-lactoglobulin fibrils shortened by shear stresses. The physical behavior of these new cholesteric materials exhibits unprecedented structural complexity, with confinement-driven ordering transitions between at least three types of nematic and cholesteric tactoids. By nucleation and growth, first homogeneous nematic tactoids emerge that further transform to tactoids with a bipolar director field and later develop to uniaxial cholesteric droplets. These phase transitions can be explained using a scaling form of the Frank-Oseen elasticity theory.



As predicted by the theoretical model, two phase transitions could be experimentally confirmed using cross-polarized optical light microscopy (see Fig. 1). Further, the critical size, where the tactoids start to develop a right-handed cholesteric twist, was observed. Keeping the left-handedness of the single amyloid fibril in mind, an inversion of the chirality from single particle to cholesteric liquid crystalline phase is observed. These findings deepen our understanding of cholesteric phases advancing their use in soft nanotechnology, nanomaterials templating and self-assembly.

Gustav Nyström, Mario Arcari, Raffaele Mezzenga, *Nature Nanotechnology,* **2018,** 13, 330–336.

Self-Assembly of Janus Nanoparticles into Suprastructures

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Amphiphilic Janus nanoparticles (JNPs) have attracted significant interest for their enhanced interfacial activity as compared to simple homogeneous nanoparticles, and therefore potential use in applications such as emulsification or bulk to surface carriers of actives.[1] In addition, a subclass of JNPs is capable of self-assembly into suprastructures resembling those generated by molecular surfactants. Computer simulations demonstrate a rich potential and diverse landscape of suprastructures that can be obtained from JNPs, but this aspect has not been fully explored experimentally. Here we present our latest experimental results showing that indeed snowman type JNPs are capable of self-assembly into a variety of structures, from micelles, to capsules, bilayers, giant mono-walled and multi-compartmented vesicles.[2,3] Some of these suprastructures resemble those produced by molecular surfactants, but some are you unique to JNPs; these key differences will be discussed and compared. The diversity of the self-assembled structures can be controlled by adjusting the geometrical parameters of the snowman JNPs, such as size, phase separation, relative ratio between the Janus lobes, etc. The obtained self-assembled suprastructures can be reversible transformed into other types of structures by controlling the experimental conditions, such as temperature, shear or solvent concentration.

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Ion speciation at nanoscale hydrophobic/water interface is diverse, occurs at millimolar concentrations and is correlated with stability

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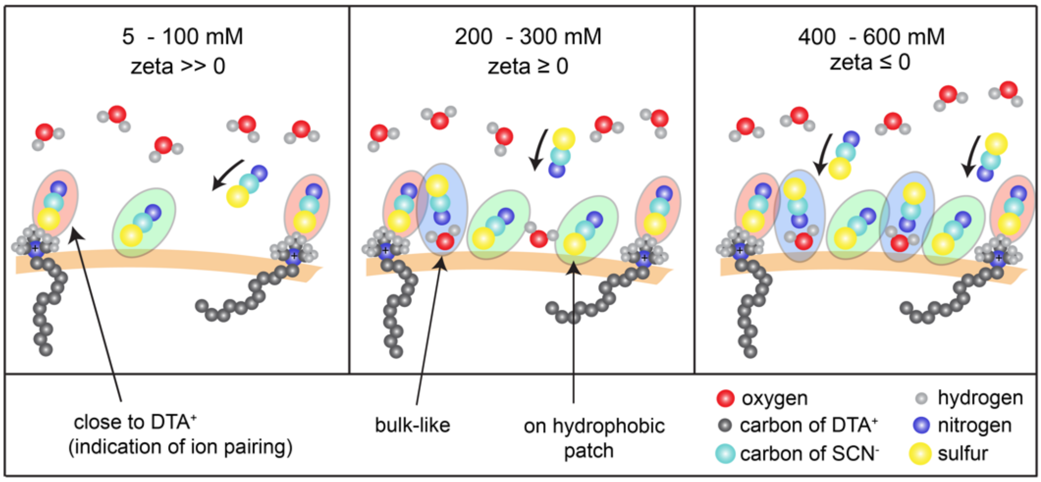
The vast majority of biologically active molecular interfaces are comprised of nanoscale structures with hydrophobic and hydrophilic groups adjacent to one another, and in contact with aqueous ionic solutions. The distribution of ions/ionic groups across interfaces, and the interaction of ions both with the hydrophobic and the hydrophilic parts are of fundamental importance for life, as they determine the chemical functionality of the interfaces. Although many studies have focused on characterizing planar extended (often air/water) interfaces, little is still known about the speciation of ions at the biologically-relevant buried liquid nanoscale surfaces. To understand the complex mechanisms involved, here we study a hexadecane nanodroplet system stabilized with a dilute monolayer of positively charged (DTA$^+$) groups in contact with electrolyte solutions (NaSCN). We used the techniques of vibrational sum frequency scattering, second harmonic scattering, ζ-potential measurements and quantum density functional theory to investigate ion speciation, molecular conformation, hydration structure and charge at the nanodroplet interface.



We find DTA$^+$-SCN$^-$ion pairing at concentrations as low as 5 millimolar, while a variety of ion species emerge at different ionic strengths, with differently oriented SCN$^-$groups adsorbed on hydrophilic or hydrophobic parts of the surface. This diverse and heterogeneous chemical environment enhances nanodroplet stability even for charge neutral droplets that are normally considered unstable.Such heterogeneity is surprisingly different from the behavior at extended liquid planar interfaces, where ion pairing is typically detected at molar concentrations and nanoscale system stability is no requirement.

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Novel Single-layer graphene/polymer composite membrane that meets the postcombustion carbon capture target

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[1]Laboratory of Advanced Separations (LAS), ISIC, EPFL

The global CO_2 emission from the consumption of fossil fuels have risen rapidly in the last decade. Curbing CO_2 emission, to slow down the global warming, has become one of the most critical environmental and energy issues. Membrane-based CO_2 separation is one of most promising and energy-efficient solution for the postcombustion carbon capture. Single-layer nanoporous graphene is the thinnest molecular barrier, and can act as an ideal gas separation membrane yielding orders of magnitude higher gas permeance compared with the conventional membranes. However, incorporation of molecular-selective nanopores in otherwise impermeable graphene lattice has proven to be a major challenge. Recently, we succeeded in demonstrating H_2/CH_4 sieving from single-layer graphene by developing an ozone based etching chemistry that etched pores of diameter between 0.30-0.38 nm.[1] However, it is extremely challenging to etch out pores to separate CO_2 from N_2 based on the molecular sieving mechanism (kinetic diameter of CO_2 and N_2 are 0.33 and 0.36 nm). To address this separation, we report development of a novel graphene/polymer hybrid membrane, where porous graphene acts as an atom-thick and atomically smooth porous support. We created a high-density of nanopores on graphene using O_2 plasma, and subsequently CO_2-philic polymers (polyethyleneimine@polyethylene glycol) were added onto the surface of graphene for the selective transport of CO_2, as illustrated in Figure 1a. Moreover, a novel, efficient transfer method was utilized for the crack-free transfer of the functionalized graphene film onto a porous support, that is, the graphene film was coated with a thin, highly permeable PTMSP layer. As a result, a remarkably high CO_2 permeance of 4030 GPU, and gas selectivities of 22.6 for CO_2/N_2, were achieved. The proposed approach of functionalizing nanoporous graphene with a specific "gate" having selective solubility or adsorption towards target molecule could pave the way for high-performing single-layer graphene membrane in a wide range of applications.

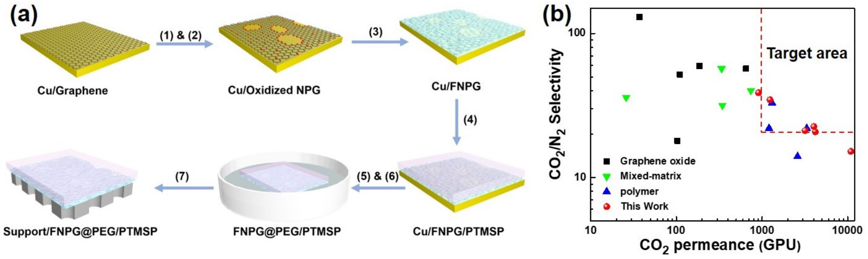

Figure 1. (a) Schematic illustration of preparing the functionalized graphene/PTMSP membrane, (b) CO_2/N_2 selectivity versus permeance diagram comparing our data with the state-of-art membranes.

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Bio-inspired Force-responsive Polymersomes

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Block copolymer vesicles find widespread applications as drug delivery vehicles, as nanoreactors and as nanocapsules [1-6]. Here, we present strategies to change the permeability of their membrane by externally applied mechanical forces. The force-responsive polymersomes can release cargo on demand when a polymersome suspension is vigorously mixed. By encapsulating enzymes into the vesicles, nanoreactors were obtained that allow to control biotransformations by applying shear forces. The resulting bio-inspired nanoreactors produce bioluminescence when shaken, similar to the behavior of bioluminescent dinoflagellates in the sea.

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Reverse Engineering of Simple Life Forms in Fully Synthetic Hydrogel Microsystems

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[1]Institute of Mechanical Engineering, École Polytechnique Fédérale de Lausanne (EPFL)

Implementing naturally occurring features such as soft materials, hierarchical organization, adaptive gaits, and control mechanisms in artificial settings can improve performance of robotic devices and reveal novel insight on biological design and evolution [1, 2]. One of the most important bottlenecks in this endeavor is the development of soft microactuators replicating the high-resolution complex movements of biological muscles. Photothermal effect of gold nanoparticles can efficiently transduce near infrared light into localized heat that drives rapid and powerful polymer collapse at the nanoscale. We developed a series of bioinspired soft manufacturing techniques for hierarchical assembly of arbitrarily-shaped microactuators from nanoscale building blocks. Sculpturing soft structures with well-defined architecture from nanoscale contractile elements requires fine control over surface chemistry and integration of a number of methods such as template-assisted microfluidic self-assembly, magnetic and acoustic levitation, additive manufacturing, origami-based folding techniques, and optofluidic manipulation. Structured illumination of samples using a programmable digital mirror display provides spatiotemporally resolved control for actuation. The input power delivered by the actuators is transformed into a desired set of movement of the micromachines using rationally designed compliant mechanisms. With the computational models informing the experimental design and assembly procedure, we provide a rapid prototyping platform for the development of synthetic constructs mimicking the structural design, kinematics, and body-fluid interactions of biological systems.

Acknowledgements: This work is supported by the European Research Council (ERC Starting Grant 714609).

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