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Ag nanoencapsulation for antimicrobial coatings

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Since long time silver is known for its good antimicrobial properties and biocompatibility. Silver nanoparticle based antimicrobial coatings can make use of these properties to fight medical device related infections by preventing biofilm formation especially if they show activity against multi resistant bacteria strains. In this context different types of Ag@metaloxide nanoparticles are investigated for their antimicrobial properties in correlation with the particle morphology. The metal oxide shells made of TiO_2 or SiO_2 protect the Ag particles from aggregation and might give control over the release rate of Ag^+ as antimicrobial active species. Moreover encapsulation offers ways to covalent attachment to implant surfaces as well as to sol gel coatings.

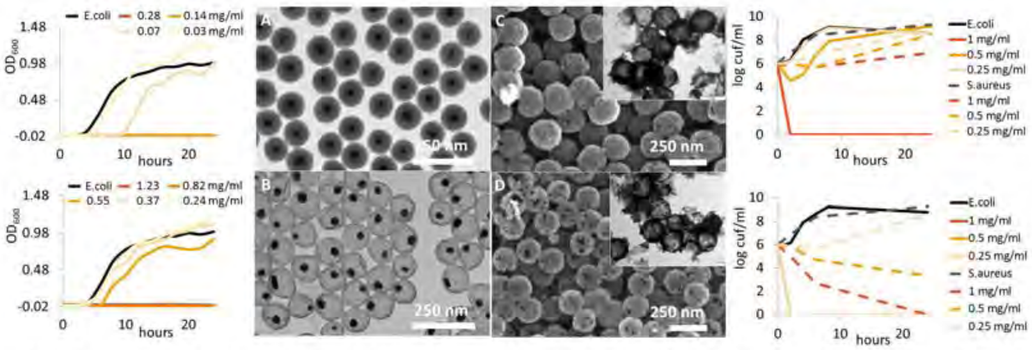

Fig 1: Electron micrographs of $Ag@SiO_2$ core shell particles (CS, A) and nanorattles (NR, B) and Ag-TiO_2 nanocontainers in amorphous (C) and anatase phase (D) and their antimicrobial effect on *E.coli* and *S.aureus*.

100 nm $Ag@SiO_2$ core shell particles (CS, Fig. 1 A) have been realized by coating Ag nanoparticles synthesized by the polyol process with a silica shell by a modified Stöber method. In a second step the inner part of the silica shell was removed by a surface protected etching process[1] which changes the particles' morphology towards a so called nanorattle (NR, Fig. 1 B). In a second synthesis, Ag nanoparticle containing amorphous TiO_2 nanocontainers of about 200 nm were synthesized by removing a polystyrene template (Fig. 1 C). A subsequent calcination step transforms the amorphous shell into crystalline anatase (Fig. 1 D). Depending on the particles' morphology different Ag^+ release kinetics could be observed by measuring ICP-OES. In the case of silica as shell material the nanorattles show a stronger release than the core shell particles over a long time period, but within the first 24 hours the reverse trend can be observed (Fig. 1, left). This correlates to the core shells better antimicrobial activity. Tests against *E.coli* show that they are killing at concentrations of about 0.14 mg/ml whereas 0.82 mg/ml of nanorattles are needed to see the same effect. In the case of TiO_2 nanocontainers the anatase particles are able to release more Ag^+ which is clearly reflected in their better antimicrobial efficiency against both, *E.coli* and *S.aureus* (Fig.1, right). In both cases no Ag related cytotoxicity was found against fibroblasts and macrophage cells. Antimicrobial tests against a multi-resistant *S.aureus* strain are ongoing. Both types of silver-containing particles thus fulfil the requirements for the development of novel antibacterial nanocoatings on biomaterial surfaces. Currently we are developing strategies to link them to implant model surfaces of titanium or to incorporate them into polymer matrices.

[1] Feng Hu, Yan Zhang, Guangcun Chen, Chunyan Li, Qiangbin Wangu *small* **2015,** 11, 985-993.

Synthesis of $(FA/Cs)Pb(Br/I)_3$ Perovskite Nanocrystals with Controlled Emission Properties through Adaptive Sampling in a Microfluidic Reactor

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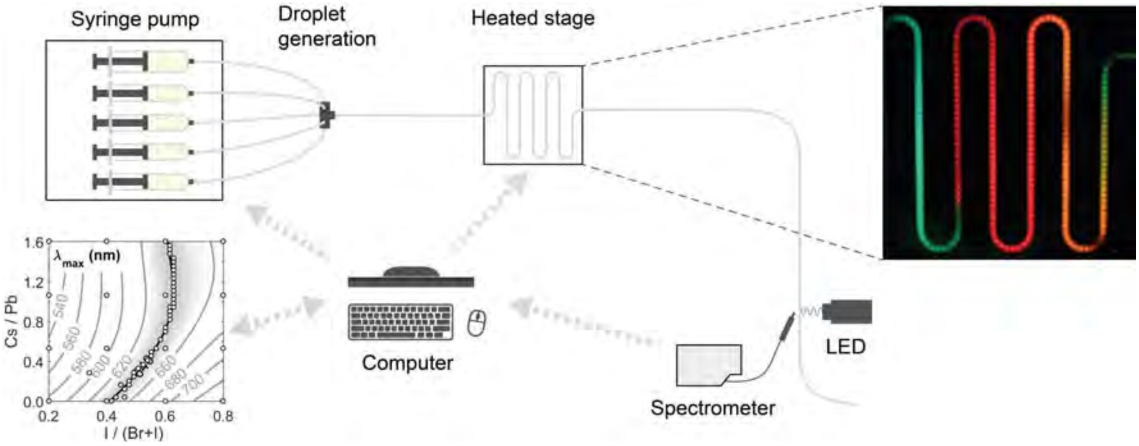
All-inorganic as well as mixed organic-inorganic metal halide perovskite nanocrystals possess attractive optoelectronic properties which make them promising targets for a wide range of applications. In particular, the development of these materials as emitters for next generation displays requires precisely controlled emission properties achieved through compositional tuning. We present a Kriging-based adaptive sampling algorithm in conjunction with an automated microfluidic reactor equipped with real-time fluorescence detection. This system allows us to rapidly identify compositions within the compositional parameter space resulting in pure-red emitting $(FA/Cs)Pb(Br/I)_3$ nanocrystals (FA = formamidinium). The algorithm iteratively computes optimal sampling points at each stage of the experiment to reach the target emission wavelength, based on spectroscopic measurements at previously visited experimental conditions. The procedure enables a statistical evaluation of reagent concentrations and temperatures yielding the desired emission wavelength in a rapid manner while using minute amounts of reagent and ensuring high reproducibility.



Formation of functionalizable DNA sheets via phenanthrene sticky ends

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In nanotechnology DNA is used to create one-, two-, or three-dimensional assemblies due to its unique molecular recognition properties which opens opportunities to precisely organize materials within those structures.[1] Combining DNA building blocks with other molecules can influence the structure and introduce other functionalities. Such functional supramolecular polymers have potential for biomedical, biomimetic and electronic applications.[2] In this contribution we show that complementary DNA strands with each three phosphate-linked dialkynyl-phenanthrenes at their 3'-ends form duplexes with amphiphilic overhangs. In presence of spermine, those overhangs act as sticky ends which link the duplexes in two dimensions. Supramolecular two-dimensional sheets with altering DNA and phenanthrene parts are formed. Fluorescence measurements show that the assembled phenanthrene units act as light harvesting antennae and transfer absorbed energy to an acceptor which is either directly added to the polymer or added attached to a complementary DNA strand. Those DNA architectures allow constructing and investigating light harvesting antennae with acceptors at defined distances to the donors. In addition, the DNA part opens other possibilities for functionalization.

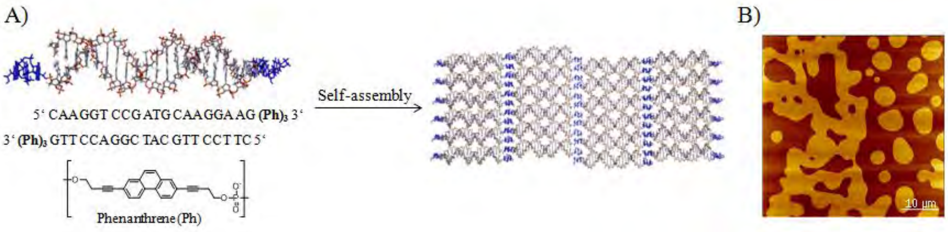

Figure 1: A) Structure and sequences of the duplex with phenanthrene overhangs and putative model of the self-assembly into two-dimensional sheets. B) AFM picture of supramolecular DNA sheets.

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Homoconjugation in Poly(Phenylene Methylene)s

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Poly(phenylene methylene) (PPM) exhibits pronounced blue fluorescence in solution as well as in solid-state (Fig. 1(a)), despite its non-conjugated nature along the backbone since the methylene groups interrupt π-conjugation between the phenylene groups. We extensively used optical spectroscopy to explore the characteristics of PPM, namely absorption between 350 nm and 450 nm with the corresponding photoluminescence in the 400-550 nm spectral region [1]. Given the evidence, π-stacking and aggregation, as well as the formation of fluorescent impurities, are excluded as the probable origins of the optical properties. Instead we have shown that its unexpected fluorescence originates in a phenomenon called homoconjugation, specifically the π-orbital overlap of adjacent phenylene groups across the non-conjugating methylene group mediated by particular chain conformations (cf. Fig. 1(d)) [2]. To further confirm the generality of the spectroscopic properties of PPM, two derivatives poly(2-methylphenylene methylene) and poly(2,4,6-trimethylphenylene methylene) were synthesized and found to exhibit comparable spectroscopic properties (Fig. 1(b-c)). Notably, PPM features a relatively high photoluminescence quantum efficiency (41%) and a substantially longer photoluminescence lifetime (>8 ns) in the solid state than other typically blue emitting conjugated polymers [3]. This first demonstration of fluorescent properties in macromolecules enabled by homoconjugation along the backbone opens new strategies for the design of next-generation light-emitting polymers.

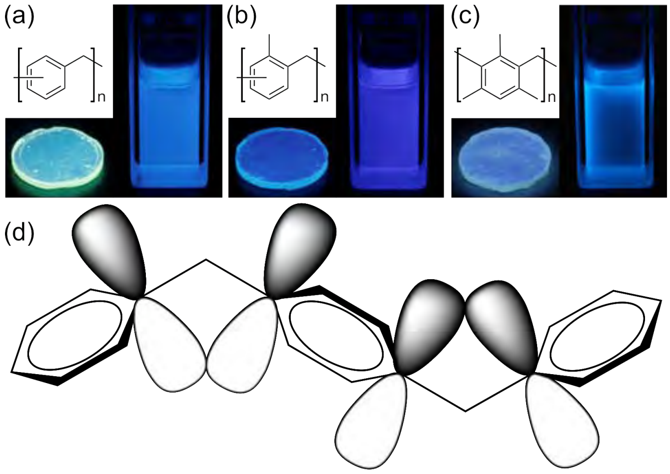

Fig. 1. Chemical structures and photographs taken under UV-light (~365 nm) illumination of polymer plaques and polymer solutions in chloroform of (a) poly(phenylene methylene), (b) poly(2-methylphenylene methylene) and (c) poly(2,4,6-trimethylphenylene methylene). (d) Schematic representation of homoconjugation via π-orbital interaction in a PPM chain segment.

[1] A. Braendle, A. Perevedentsev, N. J. Cheetham, P. N. Stavrinou, J. A. Schachner, N. C. Mösch-Zanetti, M. Niederberger, W. R. Caseri, *J. Polym. Sci. Part B Polym. Phys,* **2017**, 55, 707-720.
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Colloidal synthesis approach for energy conversion electrocatalysts

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Colloidal synthesis is a promising approach for the preparation of supported and unsupported catalysts. For electrocatalytic energy conversion the catalysts are predominantly precious metal based. In the presented work, we investigate colloidal Pt and Ir catalysts for oxygen reduction and oxygen evolution, respectively. In particular we investigate redispersion and stability of iridium nanoparticles (IR-NPs) synthesized by an established ethylene glycol (EG) route [1]. The particles are precipitated from the synthesis suspension by acidic washing in order to observe „surfactant-free“ NPs. After particle separation from the solvent by centrifugation the NPs can be redispersed in different solvents. Focusing on the stability of these colloidal systems we analyze the influence of the use of different acids for the washing step. Traditionally 1M HCl is used for this step, which however is a well-known catalyst poison inhibiting catalytic reactions and promoting metal dissolution. Stable colloid systems are essential for their further use to prepare electrode structures for example via spray coating.

[1] Yuan Wang, Jiawen Ren, Kai Deng, Linlin Gui, Youqi Tang, Preparation of Tractable Platinum, Rhodium, and Ruthenium Nanoclusters with Small Particle Size in Organic Media, *Chemistry of Materials,* **2000**, 12, 1622-1627.

Cryo 3D printed nanofiber based aerogels

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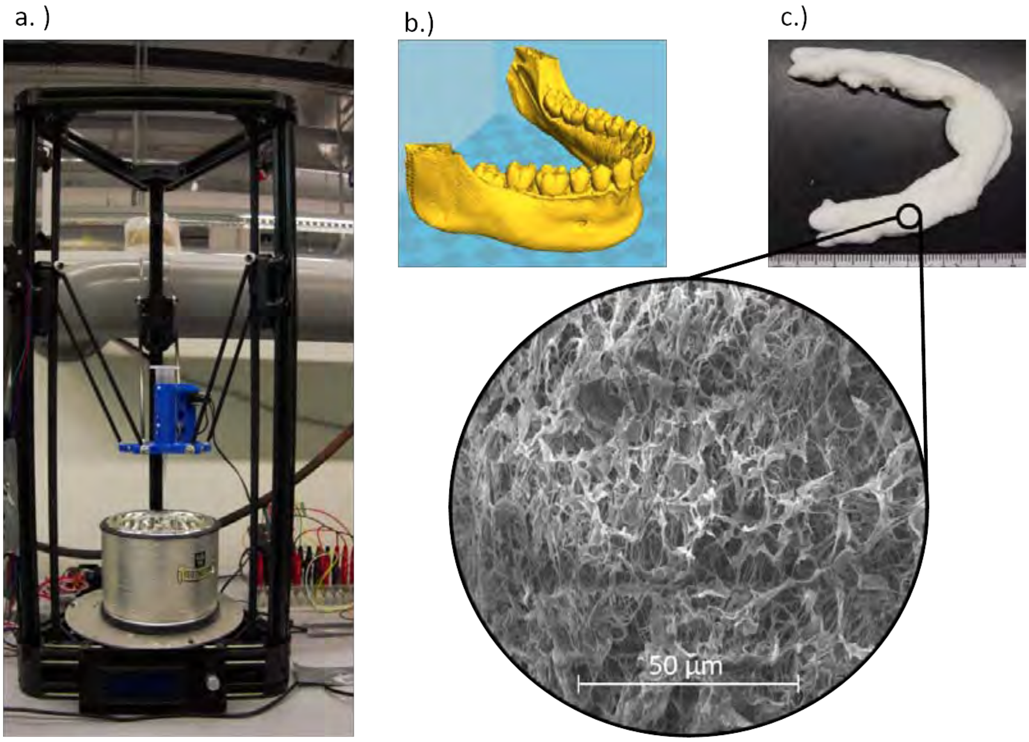
The preparation of 3D sponges or aerogels from electrospun nanofibers was recently reported [1].These freeze-casting based technologies allow the control of pore sizes and mechanical properties [2], but are restricted to casted geometries. We therefore developed a 3D printing platform for the preparation of nanofiber based aerogels. Polyacrylonitrile (PAN) nanofiber suspensions in water were used as printing material. Printing was done with a modified commercially available 3D printer (Afinibot, MicroDelta) which was equipped with a custom-made printing head hosting the suspending device. Here we describe the printing resolution, printing in 2D and the printing capabilities were described. Furthermore several cylindrical objects were printed and compared with their freeze-casted counterparts regarding mechanical properties and morphology. Moreover the influence of additives used in the printing process was investigated. For a future application as tissue scaffolds a model of a jawbone was successfully printed from a 3D model. Scanning Electron Microscopy confirmed porosity and nanostructure of the printed scaffold.



a.) Printing setup including the custom-made printing head. b.) 3D image of a jawbone to be partially printed. c.) Printed sample of a nanofiber aerogel jawbone with SEM image confirming individual nanofibers.

[1] Yang Si, Jianyong Yu Xiaomin Tang, Jianlong Ge Bin Ding, *Nature Communications*, **2014**, 5:5802

[2] Fabian Deuber, Sara Mousavi, Marco Hofer, Christian Adlhart, *Chemistry Select*, **2016**, 1, 5595–5598

DNA functionalized supramolecular nanosheets

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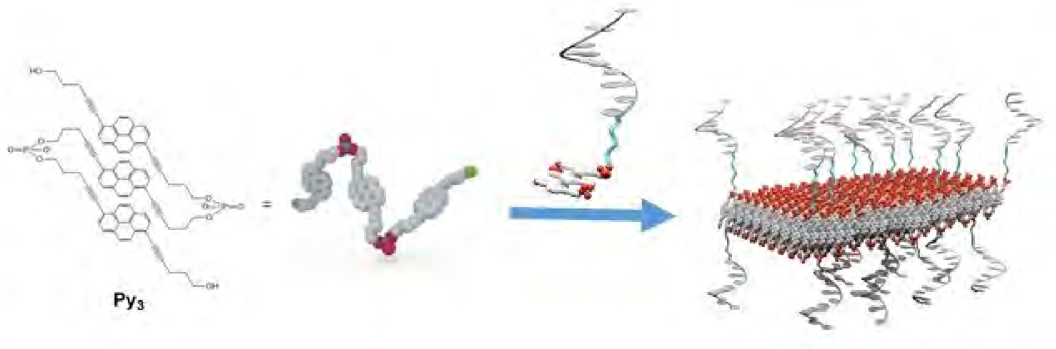
2D supramolecular polymers may find application as functional platforms. Previously it was shown that the phosphodiester-linked trimers of 1,6-dialkynyl-substituted pyrene **Py$_3$** self-assembled into supramolecular nanosheets in aqueous medium [1]. Here we doped the supramolecular nanosheets with pyrene DNA conjugates to functionalize the nanosheets. Further the functionalized nanosheets were hybridized with Au nanoparticles modified with the complementary DNA strand of the pyrene DNA conjugates. The two-dimensional supramolecular nanosheets were characterized by UV-vis spectroscopy and atomic-force microscopy (AFM).



[1] M. Vybornyi, A. V. Rudnev, S. M. Langenegger, T. Wandlowski, G. Calzaferri and R. Häner, *Angew. Chem. Int. Ed.*, **2013**, 52, 11488–11493.

Side-group modified high permittivity silicone elastomers for dielectric elastomer actuators

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The technology of dielectric elastomer actuators requires 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 based elastomers which are 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 and cyano-functionalized polymers. Thin elastic films were prepared by either using tin catalyzed condensation reactions with alkoxysilanes as cross-linker or photoinduced thiol-ene click reaction, respectively. Both approaches allowed preparation of silicones with well-balanced dielectric and mechanical properties. The thickness of the silicone films can be tuned from 100 microm to 20 microm using doctor blade techniques. Actuators show lateral actuation strains of more than 25% at an electric field of 24 V/microm and reached lifetimes of over 50.000 cycles (2Hz). The impact of thioether and cyano side groups on the elastic modulus and viscoelasticity, permittivity, conductivity, dielectric breakdown and actuation strain of the silicone films will be presented in detail.

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[2] P. Caspari, F. A. Nueesch, A. Neels, D. M. Opris, *RSC Adv.*, **2016**, *6*, 98059-98065

Investigating the extended hydration of a polyelectrolyte with second-harmonic scattering

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Natural polyelectrolytes form a key part of living tissue while synthetic ones find many industrial applications. However, the behavior of aqueous polyelectrolyte solutions is an ongoing question that relates to the function polyelectrolytes in their respective environments. We investigate the hydration of a naturally occurring polyelectrolyte – hyaluronan (HA), using angle-resolved femtosecond elastic second-harmonic scattering. Our measurements show that the structure of water in a solution of HA is altered in a specific manner compared to the structure of pure water or salt water. Hyaluronan chains are hydrated by a shell of water extending up to hundreds of nanometers. Further investigation of the effect also reveals an increase in water-water orientational correlations in the bulk - the hydrogen bond network of water is becoming stiffer. The effect of HA on the bulk water differs by an order of magnitude between H2O and D2O due to a difference in the H-bonding capacities of the two isotopes of water. The sensitivity of second-harmonic scattering to polyelectrolyte hydration offers new insight into the complex behavior of polyelectrolyte solutions. Our observations support the generally accepted idea that polyelectrolytes are well hydrated due to the presence of ionized functional groups. The measurements further show that polyelectrolytes have a longer-range effect on the bulk water than was previously hypothesized.

Direct access to primary amines and particle morphology control in nanoporous CO_2 sorbents

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Chemical tuning of nanoporous, solid sorbents for an ideal CO_2 binding requires unhindered amine functional groups on the pore walls. Although common for soluble organics, post-synthetic reduction of nitriles in porous networks often fail due to the insufficient and irreversible metal hydride penetration. Here, we synthesized a nanoporous network with pendant nitrile groups, microsphere morphology and in large scale. The hollow microspheres were easily decorated with primary amines through in situ reduction by widely available boranes. CO_2 capture capacity of the modified sorbent was increased up to four times of the starting nanoporous network with a high heat of adsorption (98 kJ/mol). Surface area can be easily tuned between 1 and 354 m^2/g. Average particle size (~50 µm) is also quite suitable for CO_2 capture applications where processes like fluidized bed require spheres of micron sizes.

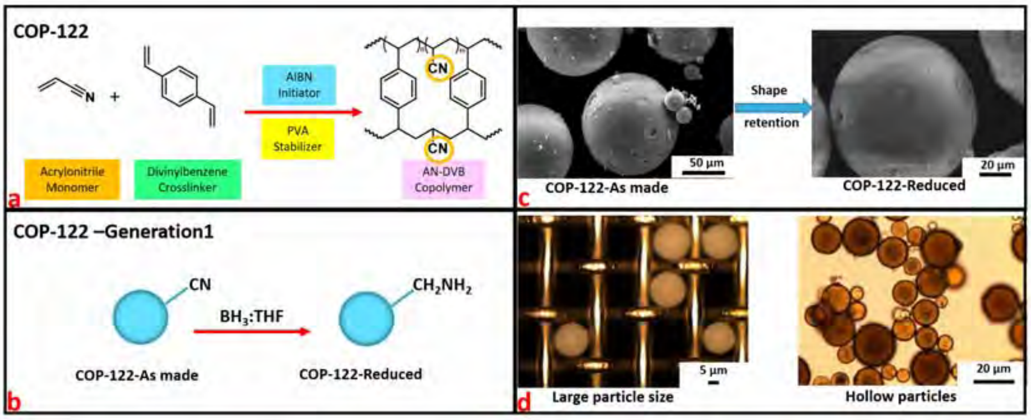

Figure 1. (a) Synthesis of acrylonitrile-divinylbenzene copolymer (COP-122) by suspension polymerization. The resulting nanoporous network polymer has the shape of spherical beads with dangling -CN groups spread out inside each polymer particle (b) Synthetic pathway to reduce nitrile groups on COP-122. After reduction, amine groups are obtained on polymer surface and inside the pores (named as COP-122-Generation1). (c) SEM picture of a single polymer particle surrounded by other particles. Morphology of COP-122-Generation1 is retained after reduction. (d) Optical microscope image of COP-122 particles. Large particle size of COP-122 makes it suitable for industrial applications.

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Biomimetic engineering of stimuli responsive artificial cell organelle membranes

T. Einfalt[1], D. Witzigmann[1], A. Najer[1], S. Sieber[1], R. Goers[1], C. G. Palivan[2]*, J. Huwyler[1]*

[1]University Basel, [2]University of Basel

Recent advances in engineering of robust polymeric compartment spaces with catalytic activity have led to the development of the first polymersome based artificial cell organelle[1]. However, several challenges still remain when mimicking the nature of organelles, such as the development of compartmentalized reaction spaces capable of interacting with the dynamic intracellular environment. In this respect systems more comparable to biological cell membranes ideally present triggered activity, whilst preserving the nanocompartment architecture of the system[2]. We present here a new type of artificial cell organelle, which is based on PMOXA-*b*-PDMS-*b*-PMOXA polymersomes, whose synthetic membranes are equipped with chemically modified channel proteins, in a stimuli responsive manner. Outer membrane protein F, previously used for the development of the first artificial peroxisome[1,3], was chemically modified with a stimuli responsive molecular cap in order to serve as a reduction responsive molecular "gate". After extensive structural characterization and confirming the ability of the system to act in a stimuli responsive manner was confirmed *in vitro* functional *in vivo* assays preformed on Hela cells show the successful enzymatic regulation and activity *in vivo* for up to 48h, whilst preserving synthetic organelle architecture.

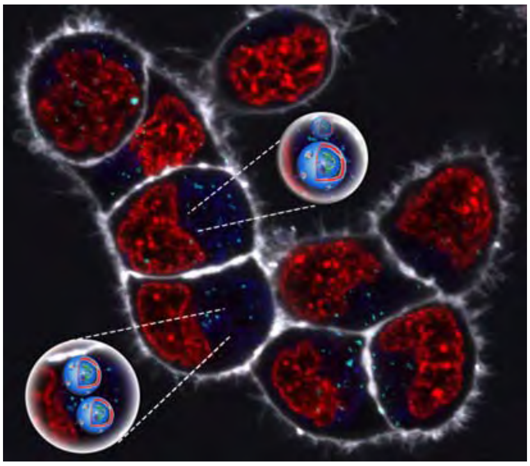

Fig. 1: Schematic representation of life-like stimuli responsive artificial cell organelle activity.

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Biopolymer-silica aerogel nanocomposites with improved thermo-mechanical properties

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Silica aerogel is an outstanding thermal insulator, but it’s brittle and rather dusty nature restricts the applications[1] [2]. Here, we report on monolithic, lightweight and nanostructured superinsulating aerogel nanocomposites that are reinforced by cogelation with biopolymers. Polysaccharides (pectin and chitosan) are dissolved into an aqueous silicic acid solution, followed by co-gelation, polymer coagulation, hydrophobization and supercritical drying. The morphology and properties of the resulting materials can be tuned by adjusting the gelation pH and biopolymer concentration. The specific surface area, porosity, microstructural and mechanical properties, as well as thermal conductivity and humidity uptake were systematically evaluated. Aerogel nanocomposites made at low acidic pH (~1.5 for pectin and ~3 for chitosan) exhibit a high plastic deformation region with no rupture until at least 80% strain, in addition to a greatly increased yield strength (2-27 MPa versus 1 MPa for silica aerogels) and compressive modulus (up to 9.0 MPa). Importantly, the reinforcement does not significantly increase the density (ρ=0.11-0.18 g/cm^3) and thermal conductivity (λ=14.2-18.3 mW·m^{-1}·K^{-1})[3]. The changes of thermo-mechanical properties are linked to a ‘neck-free’ nanoscale network structure with thicker struts compared to the classical pearl-necklace structure of silica aerogels. This new class of biopolymer-silica nanocomposite aerogels opens up new perspectives for a wide range of thermal insulation, sorption, catalysis and other applications, where structural integrity is indispensable.

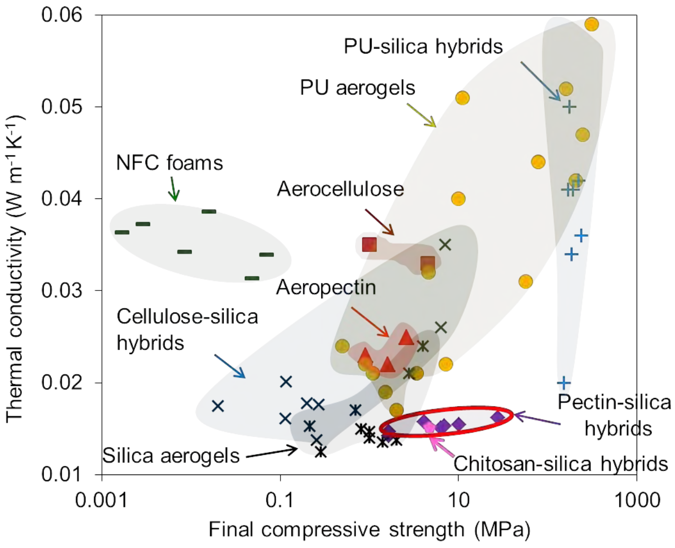

Figure 1. Thermal conductivity versus final compressive strength for aerogel-like materials. [3]

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The effect of hard phase crystallization on the microphase segregation of supramolecular polymers

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Supramolecular polymers (SPs) are macromolecular assemblies of monomeric units, which are connected by reversible and directional non-covalent interactions such as H-bonding, metal-ligand complexation and π-π stacking.[1] SPs are typically synthesized via the functionalization of telechelic oligomers with supramolecular units (e.g. hydrogen bonding groups) at the chain ends. The assembly of the resulting macromonomers through chain-end interactions affords supramolecular polymers with apparent molecular weights that are dictated by the corresponding association constant. Chain-extension is often accompanied by microphase segregation into two phases that are formed by the supramolecular motifs and the telechelic cores, respectively. In many cases the latter displays a low glass transition temperature, whereas the former constitutes a crystalline hard phase that provides physical cross-links. As a result, such SPs display elastomer-like properties. While the mechanical properties of such phase segregated SPs are well established, the role of the crystalline phase on their microstructure is less well investigated.
A new class of phase segregated SPs based on the isophthalic acid-pyridine (IPA-Py) H-bonding motif was recently reported.[2] These SPs are synthesized by mixing two components, a telechelic poly(ethylene-*co*-butylene) terminated with isophthalic acid units and a bipyridine (Figure 1). In these SPs, the hard phase is formed by the crystallization of the IPA-Py motifs, and the properties of the hard phase can be controlled by simple variation of the bipyridine component. In this contribution we report the results of an experimental study in which the influence of the hard phase's composition on the microstructure of IPA-Py-based SPs was explored. Through the combination of small angle X-ray scattering (SAXS), electron microscopy (TEM), thermal and thermomechanical analyses, we discovered that very subtle changes in the hard phase composition can cause considerable changes of the SPs' morphology. Temperature-dependent SAXS studies revealed that most of these SPs feature a hexagonal microstructure arrangement above the melting temperature of the hard phase. However, when cooled from the melt, the observed mesophase is either retained or lost, depending on the nature of the bipyridine component. The results show strikingly that the crystalline structure of the hard phase has a strong influence on the phase behaviour of nanophase-segregated SPs.

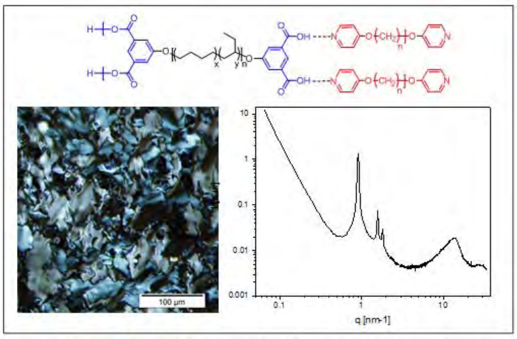

Figure 1. General chemical structure of IPA-Py based supramolecular polymers (top), POM micrograph (bottom left) and SAXS-WAXS spectrum (bottom right) of a phase-segragated SP with hexagonal microstructure arrangement .

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Characterization of nanomotors behaviour by Fluorescence Correlation Spectroscopy

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[1]University of Fribourg, [2]Scuola Normale Superiore di Pisa, [3]Center for Nanotechnology Innovation, Pisa

Lots of effort has been recently devoted to the synthesis and characterization of self-propelling nanoparticles, also called nanomotors. These peculiar types of nanoparticles are able to self-propel in solution when in the presence of a so-called “fuel”. Depending on the type of nanomotors, the fuel can by an acid, a base or hydrogen peroxide, among others.

We developed a new method to synthesis nanomotors based on polystyrene dumbbell-shaped nanoparticles. Upon proper functionalization with platinum nanocrystals acting as catalysts for the decomposition of hydrogen peroxide, we have been able to synthesis relatively large amounts of nanomotors. However, characterization of their self-propelling behavior is complicated, as they are too small to be directly observed by standard optical microscopy techniques. We recently started collaboration with scientists having expertise with Fluorescence Correlation spectroscopy, which proved to be a powerful method to describe the motion of nanoparticles. The first results clearly indicate that the motion of the nanomotors is a normal Brownian diffusion when they are placed in water, but when the hydrogen peroxide fuel is added, the behavior changes to super diffusion, which is a clear proof that the nanomotors are self-propelling.

Discussion about the synthetic pathways used to prepare nanomotors will be presented, together with a presentation of the Line Fluorescence Correlation spectroscopy method and the associated results.

IL@PZS Nanocomposites as Catalysts for CO_2 Conversion

Z. J. Huang[1,2], Z. F. Fei[1], Q. H. Lu[2]*, P. J. Dyson[1]*

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Cyclomatrix polyphosphazenes (PZS) can be readily synthesized through precipitation polymerization,[1] and serves as a host of nanocomposites due to their large pores and electron-rich environment.[2] Ionic liquids (ILs) are composed of ion pairs of which the anion catalyzes the cycloaddition reaction of carbon dioxide (CO_2) with epoxides.[3] CO_2 is an abundant and renewable C1 building block for the synthesis of value-added carbonates/polycarbonates.[4] Herein, we developed IL and PZS nanocomposites (IL@PZS) and applied them for CO_2 conversion.

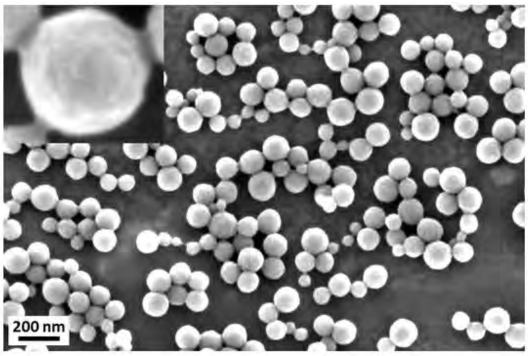

Figure 1. SEM of PZS nanophseres.

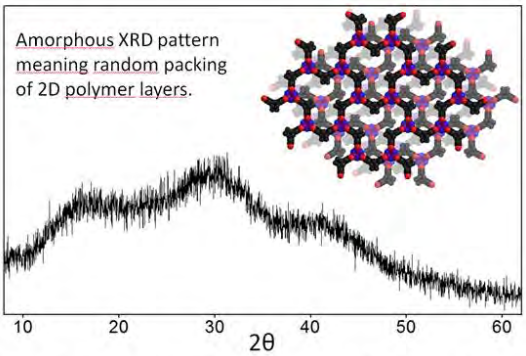

Figure 2. Powder X-ray diffraction of PZS nanophseres.

The yields of styrene carbonate are dramatically increased compared to that using only ILs as catalysts. The catalytic activity of the IL@PZS nanocomposites depends on structure matchability between the ILs and the PZS.

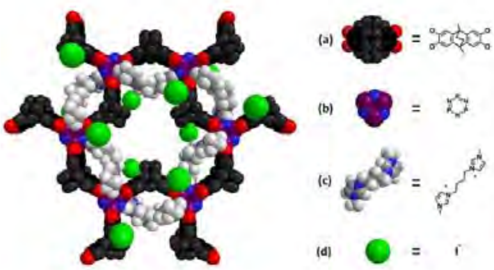

Figure 3. A typical IL@PZS nanocomposite.

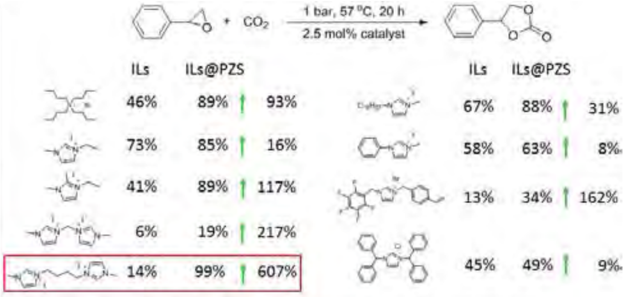

Figure 4. Catalysis comparison for CO2 conversion.

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All-Atom Models of Tobermorite 11 Å and 14 Å – Benchmarks for Realistic Modelling of C-S-H

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Calcium silicate hydrate is the main binding phase in cementitious materials. Its accurate atomic-scale models and force fields are crucial in the development of a greener construction industry. Tobermorite 11 Å and 14 Å minerals are known to be the closest crystalline structural analogs for calcium silicate hydrate (C-S-H). Therefore, dependable tobermorite models can serve as a benchmark for C-S-H, which exhibits complex poorly crystalline structures and variable surface chemistry at solid-liquid interfaces and for which nanoscale details are difficult to obtain from experiments. The Interface force field describes models that reproduce covalent versus ionic bonding and surface properties in agreement with experiment in contrast to other models. A new version of tobermorite parameters with extensive validation is presented in this study. Atomic charges of calcium ions of 1.5e in the intra-layer region and 1.7e in the partially hydrated inter-layer region were found to best describe chemical bonding. The lattice parameters of both minerals deviate less than 0.5% on average from X-ray data. The surface energy of tobermorite 14 Å (405 ± 10 mJ/m^2 least for 001 facet) agrees with available experimental measurements for C-S-H ($Ca_3Si_2O_7 \cdot 2H_2O$) of 386 ± 20 mJ/m^2, whereas other models lead to deviations over 50%. The computed bulk moduli of tobermorite 11 Å and 14 Å are 71 ± 2 GPa and 45 ± 1 GPa, respectively, matching experiment within the uncertainty. Parameters developed using the INTERFACE approach (IFF) are consistent with other important cement phases such as CH, C_3S, C_3A, CaO, water, and polymers. This platform is therefore helpful in defining full scale atomistic models of C-S-H multiphase mixtures with local and global morphologies. Brief applications to understand conformations and working mechanisms of polycarboxylate ether superplasticizers in comparison to experiment are demonstrated using these models.

Multilayered Vesicles Formed by Polyaromatic Oligoamines

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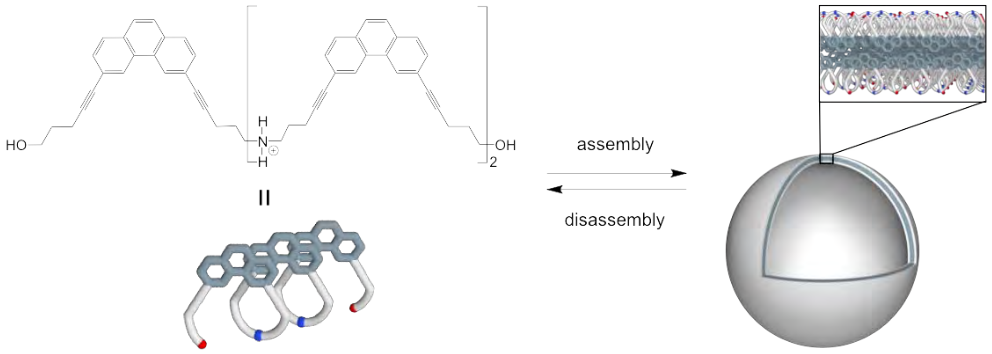
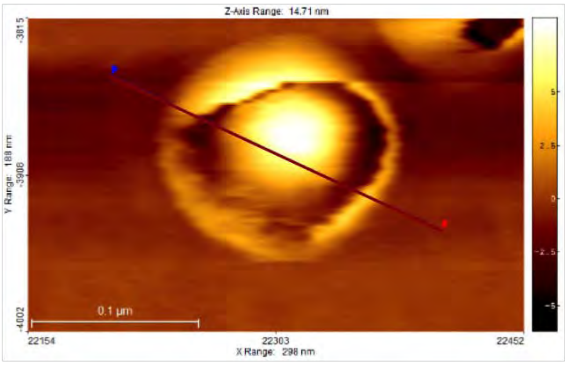
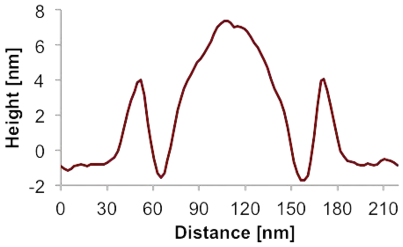
[1]University of Bern

Supramolecular phenanthrene polymers with a negative charged phosphate backbone have been synthesized in our group.[1,2] These assembled oligomers can act as light harvesting antennas. Herein we replaced the negative charged phosphate backbone by a positive charged amine one and analyzed the aggregation behavior and light harvesting properties. The self-assembly of 1,8-disubstituted amine-linked phenanthrene trimers in aqueous solution formed mono- and even multilayered vesicles based on atomic-force microscopy. The incorporation of pyrene into the vesicles allows an investigation of light harvesting properties.







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On the “soft template” effect of an enzymatic oligomerization reaction

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The oxidation of the aniline dimer, *p*-aminodiphenylamine (PADPA), with *Trametes versicolor* laccase and molecular oxygen was studied in aqueous solution at pH = 3.5. Depending on the experimental conditions used, oligomeric products are obtained, which originate from enzymatic as well as non-enzymatic follow-up reactions. The presence of dispersed anionic interfaces – also called “templates”– in the reaction mixture can have a significant and positive effect on the course of the reaction as with such templates products can be obtained which resemble the conductive emeraldine salt form of polyaniline (PANI-ES) [1-3]. Without templates, these products do not form. The effect of three different templates under their respective optimal conditions was investigated and compared in a systematic way by using UV/vis/NIR, EPR and Raman spectroscopy measurements, as well as an HPLC-MS analysis. The templates used were sulfonated polystyrene (SPS), micelles from sodium dodecylbenzenesulfonate (SDBS) – previously used by Shumakovich *et al.* [4] – and vesicles from sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Although all three templates carry a sulfonate group and yield PANI-ES-type products, there are clear differences in the properties of the product mixtures obtained. Reasons for these differences are discussed.

Acknowledgments: We thank Louis Bertschi, MS Service Lab, LOC, ETHZ for his support in the ESI – MS measurements and Reinhard Kissner, LAC, ETHZ for his support in the stopped-flow measurements. SNF project numbers: 200020_150254 and IZ73ZO_152457. The second author received financial support for this study from the Japan Public-Private Partnership Student Study Abroad Program (TOBITATE!).

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Increasing the Energy Transfer Efficiency of DNA-Photonic Wires with Light-Harvesting Supramolecular Polymers

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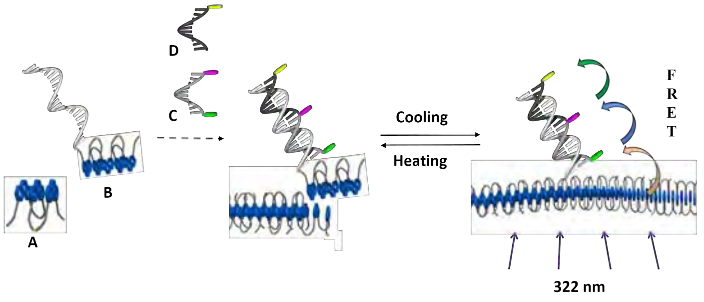
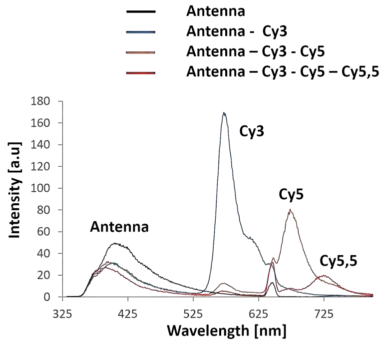
[1]University of Bern

Design of artificial light-harvesting platforms functionalized with DNA-grafted photonic wires is under great interests for designing new nanomaterials and nanodevices [1]. However there are very few DNA-bioinspired materials for the construction of multi-step FRET cascades simultaneously attached to functional light-harvesting platform. In natural light-harvesting systems the energy is absorbed by an assembly of molecules and transferred via Förster resonance energy transfer (FRET) to reaction centres where the absorption is amplified [2]. Scaffolding DNA properties as well as control over fluorophore positioning allows the creation of artificial photonic wire. Herein we demonstrate integration of such DNA-based photonic structures with supramolecular polymers for extending light-harvesting and enhancing directional FRET properties. We have recently reported supramolecular polymers (SPs) consisting of a phosphodiester-linked phenanthrene core as linear individual fibers or nanotubes [3,4]. Presented here SPs-DNA-grafted photonic wires with arranged up to 3 fluorophores along the DNA scaffold is a next step in increasing efficiency of FRET process upon phenanthrene excitation with broad potential in nanotechnology.

Assembly of phenanthrene oligomer **A** doped with 1.8 mol% of oligomer **B** composed of DNA strand (20 nucleotides) and 5`-end attached phenanthrene units yields in supramolecular light-harvesting platform upon heating-cooling process. SPs - photonic wire polymer is assemble via hybridization of DNA fragments labeled with a series of donor-acceptor cyanine dyes (**C**, **D**). Our spectroscopic studies clearly show that each addition of increasingly red-shifted dye significantly induces the consecutive quenching of the fluorescence of the previous donor-acceptor dye (Cy3, Cy5). Energy Transfer Efficiency is investigated by programing series of photonic wire configurations.





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Low Temperature Wet Conformal Metal Silicide Deposition for Transistor Technology through an Organometallic Approach

T. Lin[1], T. Margossian[1], M. De Marchi[2], M. Thammasack[2], S. Kumar[1], C. Shih[1], G. De Micheli[2], D. Baudouin[1], P. Gaillardon[3], C. Serba[1]*

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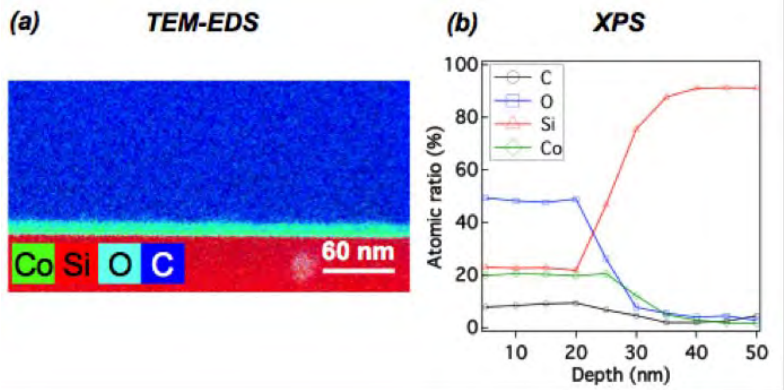
The formation of metal silicides, which are indispensable materials involved in the fabrication of all field effect transistors to reduce the contact resistance of the source and drain regions, has been identified as one of the most critical steps in current fabrication process flows. Among all the existing metal silicides, cobalt silicide ($CoSi_x$) has advantages for its low resistivity, its material compatibility, and its good stability[1]. However, the transition towards devices using advanced 3D geometries makes it challenging to form homogeneous silicides using classical silicidation processes based on sputtering. Therefore, a one-pot wet chemical approach[2] has been proposed to synthesize the metal silicide layer onto silicon wafer, exhibiting applicable electric properties and allowing a homogenous coverage of 3D-structure device.

A 20-nm Co-rich layer on Si (100) wafer was observed by electron microscopy (STEM-EDS), a layer that according to preliminary XAS results on the Si(0) model indicated to be $CoSi_x$. XPS spectroscopy showed a small amount of carbon contamination, which is similar to what is found for the pristine Si wafer (< 9%, Figure 1). Then, high temperature vacuum-treatment (~10^{-5} mbar) leads to layer having conductive behavior (Ohmic behavior) with a lower resistivity (ρ=116 μΩ.cm) measured by 4-point probe measurement confirming the presence of Cobalt silicide. In addition to forming the silicide layer onto the flat Si (100) surface, the method was applied to 3D-patterned wafers, in which the TEM results showed that a promising step coverage ratio could be obtained. This work shows that the homogeneous $CoSi_x$ layer can be deposited via wet organometallic approach at ambient temperature and that, after thermal vacuum-treatment, it exhibits an Ohmic behavior with a low resistivity, thus creating an alternative possibility for modern 3D-transistor fabrication.



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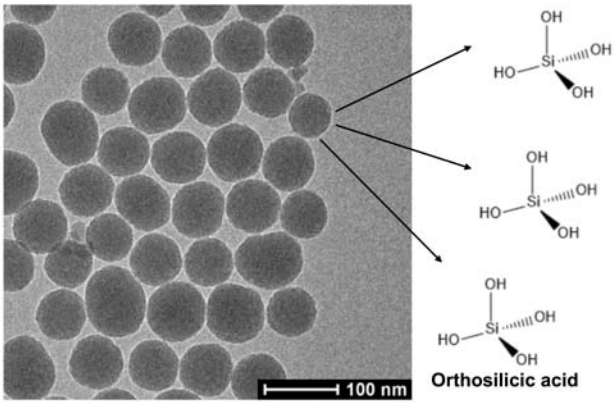
Multidisciplinary Method Development to Characterize and Quantify SiO_2 Nanoparticle Degradation in Complex Matrices

M. Maceroni[1,2], D. Bossert[1,2], L. Rodriguez-Lorenzo[1,2], D. A. Urban[1,2], A. Petri-Fink[1,2], B. Rothen-Rutishauser[1,2], F. Schwab[1,2]*

[1]Adolphe Merkle Institute, [2]University of Fribourg

Silica nanoparticles (SiO_2-NPs) and in general siliceous nanomaterials are used in a broad range of commercial products including foodstuffs and cosmetics. Recent research explores the use of SiO_2-NPs as a delivery vehicle for molecules in plants[1], which could be interesting for nano-agrochemicals, under the reservation that such SiO_2 nanomaterials degrade easily[2]. Fundamental knowledge for the development of such agricultural applications is needed to understand the SiO_2-NP behavior in the presence of plants and soil. Different parameters can influence the SiO_2-NP dissolution in aqueous solutions, or the degradation in biological/environmental media. Particle shape and size, degree of aggregation, porosity, pores size, morphology, and surface functionalization as well as mucilage and exudates of organisms can govern the dissolution/degradation rates [3]. We will present initial results of an experimental interdisciplinary approach to characterize and quantify the differential dissolution of SiO_2 NPs in media with increasing complexity, from simple aqueous solution to the highly complex soil matrix.



METHOD DEVELOPMENT:

- **Si concentration**
- **Particle size and morphology**
- **Suspension stability and surface charge**

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Magnetically controlled structure of silica monoliths for increased mechanical properties

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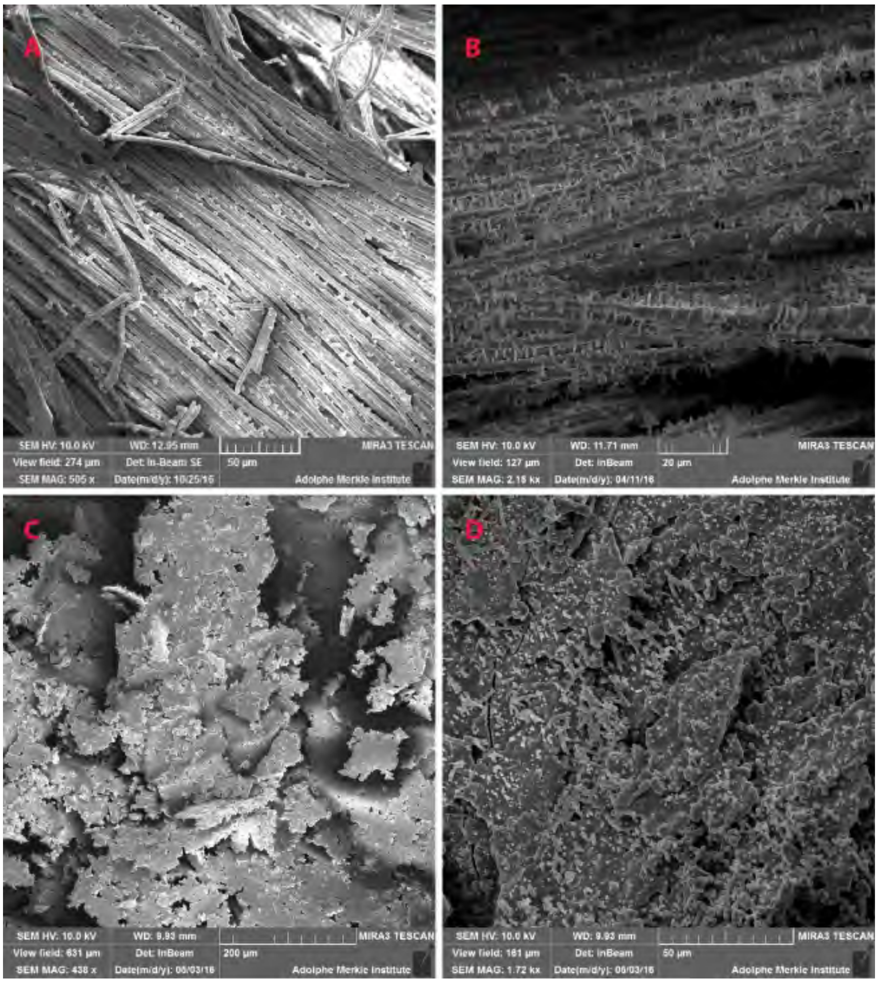
[1]University of Fribourg

The use of nanoparticles to control the structure of materials is not a new idea, but most of the time their self-assembly leads to isotropic constructs. In this work, superparamagnetic nanoparticles have been used to magnetically control the structure of monolithic silica blocks. Due to their superparamagnetic behaviour, anisotropic structures can be synthesised. Monolithic silica gels with well-defined network structure have been synthesised via a sol-gel process, where superparamagnetic nanoparticles were added to the sol solution. The superparamagnetic nanoparticles, when submitted to an external magnetic field created by an electromagnet or a permanent magnet, align along the field direction. The aligned nanoparticles dictate the structure of the gel by acting as smart templates for structure control. Silica, having high affinity for the magnetite particles, will nucleate on the top of the magnetic particles completely covering them, and gelation will fix the structure permanently. A second magnetically controlled sol-gel step can be performed by impregnation of dry monolithic blocks with a sol solution, leading to a new dimension of controlled structure. Furthermore, a composite material containing a rubbery polymer will be formed out of the structure-controlled silica monoliths. We investigated the mechanical properties of the different monolithic blocks to gain a better understanding of the structure-properties relationship.



Porous, ultralight 3D tubular scaffolds from short electrospun nanofibers

M. Merk[1], C. Adlhart[1]

[1]Zürich University of Applied Sciences (ZHAW)

Tubular organs are ubiquitously found within the human body and include blood vessel, trachea gastrointestinal tract and urinary tract. These complex tubular tissues are composed of different types of cells, extracellular matrix and proteins but share the functional purpose of transporting complex nutrients in liquid or solid form. Using active contractions of muscles placed around the organ and specific cells within the lumen, transportation requires the underlining scaffold to be adaptable to various conditions. Repair and regeneration of these tubular organs is of great interest due to the high amount of surgeries performed annually. However, the design and fabrication of synthetic scaffolds that mimic the mechanical and structural characteristics of their natural counterparts appears more difficult than expected. Here, we show the construction and comparison of different tubular structures fabricated via the combination of two-dimensional (2D) electrospinning and the freeze-casting method.[1] Together these techniques allow us to create 3D tubular scaffolds with high open porosity and adaptable mechanical properties depending upon the polymer used.

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Selective Modification of Snowman type Janus nanoparticles with Polypyrrole

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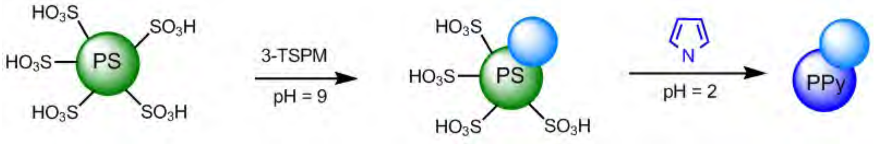
[1]Zurich University of Applied Sciences

Nanoparticles of conjugated polymers such as polypyrrole (Ppy), Poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) show many attractive features in a wide range of applications, ranging from optoelectronic to electrochemical devices.[1],[2] Homogeneous or core-shell nanoparticles of the mentioned conductive polymers have been synthesized in order to improve their processability. On the other hand Janus nanoparticles (JNPs) have received considerable attention because of their amphiphilicity, stemming from a polarity contrast between two or more surface regions. Unlike molecular surfactants JNPs can additionally carry bulk-like optical, electronic or magnetic properties. For example multifunctional JNPs that can be both amphiphilic and conductive could find use in a plethora of new applications, such as conductive inks. In this work we demonstrate that it is possible to combine such properties and obtain multifunctional amphiphilic and conductive JNPs by selective modification of only one lobe with PPy.

The JNPs were obtained starting from polystyrene (PS) seed nanoparticles (NPs) on which grew Janus lobes of different sizes via seed polymerization and phase separation of the 3-(triethoxysilyl)propyl-methacrylate (3-TSPM) monomer.[3] The selective modification of the JNPs was achieved in two steps, first selective interaction attraction of pyrrole monomer into the PS lobe followed by diffusion–interfacial polymerization resulting in the formation of a core-shell structure, see Figure. By increasing the size of the P(3-TSPM) lobe with respect to the PPy/PS lobe we were able to tune the conductivity of the powder material by an order of magnitude from 10^{-4} to 10^{-5} S cm^{-1} while in the same time there is a six-fold increase in the polarity of the material. We have therefore demonstrated the possibility to obtain new multifunctional materials by selective modification of Janus lobes.



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Removing cationic dyes from wastewaters using 3 Dimentional bio- based nanofiber aerogel

S. Mousavi[1], C. Adlhart[1]*

[1]Zurich University of Applied Sciences (ZHAW)

Nowadays, the chemical contamination of water from a wide range of chemical derivatives makes serious environmental issues. Synthetic dyes as one of the widely- used group of chemicals in various kinds of textile, paper, cosmetics and printing industries possess a significant source of pollution. Due to the high amount of color discharge in wastewater, their UV and temperature stability together with their inhibiting effects on photosynthetic activities, dye removing is essential.

Adsorption as a cost effective, easy and flexible method without any new toxic by- products is one of the best dye removing method. To overcome the difficulties such as following adsorbent separation processes beside the low efficiency of adsorbents, new promising electrospun nanofiber membranes are introduced.

Although electrospun nanofiber membranes have outstanding properties such as huge specific surface area, tailored surface functionality and fiber uniformity, they are still facing challenges such as low mechanical stability as well as unfavorable mass transport properties.

The new synthesized robust 3D aerogel, produced from short electrospun nanofiber dispersion using freeze casting method and crosslinking, has outstanding properties such as high porosity, mechanical stability, and flexibility as well as low density. The pore size of the sponge is tunable [1] and control of surface chemistry and surface properties is possible according to our previous works [2].

In this study, the pullulan based super elastic and environmentally friendly aerogel is used as a highly efficient dye adsorbent with outstanding regenerability. Effects of different parameters on batch and continuous experiments have been investigated. The adsorption process follow the Longmuir isotherm and pseudo second order kinetics is the best fit model.

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Improving the properties of alginate-based hydrogels by functionalization with bioactive ingredients

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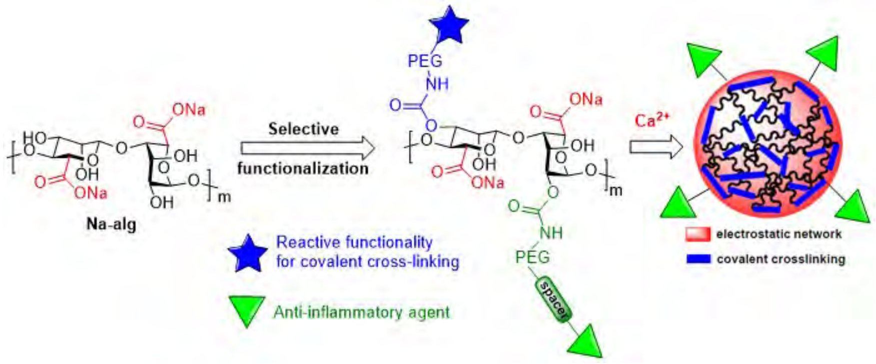
The progress of medical therapies relying on the transplantation of immobilized cells relies on both the quality of cells and the properties of the encapsulation materials. Such material has to be biocompatible, its physical characteristics have to be adjustable, and the microencapsulation process should be simple to avoid any damages to the cells. The biopolymer sodium alginate (Na-alg) presents several favorable properties for cell transplantation applications.[1] However, long term *in vivo* durability and selective permeability of alginate-based microspheres are still not optimal.[2]

The strategy that we developed to improve the performance of alginate-based hydrogels relies on the combination with other polymers such as poly(ethylene glycol) (PEG) to produce microspheres by ionotropic gelation and further reinforcement by covalent cross-linking.[2-6] Following this concept, additional bioactive ingredients can be conjugated to the hydrogel matrix to reduce inflammation response and fibrotic overgrowth which are commonly observed after transplantation, leading to cell asphyxia.[7] We report herein synthetic pathways for the functionalization of the polymeric components involved in hydrogel formation allowing conjugation of anti-inflammatory agents at the surface of the resulting microspheres for controlled release around the transplantation site. Depending on the chemical linkage envisaged for the conjugation process, different time scales for local delivery are expected.



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High permittivity thin elastomer films for low voltage actuators

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Stretchable capacitors are capable of converting electrical energy into mechanical work, however, high driving voltages are required. Reducing the thickness and increasing the dielectric permittivity of the dielectric elastomer allows reducing the driving voltage. The dielectric permittivity of an elastomer can be increased by chemical modification with polar groups. Using this approach, we have recently prepared novel polysiloxane based elastomers with a permittivity as high as 18 and excellent mechanical properties.[1] Actuators constructed with them show about 20.5% lateral strain at an electric field as low as 10.8 V/mm. Despite of this progress achieved, it turned out to be challenging to process the material into sufficiently thin films.[2] To overcome this problem, we modified first a polymethylvinylsiloxane of a high molar mass with 3-mercaptopropionitrile while leaving some vinyl groups unreacted. The resulting polymer was subsequently cross-linked in thin films whereby the vinyl groups were used. This was achieved *via* a thiol-ene reaction, but because a low volatility multifunctional cross-linker was used, the processing in thin films can be conducted using conventional techniques in any lab equipped with hoods. This allowed us to process films with a thickness below 20 microm. No further attempts were conducted to reduce thickness even more, however, processing films thinner than 5-10 microm is challenging. A lateral actuation of about 7% was measured at 300 V with a 35 microm thick film. Additionally, the actuators were able to self-repair after a breakdown which led to improved device lifetimes and increased reliability.

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Design of stimuli-responsive surfaces through layer-by-layer assembly for biomedical application

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The design of extracellular matrix (ECM) mimics is a challenging task in tissue engineering and related fields owing to its complexity in terms of structure and biochemical signaling.[1] Indeed, ECM is a dynamic and physiologically active matrix which response to physicochemical and biochemical changes of the surrounding environment. It exhibits a complex organization (both at micro and nano scales) that provides a mechanical support and insures communications between cells.[2] The synthesis of ECM bioinspired three dimensional structures may thus be relevant to create functional interfaces which are able to response to changes in the media (pH, T, I, etc). In this regard, we target to synthesize smart nanotubes using layer-by-layer (LbL) assembly and create an interface that mimic the 3D organization of ECM.

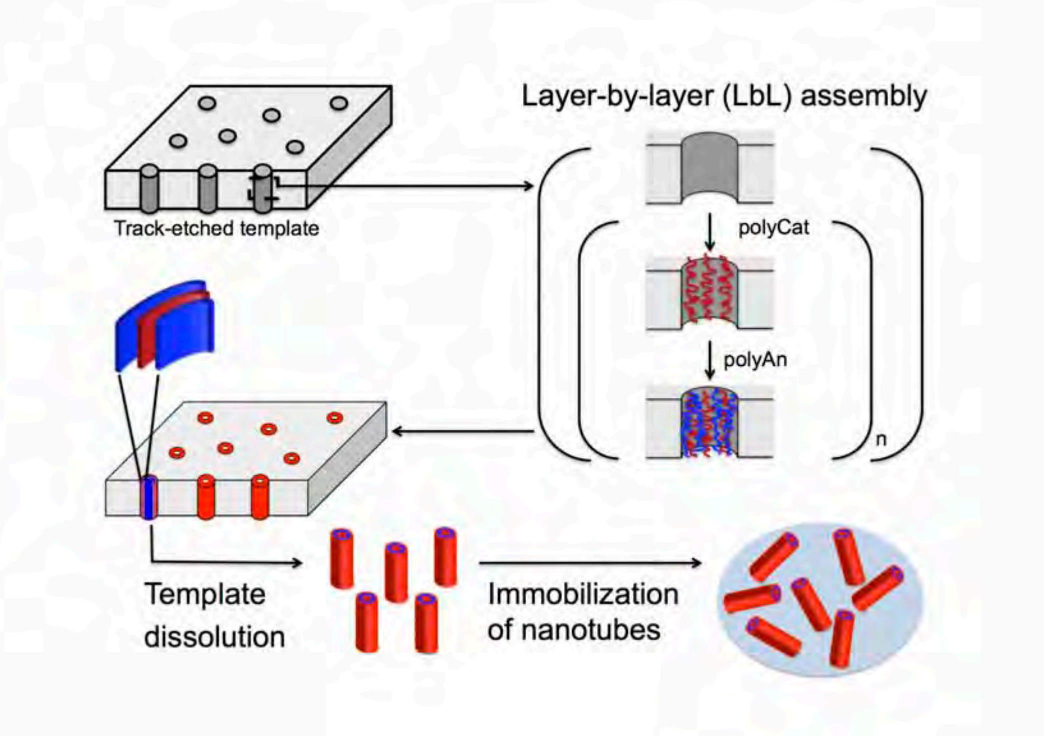

Figure 1. Combination of nanotempates and layer-by-layer assembly approaches

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Polyamides Comprising π-Conjugated Segments

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Polymer semiconductors often feature varying degrees of structural order, which plays a key role in determining their macroscopic properties. Therefore, approaches to control the balance between short-range order and overall disorder are highly relevant, to develop a better understanding of charge carrier generation and transport and, especially, to design novel high-performance materials for organic electronics. To this end, our work aims to make use of hydrogen-bonded groups attached to π-conjugated chromophores to guide the supramolecular arrangement of the chromophores in the solid state, and the morphology of thin films processed from these materials.

Our previous investigations with quaterthiophene acetamide have shown that the presence of hydrogen-bonded functional groups reinforces structural elements required for efficient π-overlap. Now we intend to use this analogy and investigate novel semicrystalline polyamides comprising π-conjugated segments. Here we report on the three-step, gram scale synthesis of bithiophene dicarboxylic acid monomer. Seven polyamides with different diamine lengths were synthesized by solution-phase polycondensation using Yamazaki-Higashi conditions. The obtained polyamides were thermally characterized and investigated regarding their chemical and supramolecular structure.

Polymer brushes on silicon: promising applications as electrochemical capacitors

G. Panzarasa[1]

[1]Empa Materials Science and Technology

Polymer brushes are dense arrays of macromolecular chains tethered on a surface by one end. Their production on different kind of substrates is enabled by the grafting-from approach, in which the polymer is grown directly from a surface functionalized with a proper initiator [1].

We already demonstrated that when the substrate is slightly-doped silicon wafer and the brushes are made of hydrophilic monomers, such as 2-hydroxyethyl methacrylate and methacrylic acid, the electrochemical properties of the former are greatly enhanced and can even be controlled by switching the pH [2,3].

Here we want to describe what happens when brushes of an hydrophobic monomer, such as styrene, are grown instead. The results for ultrathin (10 nm-thick) poly(styrene) brushes, obtained by surface-initiated atom transfer radical polymerization (SI-ATRP), showed that the modified silicon electrode behaves as an almost perfect capacitor. Moreover, in contrast with pristine silicon, this behavior is not influenced by UV irradiation.

Given the interest in the application of polymer brushes for the development of hybrid electronic components and circuitry [4], our results can open a new promising research front.

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Positron annihilation spectroscopy: a powerful approach for the advanced characterization of polymer brushes.

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[1]Empa Materials Science and Technology

Polymer brushes, dense arrays of macromolecular chains tethered on a surface by one end, are one cornerstone of contemporary polymer science and technology. Practical applications span from the biomedical field (e.g. to generate antimicrobial, antifouling surfaces) to organic electronics, passing through the development of sensors and actuators.

However, to achieve a proper characterization of polymer brushes presents great challenges for conventional analytical techniques [1].

Here we want to demonstrate how Positron Annihilation Spectroscopy (PAS) can be a powerful tool to gain unprecedented insight about these complex, fascinating systems.

Brushes made of a pH-responsive polymer, poly(2-dimethylaminoethyl methacrylate), were grown on silicon wafer by means of surface-initiated atom transfer radical polymerization (SI-ATRP). This allowed their investigation in different conditions: before and after protonation as well as before and after the incorporation of silver nanoparticles.

By means of PAS, the brush density and distribution profile of silver nanoparticles can be obtained without making the least damage to the sample.

One of the most relevant findings that will be discussed is the ability of PAS to discriminate within one analysis between brushes made from different initiators, which usually requires the combination of many different techniques.

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Entrapment of ROS Generating Quinones in Stimuli-Responsive Peptide Beads

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[1]University of Basel, [2]Weizmann Institute of Science, Israel

Quinones, specifically anthraquinones, have been reported to act as DNA intercalant and to mediate the production of reactive oxygen species (ROS), thus inhibiting cell growth [1]. These properties make anthraquinones interesting candidates for cancer therapy. However, their mechanism of action does not confer them selectivity for cancer cells. Systemic toxicity can be reduced by the use of a delivery system capable of releasing its cargo in tumor tissue.

Short amphiphilic peptides have been reported to self-assemble into various nano-structures, including multi-compartment micelles that can entrap small hydrophobic molecules. Stimuli-responsive release of the payload can be achieved, for instance, by insertion of a reduction sensitive bond between the hydrophilic and hydrophobic parts of the peptide [2].

This project aims at entrapping ROS generating quinones in peptide beads self-assembled from an amphiphilic peptide. The hydrophobic sequence of the peptide is linked to a hydrophilic oligo-histidine sequence by a disulfide bond. This system should prevent systemic toxicity and allow release of the active compound in a reducing environment such as cancer tissue.

Preliminary in vitro experiments showed reduced toxicity of the compound when entrapped in peptide beads and further experiments aim at showing an increase in toxicity in a reductive environment resulting from the release of the quinones.

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Ring-opening polymerization for 100% renewables-based Polyethylene Furanoate (PEF) towards the "Green Bottle"

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Along the shift of our societies from fossil-fuel based economies towards more sustainable civilizations, polyethylene furanoate may replace one of the world's dominant fossil-based plastics, polyethylene terephthalate (PET). Recent efforts were invariably based on polycondensation followed by solid-state polycondensation, which is burdened with the necessary removal of condensation byproducts to reach high conversions and molecular weights, and thus typically requires reaction times in the order of days [1]. We present ring-opening polymerization (ROP) as a faster and living synthesis route to reach sufficiently high molecular weight PEF for commercial applications such as bottles, textiles, medical grafts, etc. [2].

Cyclic PEF monomers (cyOEF) can be derived from the 100% renewables-based building blocks 2,5-furandicarboxylic acid and ethylene glycol via depolymerization of short PEF oligomers in suitable solvents [3]. Within 4 hours, cyOEF are formed with a selectivity of >90% towards cyOEF. The remaining unconverted linear species and solvents can be recycled to maximize material use. Purification of cyOEF from residual linears via silica gel adsorption to yield >99% cycles is essential for ROP to deliver 1) high molecular weights, 2) reproducible reaction control and 3) colorless products.

Understanding of this raw material for ROP is essential to obtain PEF that is applicable to typical commercial applications of PET: The cyclic oligomers exhibit a distribution of ring sizes, showing melting points ranging from 270 °C to 370 °C and different reactivity. Successful full conversion of all cyclic species towards bottle-grade molecular weights (Mw = 60 kg/mol) was achieved well below their melting point using 230-280°C with tin-based catalysts. Lower temperatures are actually beneficial and allow for higher achievable molecular weights, due to the more limited impact of degradation, which was observed after reaching >95% conversion. The reaction is usually complete after less than 20 min, since there are no condensation by-products that have to be removed from the viscous melt. Combined with cyOEF synthesis time, it outperforms traditional polycondensation by about a factor of 10. Preliminary economics evaluation reveals that ROP can be cost-competitive with the established polycondensation process. The material properties of ROP-PEF essential for bottle manufacture were briefly analyzed: Higher glass transition temperature (85 °C vs. 73 °C), lower melting point (215 °C vs. 260°C) and a 5x higher oxygen diffusion barrier compared with PET confirm the expected advantageous properties of PEF.

While the scale-up to larger (kilogram) volumes and processing towards actual bottles is ongoing, the advantageous synthesis of PEF via ROP opens a new and promising pathway not only towards the highly anticipated "green bottle", but also enables advanced molecular architecture control of furan based polyesters through a "living" polymerization, e.g. for branching and block copolymers, which is infeasible with the current process based on polycondensation.

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Self-Assembly Studies of Anthracene-Containing Oligomers

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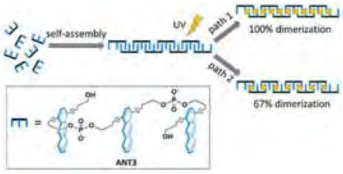
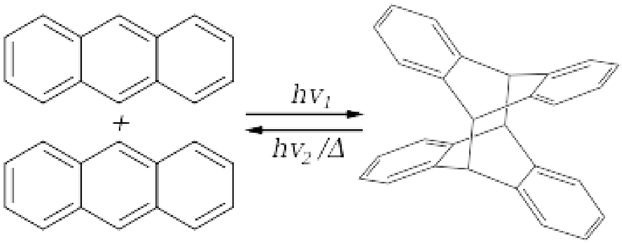
Dimers and trimers containing different isomers of anthracene were successfully synthesized through automated solid-phase synthesis and phosphoramidite chemistry. These oligomers displayed a self-assembly behavior in water, giving rise to supramolecular polymers. Atomic Force Microscopy revealed that these polymers are nanofibers, with lengths of several micrometers. One of the dimers showed a peculiar temperature-dependent spectroscopic behavior. [4+4]-cycloadditions between anthracenes did not result in a change of shape for one of the trimers, but a dimer changed dramatically, and this could give us better understanding of the self-assembly behavior of these oligomers.





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Hydrogel preparation using polyetylene glycol potassium acyltrifluoroborates (PEG-KAT) and amine containing molecules as chemical-cross linkers.

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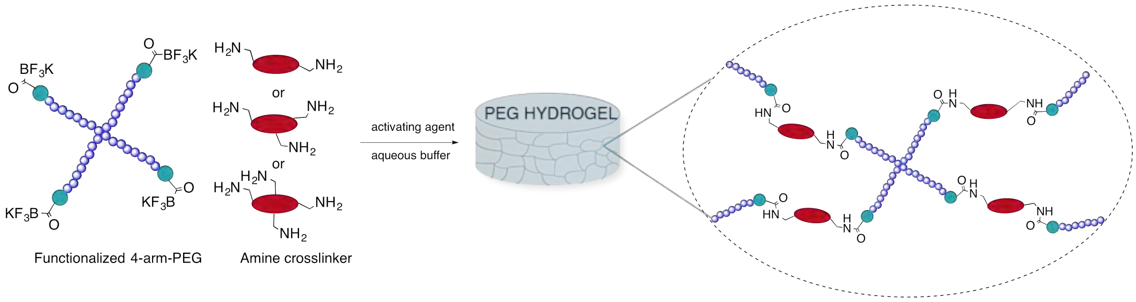
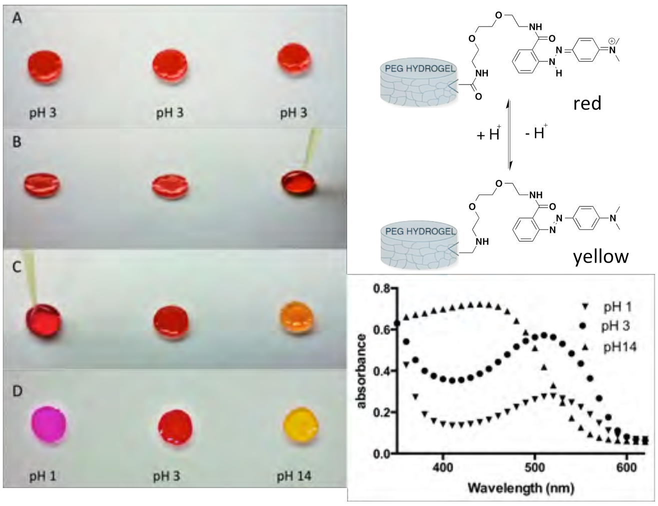
A method for the formation of chemically cross-linked hydrogels using polyethylene glycol potassium acyltrifluoroborate (PEG-KAT) with a wide range of commercially available di-, tri- or tetra-primary amine-containing molecules has been established. This protocol utilizes a chemoselective reaction that proceeds rapidly under a variety of mild conditions in acidic aqueous buffer, creating highly defined and multifunctional materials.





A broad range of amines are applicable in this procedure, from simple aliphatic diamines to complex natural products as Polymyxin B or Gramicidin S. Dyes such as Sulforhodamine B and pH switchable azo compounds could be covalently immobilized in the hydrogel network.

Reactive Hexayne Precursors for Microfluidic Production of Carbon Microcapsules

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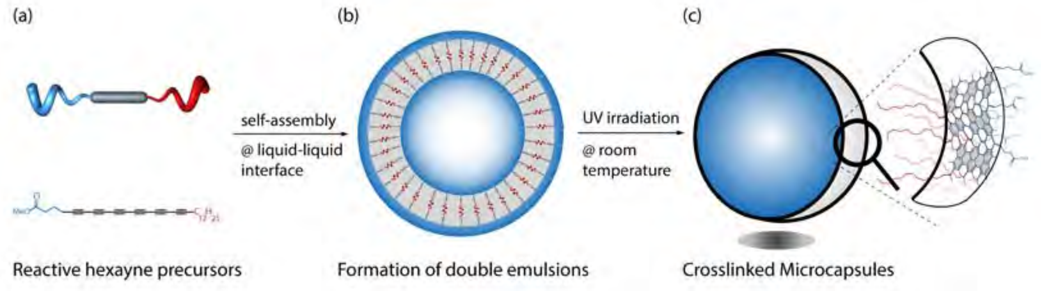
Liposomes are defined vesicular aggregates formed from small amphiphilic organic molecules. The formation of liposomes is an important way to achieve compartmentalization in nature, and synthetic liposomes often serve as simplified model systems to study the behavior of biological membranes with regard to their permeability and their uptake-and-release properties. The work presented here has aimed to prepare “carbosomes” as a novel type of vesicular, synthetic materials that resemble liposomes but have a carbon shell. The "carbosomes" we have prepared represent microcapsules that are fabricated from carbon-rich, amphiphilic precursor molecules (Figure 1).



These precursors have a polar head group, a reactive segment of twelve *sp*-hybridized carbon atoms, and a hydrocarbon tail. Previous investigations of the self-assembly of carbon-rich amphiphiles at the air-water interface showed that flat carbon nanosheets are accessible already under mild conditions, such as UV irradiation at room temperature [1, 2]. We self-assembled these precursor molecules at the oil-water interface using microfluidic drop emulsification, which allows us to create oil-in-water single emulsion or water-in-oil-in-water double emulsion droplets with defined size and composition. The goal is to obtain extensively cross-linked carbon-rich capsules with a diameter on the order of micrometers that have a defined chemical surface functionalization and are constituted from an ultrathin carbon shell with a thickness of 2–4 nm. Such microcapsules are expected to combine a low shell thickness similar to biological cells or synthetic liposomes with the mechanical rigidity and electrical properties of carbon nanomaterials. Thus, the project is expected to deliver insights into the mechanical stability and porosity of these microcapsules. Furthermore, it provides an interesting platform to study fundamental questions of surfactant self-assembly, such as the effect of an ionic or non-ionic precursor on the shell density of the crosslinked microcapsule and the carbon microstructure within the shell.

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Electrovariable Nanoplasmonics at Liquid-Liquid Interfaces: the Case of Marangoni Shutters

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Ongoing climate change requires enormous amount of energy rather to cool our building then to warm them up. Thus, smart systems capable to switch between “mirroring” and “transparent” states on demand can significantly reduce the energy costs. In this case, nanoplasmonic devices are of high practical importance due to tunable adsorption and reflectance. In its turn, a liquid-liquid interface (LLI) represents almost an ideal platform to realize such devices due to surface energetic homogeneity, flexibility, self-healing nature, and possibility to control nanoparticles position by an external electric field (the case of two immiscible electrolytes solutions, ITIES).
Previously, the research in the field was focused on “vertical” landing of nanoparticles from the bulk of one phase to ITIES in order to form mirror-type films.[1,2] However, this approach has two major restriction limiting practical applications: slow diffusion and low concentration of the nanoparticles. In contrast, we propose here to use “horizontal” or in-plane movements of nanoparticles driven by changes in interfacial tension. The latter is caused by interfacial transfer of surfactant molecules (SDS) upon applying of the external electric field. We called such systems “*Marangoni-type shutters*”. In fact, the Marangoni effect (the mass transfer along an interface between two fluids) has been used previously to power movements of capsules at LLI.[3]
We observed that Marangoni effect induces migration of citrate covered gold nanoparticles located close to the ITIES from the middle region of the cell to its periphery with polarizing of the ITIES.[4] In this work we showed that moving of nanoparticles in-plane of the interface can be performed repeatedly (up to 20 cycles) with significant change of the reflectivity (Fig. 1). This type of electrovariable nanoplasmonic device does not have diffusion limitation and the entire movement of nanoparticles assemblies happened almost instantly (within a second). The present approach opens a fresh view on electrovariable nanoplasmonics and proposes new opportunities to create smart nanosystems at ITIES driven with electric field.

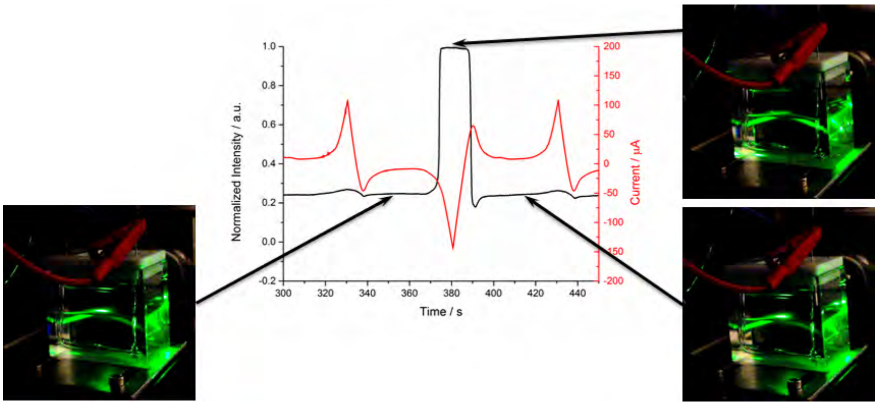

Fig. 1. Marangoni shutter in action: cyclic voltammogram and corresponding reflection of the film.

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Functionalization of Sodium Alginate Hydrogels for Cell Microencapsulation

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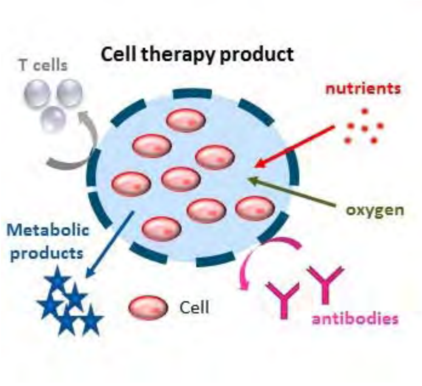
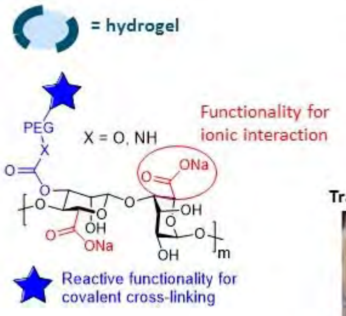
Cell based therapies, especially transplantation of microencapsulated cells, open doors for new medical and clinical modalities, and offer an alternative solution to whole organ transplantation for the treatment of various diseases, such as type 1 Diabetes Mellitus or acute liver failure. The success of the cell transplantation highly depends on the quality of both the encapsulating biomaterial and the source of cells.

Encapsulation materials should fulfill many requirements, including biocompatibility, adjustable physical characteristics, and the microencapsulation process must be simple and not harm the cells.[1] While sodium alginate (Na-alg) benefit from the spontaneous formation of hydrogels in the presence of divalent cations (Ca^{2+}, Ba^{2+}) and present high biocompatibility, its mechanical and permselectivity properties are not optimal. To improve the properties of hydrogels formed from Na-alg, our group has developed a variety of hybrid hydrogels combining the alginate backbone with poly(ethylene glycol) derivatives.[2–7] The simultaneous presence of the electrostatic ionic crosslinking of alginate with divalent cations (such as Ca^{2+}) provides fast gelation and spherical beads, while the chemical crosslinking through covalent linkages of the PEG chains is responsible for the reinforcement of the hydrogel.

We herein present the synthesis of heterobifunctional PEG derivatives, their conjugation to the alginate backbone through a variety of covalent linkages and the preparation of hybrid microspheres. Physical characterization of the formed beads as well as *in vivo* and *in vitro* evaluation of their potential for cell immobilization and transplantation will be discussed.





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Ion specificity on the dynamics of ion-induced surface charge asymmetry of freestanding lipid membranes

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The distribution and flow of charges in biological membranes dictate the electrostatic environment essential for the activity of fundamental membrane processes such as signaling and transport in cells. These membranes reside in an aqueous environment and are stable because of the hydrating water that drives the membrane structure intact. The presence of charges on the membrane orients the hydrating water through electrostatic charge-dipole interaction. We use this universal phenomenon to image the orientational ordering of water molecules with a non-resonant optical second harmonic microscope[1]. Second harmonic generation is a coherent method that provides contrast only when a material possesses spatial non-centrosymmetry[2]. Differences in surface charge between the bilayer leaflets lead to non-centrosymmetric ordering of water molecules, thus, providing second harmonic contrast. As such, SHG imaging is sensitive to the asymmetric distribution of surface charges, and concomitantly, the asymmetric distribution of membrane potentials between bilayer leaflets. In this work, we demonstrate this imaging method and investigate the affinity of specific ions to induce asymmetric surface charge distribution in freestanding lipid bilayer membranes. The images provide insights in both the spatial and temporal distribution of ions, and on how different ions can affect the electrostatic membrane environment that cannot be explained by simple electrostatic interaction alone.

Keywords: interfaces, membrane potentials, surface charges, aggregation, membrane asymmetry, freestanding lipid membranes

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Designing artificial soft materials exhibiting mechanochemical activity

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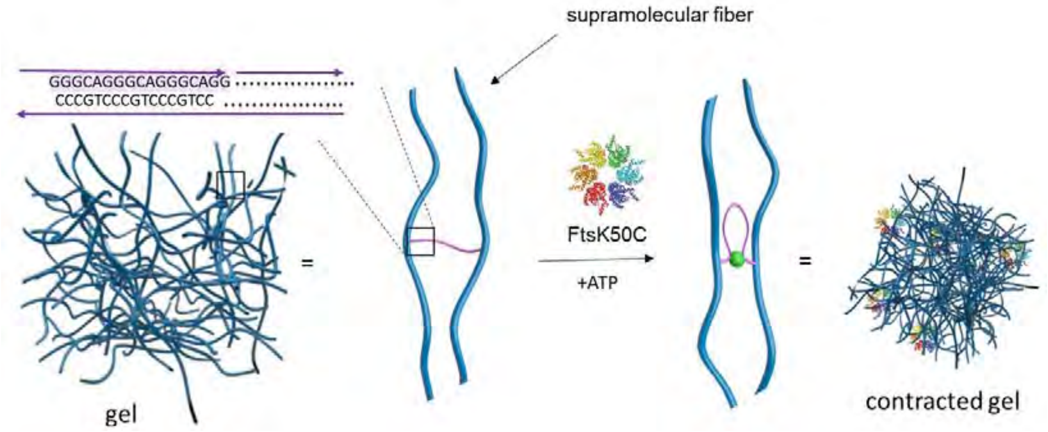
Herein, we explore the possibility to transfer mechanochemical activity exerted by motor proteins to a synthetic hydrogel. Water-soluble supramolecular polymers are excellent candidates for this purpose, since they possess numerous properties intrinsic to extra- and intracellular matrices – biocompatibility, tunable rheological properties, dynamic behavior of components, and adaptability to stimuli.[1] The model material in this study is a hybrid DNA hydrogel assembled from one-dimensional supramolecular polymers (structural scaffold), in which the filaments are held together by complementary DNA strands (crosslinking motifs). The supramolecular polymers consist of two kinds of co-assembled benzene-1,3,5-tricarboxamides, one of which is conjugated to a short DNA handle. The self-assembly exhibits two regimes of the supramolecular polymerization. Moreover, the usage of two components allows to adjust the dynamics and crosslinking density of the material. Based on the previous results, we foresee that such hydrogels can be rendered active, i.e. change their stiffness and exhibit spontaneous mechanical fluctuations in the presence of the DNA translocase motor protein and ATP.[2] We believe that our system can provide a convenient tool to establish design principles for the preparation of adaptive and responsible artificial soft matter. The project offers opportunities for studying the diverse properties of active materials which are difficult – if not impossible – to modulate in entirely natural objects.



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Kinetics of Monoclonal Antibody Aggregation - Going From Elevated Towards Lower Temperatures

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Monoclonal antibodies and other therapeutic proteins are gaining increasing importance as pharmaceutical compounds due to recent advances in biotechnology and their very specific mode of action, resulting in higher drug efficacy and reduction of adverse side effects [1]. Modern production processes yield the protein of interest at very high purity. However, under a broad range of conditions proteins could be only marginally stable in solution, and preserving their stability under long-term storage represents a challenge in product development [2]. Aggregation of the protein molecules into soluble oligomers as well as micron-sized precipitates is viewed as the largest threat to product safety due to the potential immunogenicity of the protein aggregates and the resulting danger to the patient. In this respect, a large effort is dedicated in liquid formulation development to the optimization of the composition of the final product in terms of solution pH, buffer species and potential additives. This optimization is both time and effort consuming, since the resulting parameter space to be investigated is very large [3].

In this context, accelerated studies at elevated temperatures represent a common strategy to test the aggregation and other potential degradation reactions of biopharmaceuticals. The possible drawback of this approach is, however, the question about the validity of the information gathered at higher temperatures for the actual temperatures encountered in storage and shipment, as well as the extrapolation of the degradation rates observed at elevated temperatures to lower temperatures [4].

Gaining a fundamental understanding of the aggregation process at the microscopic level would be highly beneficial to overcome limitations of accelerated studies as well as to design rationally optimized formulations [5,6]. The scope of this work is to apply a combination of model simulations and experimental data to investigate the mechanistic details of the aggregation process of a model monoclonal antibody over a broad range of temperatures.

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Surface Energy of Janus Nanoparticles and Their Application in Pickering Emulsions Polymerization

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Surface energy of nanoparticles is an important physicochemical parameter because it controls the colloid stability, surface adhesion, flowing ability, aggregation, etc. However, direct measurement of the surface energy of nanoparticles is not as easy as for bulk materials. Currently, the common method for measuring surface energy of particles is by measuring the contact angle *via* Washburn method. But this method has significant drawbacks, while it works relatively well for micro-particles, it often fails in the nano-range, due to packing reproducibility and limited solvent intake by the nano-capillaries.

Alternatively, we propose a new method to measure the interfacial energy of nanoparticles. For this we have synthesized a homologous series of varying polarity Janus nanoparticles (JNPs) consisting of a hydrophobic polystyrene (PS) lobe and more polar P(3-TSPM) lobe by surfactant-free seeded emulsion polymerization. In this case the P(3-TSPM) lobe is more polar than the PS lobe due to the presence of polar -OH functional groups on its surface. The size of the PS lobe was kept constant, while that of the P(3-TSPM) lobe was changed, thus the overall particle polarity of the surface also changed systematically in the homologous series.

Next, we employed the homologous series of JNPs to emulsify several oils, with varying polarity, such as heptane, toluene, styrene, dichloromethane and methyl methacrylate in water. In the phase diagram of oil-to-water ratio vs. JNP lobe size both transitional and catastrophic emulsion phase inversions from o/w to w/o could be observed. From the evolution of these phase transition lines with different polarity oils we were able to calculate the relative interfacial energy of each JNP with water and oil.

The relative interfacial energy of JNPs with water decreased by 92% and increased by 100% with respect to heptane in the homologous series. The obtained result clearly demonstrates that the polarity of JNPs significantly increases with the size of the P(3-TSPM) lobe. Furthermore, the new method employed here can be universally applied to estimate the polarity of different types of particles.

Finally, the obtained JNP-Pickering emulsions, from styrene and methyl methacrylate, were polymerized in the presence of a hydrophobic radical initiator. Depending on the starting emulsion, o/w or w/o, we obtained either surface-nanostructured colloidosomes or polymeric hollow structures. Such hollow materials with closed cavities could be used as long-term storage containers for water-soluble actives such as proteins, enzymes, or pharmaceuticals.

Increased heat stability of α-chymotrypsin through its confinement in liposomes

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For applications of enzymes in confined space, for example inside liposomes (lipid vesicles), the enzyme stability is a critical issue [1]. During the course of our investigations on the entrapment of enzymes inside submicrometer-sized liposomes, we found that the confinement of α-chymotrypsin in liposomes formed from POPC (1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine) leads to a significantly increased thermostability of the enzyme. Since through the method used – dispersing a dried POPC layer with an aqueous enzyme solution, followed by polycarbonate membrane extrusion – the enzyme entrapment in the liposomes occurs during liposome formation, a stochastic enzyme distribution among the liposomes is obtained. Heat stability experiments showed that a considerable fraction of liposomal α-chymotrypsin is still active after being treated at 80 °C for 30 min, whereas the free enzyme is completely deactivated. For liposome-confined α-chymotrypsin, the heat stability increases as the average number of enzyme molecules per liposome decreases. This high heat tolerance can be explained by a decrease in interactions between partially unfolded enzyme molecules as a result of a decrease in the number of enzyme molecules per liposome compartment. In the extreme case, there is no opportunity for the irreversible formation of enzyme aggregates – which leads to enzyme deactivation – in the case of single enzyme molecule confinement. Whether this finding also holds for other monomeric enzymes is currently under investigation.

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The selective transport of functional nanocarriers into cell nuclei via nuclear pore complexes

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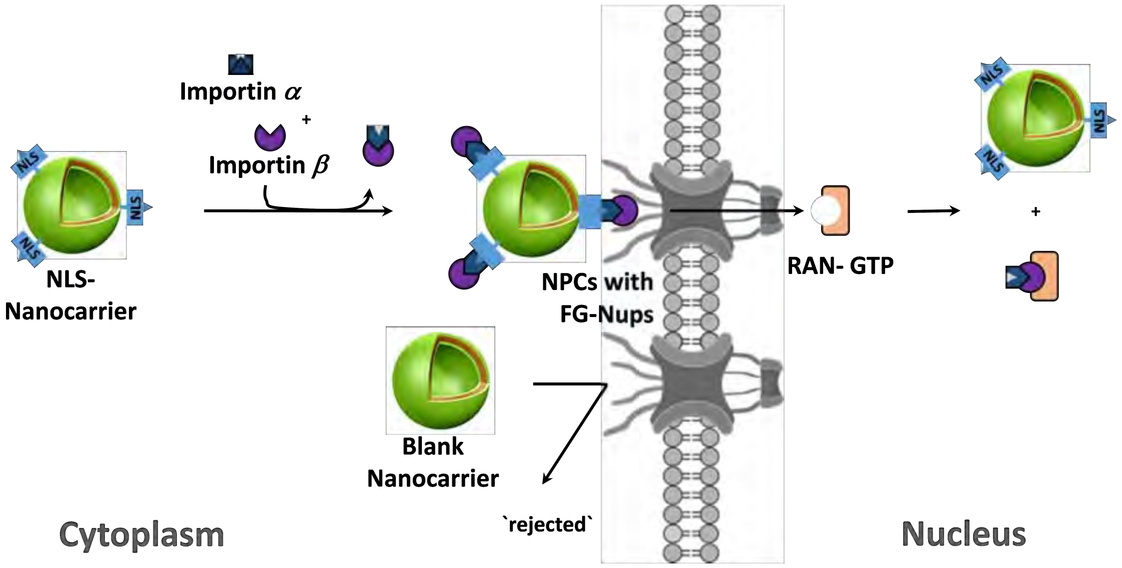
In eukaryotes, the selective substance exchange between the cytoplasm and the nucleus is an essential process to execute cell function and proliferation. Bio-macromolecules, when tagged with a nuclear localization sequence (NLS), are recognized by the cell intrinsic nuclear import machinery and form stable complexes with transport regulating receptors (e.g. importins).[1] For a cargo to be actively transported into the nucleus, it has to cross the nuclear envelope and thereby, it transverses through ~ 50 nm wide channel-like protein arrangements termed nuclear pore complexes (NPCs).[2] Here, multivalent interactions between the NPC constructing nucleoporins (FG-Nups) and the cargo on-bound importins drive its initial up-take into the NPC whilst RAN-GTP finalizes the release of the cargo into the nuclear cavity. Although nucleocytoplasmic transportation mechanisms have been studied extensively during the last decades, it remains challenging to analyze how large, deformable objects enter into the NPC.[3] On this account, we are applying a bottom-up strategy to fabricate artificial `cargoes` that mimic natural translocation mechanisms. Specifically, we are engineering nanometer-sized hybrid-polymer vesicles that are easily tuneable in size, membrane flexibility and allow for their surface-attachment with transport receptors. With this in hand, we are studying how structural cargo properties translate to the NPC uptake kinetics and uptake efficiency.



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Pseudomorphic transformation of SBA-15 and SBA-16

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Pseudomorphic transformation is an elegant way to alter the pore size of a mesoporous material without affecting its particle size and shape. This pathway uses a structure-directing agent (SDA) to rearrange the pore system of a porous material. Functional groups can be introduced during the transformation and the pore size can be adjusted to a certain degree by using differently sized SDAs. Mesoporous silica with bimodal pore size distributions were prepared by pseudomorphic transformation of SBA-15 and SBA-16 in the presence of hexadecyltrimethylammonium ions as a structure-directing agent. Partial pseudomorphic transformation was shown to alter the structure of the porous starting material from the outside to the inside, thus virtually creating a shell with a reduced pore size. The pH thereby governs the equilibrium between dissolution and reprecipitation of the silica matrix. Analysis of the products by gas sorption and small-angle X-ray scattering (SAXS) revealed hybrid pore structures, which featured – depending on the degree of transformation – variable contributions from the original and the newly introduced pore systems. This leads to the conclusion that the pore structure of the starting material significantly affects the outcome of the pseudomorphic transformation, thus opening possibilities for the synthesis of new porous materials with complex pore systems.

Functional surfaces through immobilization of polymersome nanocompartments

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Amphiphilic block copolymers possess the ability to self-assemble into planar membranes and nanometer-sized spherical architectures such as micelles and vesicles.[1,2] The intrinsic properties of polymers and the variety of monomers available to synthesize block copolymers give access to a library of functionalities that are explored to specifically modulate interactions. The covalent immobilization of polymer vesicles on solid support is realized using a thiol-ene reaction, and the conditions are optimized towards maintaining structural integrity of the hollow polymer architectures.[3] Thus, functional surfaces can be generated when immobilized polymer vesicles act as protected compartments to perform enzymatic reactions.

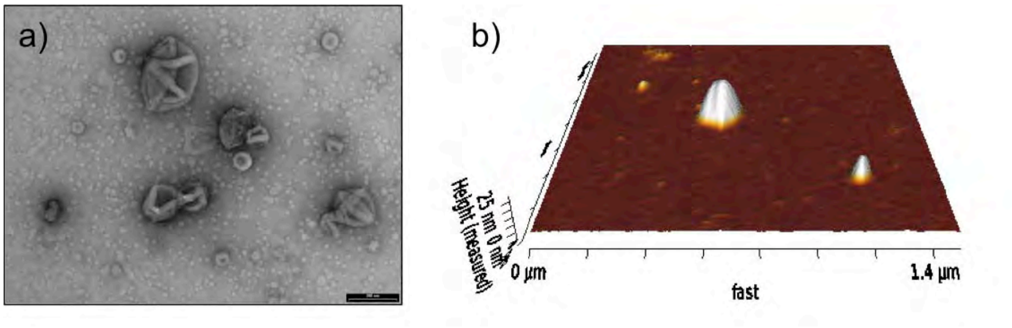

Figure 1. a) Visualization of polymer vesicles composed of polydimethylsiloxane-polyoxazoline triblock copolymers by transmission electron microscopy (scale bar 200 nm) and b) visualization of a surface immobilized polymer vesicles by atomic force microscopy.

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