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Click-Thiols as an approach to implement novel functionalities within bio-derived scaffolds

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As a result of dwindling fossil resources and pressing environmental issues, the utilization of sustainable materials gains more and more impact nowadays. Among various natural resources, wood and wood-based materials will certainly be an essential part of the future challenges. The benefits of this green material are ease of processability, light weight, low cost, wide availability, excellent mechanical properties, and attractive appearance. In addition, wood possesses a unique hierarchical microstructure, which itself allows the design of future bio-derived materials. However, dealing with wood also bears some drawbacks, mainly due to its hygroscopic and anisotropic behaviour. Chemical modifications of the lignocellulosic scaffold are a simple yet versatile tool to alter wood properties.

In this work, Thiol-Michael additions were chosen as a promising candidate for a “grafting to” method to modify lignocellulosic materials. It was shown in our previous studies (using EDX mapping, Raman and FTIR) that acrylated wood can be modified by simple click thiol approach. Given the availability of more complex alkene containing structures (such as organosilane vinyl, polymer-brushes and dendrimers), there is a large potential for further modification by click-thiols. The structural and chemical anisotropy of the wood surface represents a challenge for the implementation of such a technique. We currently aim to develop a straightforward protocol in green conditions to adapt the approach to wood. While preserving the surface and the wood scaffold intact, the goal is to bring novel functionalities to the wood surface, such as superhydrophobicity through microstructuring inspired by plant surfaces. Such a modification would be highly desirable to protect wood from external aggressions.

LDH-polyelectrolyte nanocomposites as novel materials or enzyme carriers

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Layered double hydroxides (LDHs) have been extensively investigated due to their promising applications as flame retardants, photocatalysts, enzyme supports and drug or gene vectors. In many of such utilizations these layered materials are used in dispersions, where colloidal stability plays a major role. Therefore, we have investigated aggregation of LDH particles in presence of different polyelectrolytes, namely, negatively charged MacroRAFT random copolymers and naturally occurring anticoagulant heparin.^{1,2} Aggregation processes were followed in time-resolved dynamic light scattering experiments to probe the dispersion stability of the system (stability ratio values close or equal to unity correspond to the fast aggregation), in addition to electrophoretic mobility measurements. All polyelectrolytes adsorbed strongly on the surface of oppositely charged LDH platelets leading to charge neutralization and unstable system. However, further addition of polyelectrolytes resulted in overcharging and significantly more stable nanocomposites in comparison to the bare nanoparticles (Fig. 1). As a result, we were able to make highly stable LDH-MacroRAFT nanocomposites even at high ionic strength. On the other hand, the enormously stable, biocompatible LDH-heparin composites can be used in biomedical processes (e.g. drug delivery and enzyme formulations).

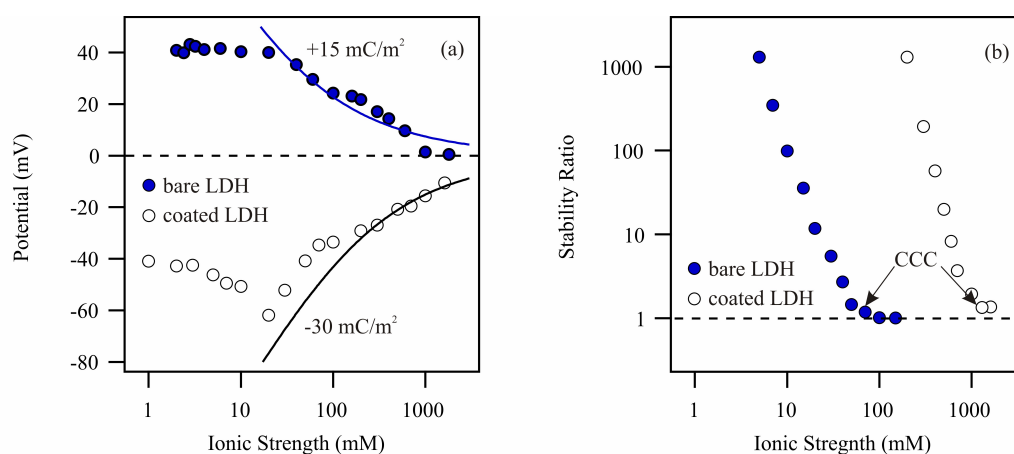


Fig. 1. Electrokinetic potential (a) and stability ratio (b) values for the bare (filled symbols) and heparin coated (empty symbols, at a dose of 100 mg/g) LDH particles at different ionic strengths. The solid lines in (a) indicate the potentials calculated using the Debye-Hückel model.

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Ag nanoencapsulation for antimicrobial implant coatings

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Medical progress and an ageing world population have led to an increasing use of foreign materials inside the human body. Consequently also the number of infections related to these implants has grown significantly.¹ Antimicrobial coatings that prevent the formation of infectious biofilms on the surface of the implants could make an important contribution to overcome that issue. Silver is known for its good antimicrobial and biocompatible properties and could therefore play an important role in the fight against implant infections, especially if they are caused by antibiotic resistant bacteria.²

This project investigates Ag@SiO₂ nanorattles as antimicrobial agent for implant coatings. These nanoparticles are characterized by a void between a silica shell and a silver nanoparticle as cargo.³ The silica shell protects the Ag cores from aggregation and prolongs the release of the antimicrobial active Ag⁺ ions. Moreover it provides reactive sites to functionalize the nanocontainers in order to attach them covalently to implant surfaces or to incorporate them into polymer materials.

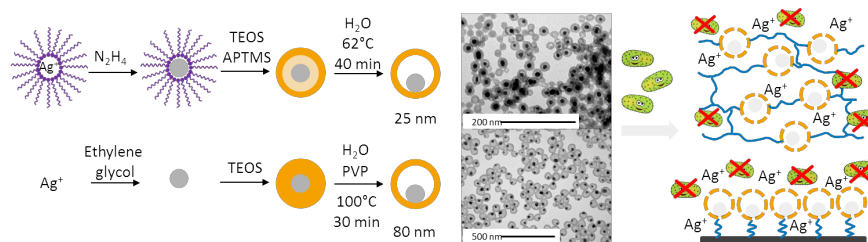


Fig. 1: Synthesis and antimicrobial Ag⁺ release of Ag@SiO₂ nanorattles: microemulsion method (top) and Stöber conditions followed by surface protected etching (bottom).

We have developed two different synthetic routes to Ag@SiO₂ nanorattles of different sizes. The microemulsion method⁴ gives access to nanorattles with a diameter of about 25 nm (Figure 1, top) that were evaluated for their Ag⁺ release properties, antimicrobial potential and for their impact on cells of the immune system (in collaboration with C. Bourquin, University of Fribourg).⁵ The second synthetic approach is based on the coating of Ag nanoparticles with silica under classical Stöber conditions followed by a surface protected etching protocol. This results in very homogeneously filled Ag@SiO₂ nanorattles with a diameter of about 80 nm (Figure 1, bottom). Cytotoxicity tests showed a good biocompatibility determining a nontoxic concentration of ≤0.113 mg/ml. Their antimicrobial efficiency is currently under investigation. First tests against *E.coli* suggest a therapeutic window from 0.003 mg/ml.

Both types of silver-containing silica nanorattles thus fulfill several requirements for the development of novel antibacterial nanocoatings on biomaterial surfaces. Further investigations will compare their Ag⁺ release kinetics and develop strategies to link them to implant model surfaces of titanium, gold or polymers.

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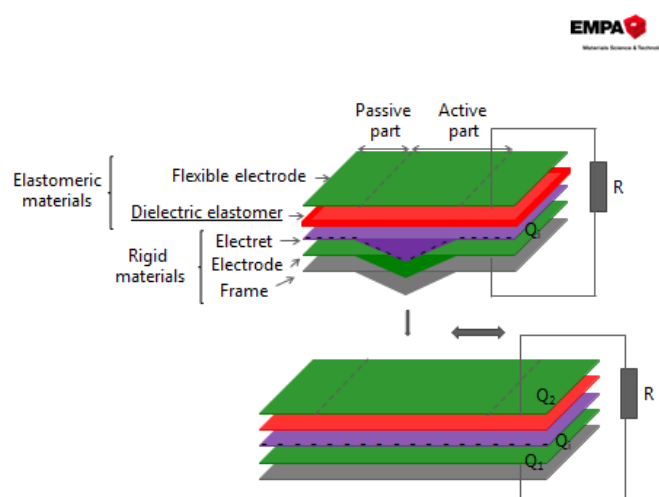
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Development of high permittivity siloxanes for dielectric elastomer generators

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Electret-based dielectric elastomer generators (DEG) consist of a thin elastomeric film coated with two compliant flexible electrodes. When properly charged the devices are able to convert mechanical into electrical energy.^[1] An electret-based DEG operates without an external voltage source. The rigid part has an accordion like structure which allows unfolding and expansion. The elastomeric part is made of a high permittivity dielectric elastomer coated on one side with a stretchable electrode. In the relaxed state, the capacitance is smaller as compared to the capacitance in the strain state ($C = \epsilon \epsilon_0 A/d$), where ϵ is the permittivity of the elastomer, ϵ_0 is the permittivity of air, A is the surface area of the flexible electrode and d is the thickness of the dielectric elastomer). When the device is strained by external forces, the accordion like structure deforms. Variation in capacitance leads to rearrangement of charges between the two electrodes and an alternative current. Dielectric elastomers with increased permittivity are more strongly polarized by the electret and harvest more energy per cycle than low permittivity elastomers.



Polysiloxanes $(R_1SiR_2O)_n$ are ideal candidates as dielectric elastomers due to their thermal and chemical stability, low glass transition temperatures and mechanical robustness. The major disadvantage of siloxane elastomers is their low dielectric permittivity ($\epsilon \sim 3$).^[2] One approach to increase permittivity without affecting the excellent elastic properties of the cross-linked siloxane is the chemical modification of siloxane with polar side groups. When this material is exposed to an electric field, the polar side groups align with the electric field. An increase in permittivity is usually accompanied by a decrease in electric breakdown field. It is important to find the right degree of modification with polar groups which increases permittivity while barely affecting the electric breakdown field. A deeper understanding of the impact of various functional groups on permittivity, elasticity, electric breakdown field etc. and the correlation between those properties is needed for targeted development of ideal siloxane elastomers. Post-polymerization modification of polymethylvinylsiloxane with various thiols is a promising pathway to high permittivity polysiloxane elastomers.^[3]

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Effect of aging on silica aerogel properties and study of the structure of glass wool aerogel composites by X-ray tomography

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Silica aerogels unique physical and chemical properties make them fascinating materials for a wide variety of applications. In addition to silylation, aging is very important in the synthesis of silica aerogel by ambient pressure drying. Here, we systematically study the effect of aging on the physio-chemical properties of silica aerogel. Silica aerogels were aged for different times and temperatures in the gelation liquid (without solvent exchange), hydrophobized in hexamethyldisiloxane and subsequently dried either at ambient pressure or by supercritical CO₂. The specific surface area decreases with increasing aging time and temperature as a consequence of Ostwald ripening processes during aging. With increasing aging time and temperature, the linear shrinkage and bulk density decrease and the pore size and pore volume increase for the ambient dried gels, but remain nearly constant for supercritically dried gels. The Small Angle X-ray scattering data indicate that the aging process affects the structure of aerogels mostly at length scales of hundreds of nanometers, while no significant change is noticeable at smaller length scales. Our results highlight the importance of aging to increase the ability of the gel particle network to withstand irreversible pore collapse during ambient pressure drying. This study was further expanded to see the influence of aging and drying processes on the thermal conductivity of fiber reinforced silica aerogel composites. The trends in thermal conductivity of glass wool-silica aerogel composites prepared at different aging times were linked to the structure of the samples as determined by X-ray tomography. The findings of this study provide the means to correlate the 3D quantitative characterization of drying shrinkage cracking in fiber reinforced aerogel composites by X-ray tomography with the thermal conductivity.

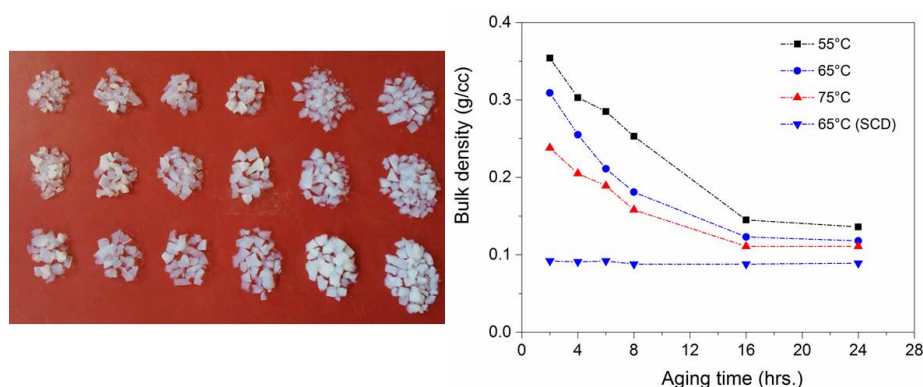


Figure 1. Influence of aging time and temperature on the bulk density of silica aerogels.

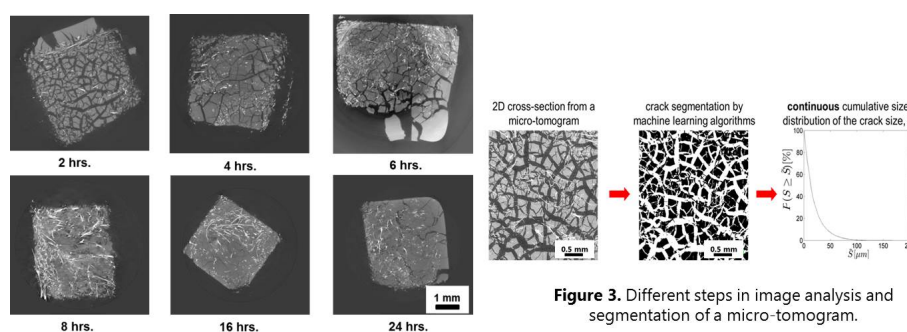


Figure 2. 2D cross section from micro-tomogram of ambient dried glass wool-silica aerogel composites at 6 aging times.

Figure 3. Different steps in image analysis and segmentation of a micro-tomogram.

Excitation energy transfer over base pairs in DNA based light-harvesting antennae

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In light-harvesting systems, energy is absorbed by chromophores and subsequently transferred to an acceptor. The design and construction of efficient artificial systems is a continuing field of study.[1] In previous work we described different light-harvesting systems based on DNA-organized chromophores.[2-4] In this contribution we will present DNA based light-harvesting antennae which consist of a stack of light-harvesting phenanthrene units and one pyrene as acceptor. Excitation of phenanthrene leads to efficient excitation energy transfer to pyrene. Different DNA duplexes were prepared in which the stack of phenanthrene is separated by different numbers of base pairs (0-5). Fluorescence measurements show that even in separated DNA based light-harvesting antennae excitation energy is transferred from one stack of phenanthrene to the other (pink arrow in Figure 1 B)). Quantum yield measurements indicate that the observed energy transfer cannot be explained by a Förster resonance energy transfer mechanism alone. Coherent energy transfer is more reasonable as the incorporated phenanthrene units should couple strong enough. Investigation of the energy transfer mechanism will be done by DUV-to-Vis femtosecond transient absorption spectroscopy.

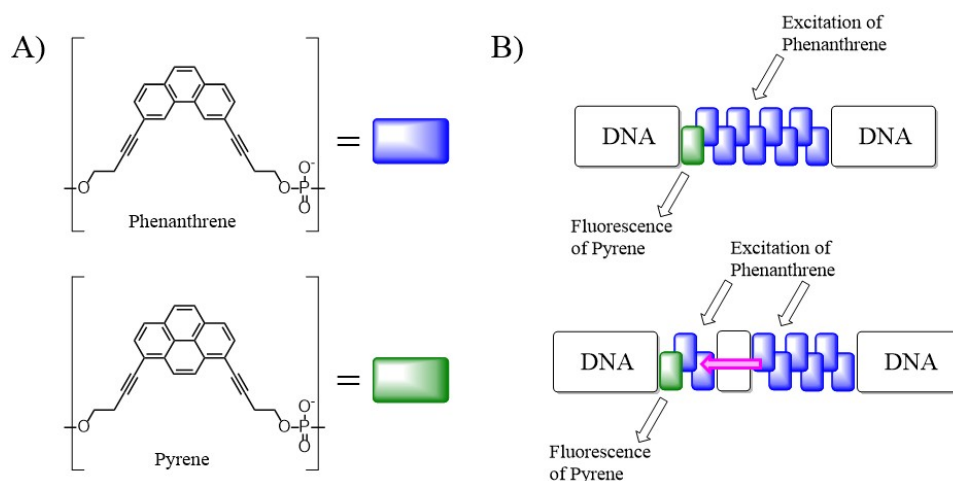


Figure 1: A) Structures of incorporated phenanthrene and pyrene building blocks. B) Schematic illustration of DNA based light-harvesting antennae without (top) and with (below) separating base pairs between phenanthrene units.

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Surface functionalisation of titania nano-objects for biocatalytic applicationsP. Rouster¹, M. Pavlovic¹, I. Szilágyi¹¹University of Geneva

During the past decades, titania has received more and more considerations in various fields i.e. drug delivery, photocatalysis... However, a major issue in the use of titania nano-objects lies in their colloidal stability. Indeed, in order to be an efficient nanocarrier for drug delivery, the colloidal suspension of titania nano-object should be stable and not aggregate[1]. As a consequence, aggregation could prevent the successful use and/or inhibit the delivery of the target molecules from the titania nano-objects.

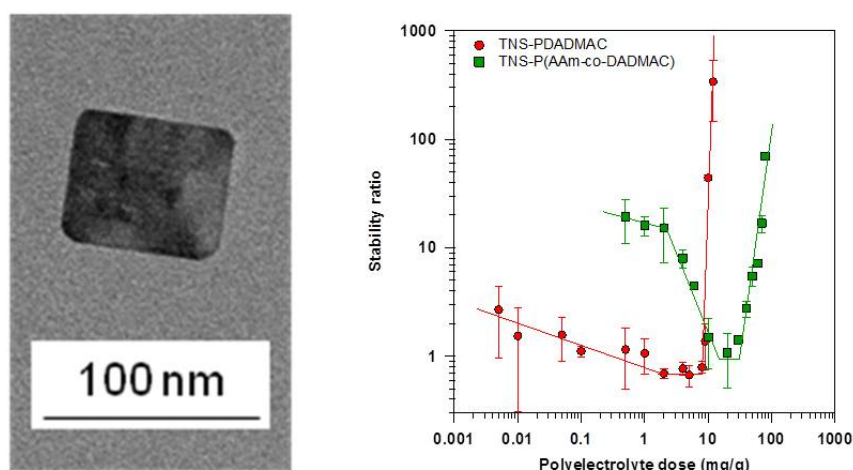


Figure 1. Transmission electron microscope image of a TNS (left) and stability ratio of poly(diallyldimethylammonium chloride) and poly(acrylamide-co-diallyldimethylammonium chloride) coated TNS (right). Please note that the values close to unity correspond to fast aggregation of the particles while higher values indicate a stable system.

Here, titania nano-objects were synthesized using a hydrothermal treatment. Depending on the experimental conditions, various kinds of titania nanostructures could be obtained (titania nanosheets (TNS), titania nanocubes...). The structure and morphology of the nano-objects were determined to ensure the formation of the anatase phase of titania. The functionalisation of the TNS was then performed by adsorbing different polyelectrolytes. Depending on the polyelectrolyte dose used, its adsorption on the TNS led either to charge neutralization and therefore to an unstable colloidal suspension where aggregation occurred or to charge reversal where a stable TNS suspension was obtained. The electrophoretic mobility and stability ratio of the TNS were measured in order to determine the polyelectrolyte dose required to have a stable dispersion prior to their use as nanocarriers.

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DNA-grafted supramolecular polymers: self-assembly, dynamics and potential applications

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The unique self-recognition properties of oligonucleotides laid the foundation of modern DNA nanotechnology. Over the last two decades, man-made DNA assemblies led to the development of numerous biocompatible functional materials, including drug carriers, nanorobots, and scaffolding platforms. A standard toolbox of building blocks used by chemists in the field is largely limited to four units – A, G, C, T. To further develop the functional potential of synthetic DNA systems, the use of DNA-chromophore conjugates emerges as an exciting approach. Following our previous findings, we demonstrate herein the pathway complexity in a temperature-induced self-assembly of the DNA-pyrene oligomers. Thermodynamically favoured DNA-grafted supramolecular polymers assemble into metastable networks through hybridization between DNA sticky ends followed by the subsequent re-assembly into individual DNA-grafted polymers through monomer exchange (see Figure 1). Such systems become increasingly important for the creation of dynamic and stimuli-responsive materials targeting various applications such as delivery and precise scaffolding.

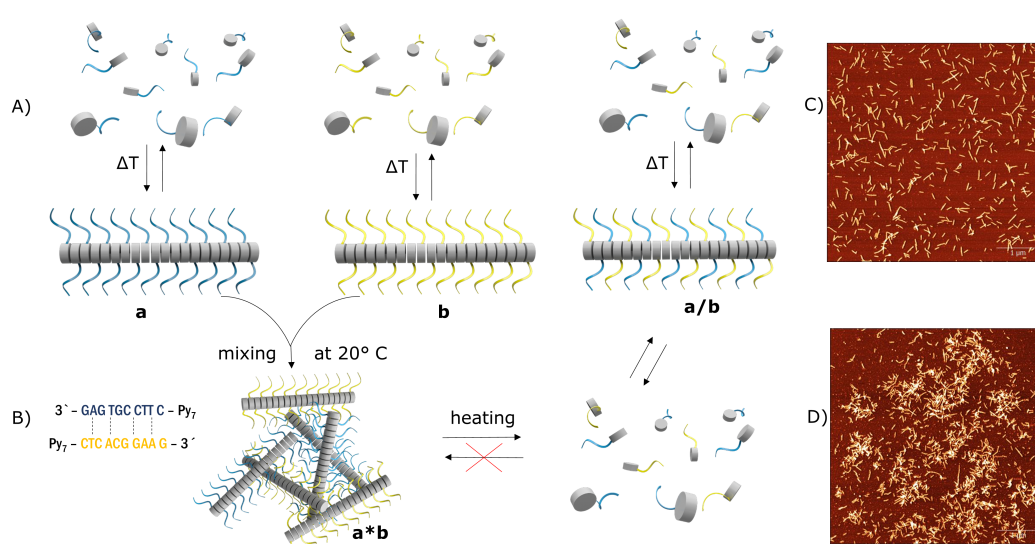


Figure 1. Schematic representation of the self-assembly of molecularly dissolved pyrene-DNA hybrids (A) into 1-dimensional DNA-grafted supramolecular polymers **a/b**, **a** and **b**. Mixing of the pre-annealed SPs **a** and **b** at 20 °C results in the formation of the networks **a*b** via hybridization between complementary DNA strands (B left). This scheme also shows irreversible rearrangement of the networks into dual-component SPs **a/b** through the disassembly upon heating (B). AFM images of the DNA-grafted SPs **a/b** formed from co-assembled pyrene-DNA oligomers (C) and DNA interconnected networks formed from separately pre-annealed SPs **a** and **b** (D).

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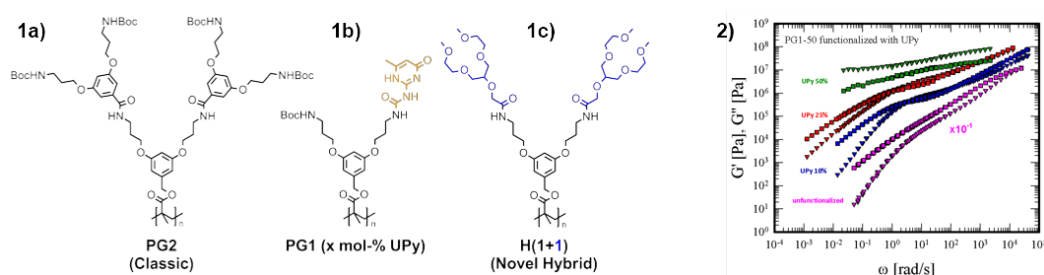
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Effect of supramolecular interactions in dendronized polymers on their thermal- and viscoelastic properties

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Dendronized polymers (DPs) represent an intriguing class of macromolecules combining the concepts of dendrimers and polymers [1]. By tailoring their thickness and persistence length through the generation number (g) and backbone degree of polymerization (P_n), respectively, DPs can be endowed with a wide range of conformations, spanning from flexible polymers to shape-anisotropic colloidal objects [2]. Thereby, the molecular dynamics of DPs are not only governed by their physical dimensions, i.e. g and P_n , but further complicated by the possibility for supramolecular interactions, such as hydrogen bonding or π - π stacking. According to MD simulations [3], these interactions are relevant for the interdigitation dynamics of the outermost dendritic branches of neighboring molecules, which exist to minimize local density gradients that are inherently present in the periphery of DPs.



In order to approach the intrinsic properties of these interesting materials, we performed modifications to our prototype “classic” DPs [2] (Fig. 1a) aimed at enhancing or suppressing their intermolecular hydrogen-bonding interactions through incorporation of strongly hydrogen-bonding ureidopyrimidinone (UPy) moieties (Fig. 1b) or hybridization with oligo(ethylene glycol)-based dendrons [4] (Fig. 1c), respectively. Here, we present the effects of $g = 1-3$, various P_n s and chemical modifications on the thermomechanical properties of these novel DPs, which have been systematically investigated by differential scanning calorimetry and linear viscoelastic measurements. The studied DPs undergo very slow ageing owing to the reduced global mobility of these bulky molecules. Even so, their segmental mobilities are increased in the hybrid DPs and constrained in the UPy DPs, which translates into vastly different equilibration times and glass transition temperatures. The very large entanglement molecular weight of the classic DPs causes a frequency dependent rheological response, which is typically characterized by low values of the entanglement plateau modulus in the low frequency regime, similarly to bottlebrush polymers but tunable through both g and P_n . At it, UPy-functionalization broadens the scope of rheological responses even further (Fig. 2). Our results demonstrate remarkable effects of the chemical structure on the viscoelastic properties of such super soft elastomers with ultra-high molar mass and pave the way into exciting applications.

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Layer-Controlled Colloidal Dispersions of Two-Dimensional Organometal Halide Perovskites for Efficient Blue Light-Emitting Diodes

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Two-dimensional (2D) organometal halide perovskites exhibit the quantum confinement effect by reducing the thickness smaller than the Bohr radius, or ~ 10 unit cell thick (i.e., $n < 10$). Their colloidal dispersion is emerging as one of the most promising candidates for printable optoelectronics and nanocomposites. However, it is not yet possible to synthesize large quantities of high-photoluminescence-quantum-yield (PLQY $> 20\%$) 2D perovskites with precisely controlled stacking, as is necessary for light-emitting diodes (LEDs). Here, we demonstrate a synthesis method for the large-scale production of monolayer ($n = 1$), trilayer ($n = 3$), and 5-layer ($n = 5$) 2D methylammonium lead bromide (MAPbBr₃) colloidal dispersions, which exhibit blue PL emissions at ~ 431 nm, ~ 456 nm, and ~ 485 nm, respectively, with high PLQYs (50% - 80%). The carefully-controlled ligand chemistry allows small lateral size and surface passivation, minimizing the effects of self-quenching and downhill energy transfer. The high PLQY has led to a record-high external quantum efficiency (EQE) of 0.2% in the blue LED devices, representing a >500 -fold increase compared to that of the best blue organometal halide perovskite LED reported so far. The solution-based process is expected to allow low-cost and high-throughput production, as well as the deposition of the new family of 2D materials onto arbitrary substrates.

PEGylated chelator-based calcium phosphate nanoparticles for gene deliveryX. Huang¹, D. Andina¹, J.-C. Leroux^{1*}, B. Castagner^{2*}

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Calcium phosphate (CaP) is a natural material and the main inorganic constituent of bone and teeth. The transfection method based on CaP-DNA co-precipitation developed in the 1970s[1] is very attractive because CaP materials exhibit low toxicity, are easy to prepare from low cost starting materials, and have high gene condensing efficacy. However, the rapid growth of calcium phosphate particles after preparation prevents their *in vivo* application. Therefore, several strategies have been used to control the growth of the CaP nanoparticles including polymer hybrid, lipid or DNA/siRNA coatings. In recent years, a PEGylated chelator coating strategy was developed in our laboratory,[2] where PEG-bisphosphonate (PEG-BP) and PEG-inositol 1,3,4,5,6-pentakisphosphate (PEG-IP5) conjugates were used to efficiently stabilize CaP-DNA/siRNA nanoparticles with a particle size between 200 and 260 nm.

Here, we present a systematic study of the impact of the chelator and preparation method on the particle size, morphology, and *in vitro* uptake and transfection activity. First, a new synthesis route involving click chemistry was developed to prepare the PEGylated chelators PEG-IP5 and PEG-BP. We then studied the binding affinity of two chelators to hydroxyapatite and the Langmuir binding isotherm demonstrated that IP5 (Langmuir constant K $3.17 \pm 0.69 \times 10^5$ L mol⁻¹) was a better CaP binder than bisphosphonates (K $1.29 \pm 0.17 \times 10^5$ L mol⁻¹). The morphology of particles prepared using the previously published method (method 1) consisted of amorphous aggregated spheres with a particle size about 200 nm. We also developed a novel particle preparation method (method 2) that yielded partially crystalline particles with needle-bundle like morphology and sizes of about 80 nm.. We further showed that PEG-IP5 stabilized nanoparticles had different uptake and transfection efficiency in HepG2 cells depending on the preparation method. The uptake was about 10 folds higher for particles prepared by method 1 vs. method 2. This greater uptake resulted in a 8-fold higher transfection efficiency. These differences are ascribed to the distinctions in size and PEG density of the two types of particles. We further showed that the uptake of the larger particles was enhanced by sedimentation. This work highlights the impact of the preparation method on particle size, morphology, uptake and transfection efficiency and provides new insights for the application of CaP nanoparticles as a gene delivery vector.

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Functionalization of arrays of silica nanochannels by post-condensationN. Zucchetto¹, D. Brühwiler^{1*}¹Zurich University of Applied Sciences, ZHAW

Functionalized arrays of silica nanochannels (ASNCs) were prepared by post-condensation of amino-functional alkoxy-silanes (NH-silanes). The method of post-condensation combines postsynthetic grafting and co-condensation - the classical pathways for the functionalization of mesoporous silica - to afford a convenient one-pot reaction in aqueous medium. The structure of the NH-silanes determines the distribution of the surface-bound groups in the ASNCs. Accumulation at the channel entrances was observed by confocal laser scanning microscopy in the case of sterically hindered NH-silanes [1], whereas smaller NH-silanes led to a more uniform distribution. In all cases, the channels remained accessible for additional postsynthetic treatment or introduction of guests after extraction of the structure-directing agent. Particle size and morphology, as well as pore size and degree of ordering of the amino-functionalized ASNCs were comparable to pristine ASNCs [2].

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Ferrocene derivatives: new mechanophore for stimuli-responsive materials

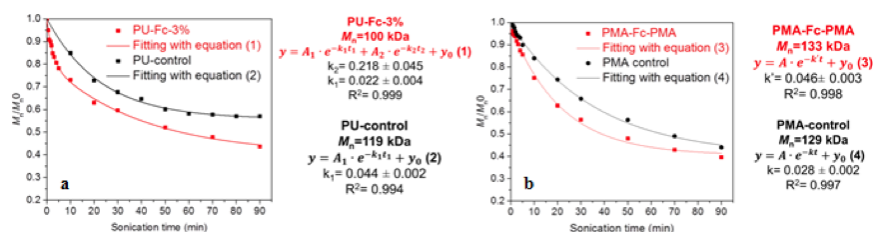
M. Di Giannantonio¹, M. Ayer², E. Verde Sesto², C. Weder², K. Fromm^{1*}

¹University of Fribourg, ²Adolphe Merkle Institute

Since long, ferrocene and its derivatives have attracted the attention of the scientific and technical community because of its fascinating chemistry. Due to its easy functionalization and unusual and attractive properties, ferrocene derivatives have found different applications in material science, such as sensors, catalysts, polymers, electro active materials and medicinal chemistry^{1,2}.

Linear poly(methyl acrylate) and polyurethanes with a number of covalently linked ferrocene units in the backbone were successfully synthesized. Upon exerting a mechanical stress (e.g. ultrasound induced degradation³, in solution), we expect the polymer to break along the weakest bonds, i.e. the ferrocene moieties. In order to verify this hypothesis, we analyze the physico-chemical properties and changes of the polymers following sonication in solution by SEC (Size Exclusion Chromatography) or using techniques such as the atomic force microscope⁴ (AFM) in collaboration with Prof. M. Borkovec (Geneva), in order to understand their potential as stimuli-responsive materials.

In collaboration with Prof. C. Weder (Adolphe Merkle Institute, Fribourg) the first mechanical tests in solution were performed with the linear polyurethane (Fc 3%) and poly(methyl acrylate), stretching the polymer in order to selectively break the weak bonds. The first results obtained by a kinetic study (**Fig. 1 a-b**) show that ferrocene moieties are potential mechanophores in a linear polymer. The synthesized ferrocene-based polymers will be further studied exploiting the AFM⁴ and other techniques to confirm these preliminary findings.



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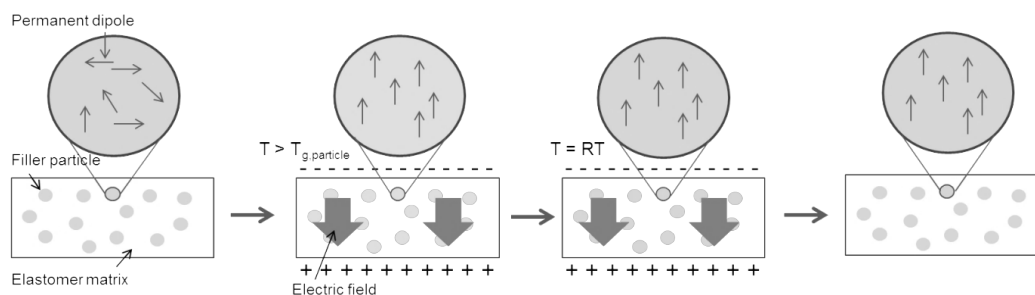
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Piezoelectric Elastomer Composites

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¹EMPA Dübendorf, ²EPF Lausanne

The aim of this work was to synthesize a piezoelectric elastomer composed of a chemically cross-linked polydimethylsiloxane (PDMS) matrix, blended with nanoparticles of poly(methyl methacrylate)-*co*-(4-[ethyl (2-hydroxyethyl)] amino]-4-nitrobenzene) copolymers which has been poled at elevated temperatures under an electric field. An overall polarization was thus imparted on the material, which upon deformation leads to a piezoelectric response. [1] The copolymer was first prepared *via* free radical polymerization and processed using nanoprecipitation [2] to obtain nanoparticles with a diameter of 50 nm, as can be proven using dynamic light scattering spectroscopy and secondary electron microscopy. The copolymer particles were homogeneously dispersed in a PDMS matrix which was cross-linked to obtain free standing films. The poleability of the constituent materials and the composite was tested with the thermally stimulated depolarization technique, as well as impedance spectroscopy. The mechanical properties of the composite were tested using tensile tests. The piezoelectric constant was measured using the Berlincourt method.



By combining different polable copolymers with elastomeric matrices a high tuneability of electrical and mechanical properties is expected. [3]

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Solid-state NMR spectroscopy of silica and silica-biopolymer hybrid aerogel

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The properties of silica aerogels, and the ability to prepare them by ambient pressure drying, hinge on their surface modification, but until now, the surface chemistry has eluded quantitative analysis. Here, we develop solid-state NMR as quantitative tool [1] and determine the surface chemistry of different archetypal hydrophobic silica aerogels/foams with ¹H, ¹³C and ²⁹Si and ¹H-²⁹Si heteronuclear solid state NMR spectroscopy [2]. The quality of the external calibration, the validation by elemental analysis and the consistency between the ¹H, ¹³C and ²⁹Si data, enable us to quantify the surface chemistry of these classical silica aerogel materials. The aerogels display remarkably similar chemistries despite their very different precursors (alkoxide, waterglass), hydrophobization agent (hexamethyldisilazane, trimethylchlorosilane, hexamethyldisiloxane) and gelation and hydrophobization solvents (water, ethanol, heptane). The trimethylsilyl content is nearly constant (22-27 wt%) and the ethoxy content is low. The ¹H-²⁹Si heteronuclear correlation spectra provide unambiguous evidence for the grafting of the trimethylsilyl groups on the silica surfaces and, for biopolymer-silica hybrid aerogels, the homogeneous dispersion of pectin [3] and chitosan on the silica surface (Figure 1).

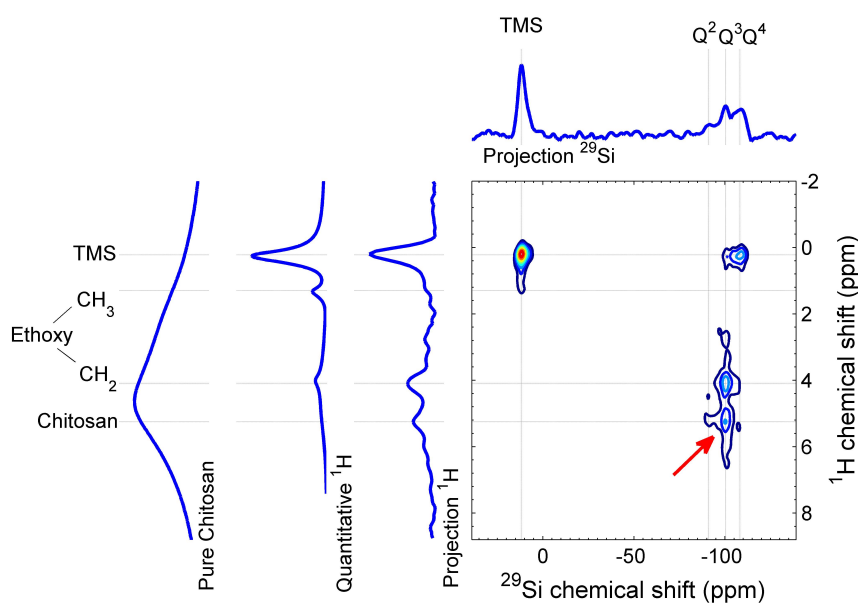


Figure 1. Solid-state ¹H-²⁹Si heteronuclear correlation NMR spectrum of a chitosan-silica aerogel hybrid. The red arrow points to the strong correlation between the chitosan protons and the silica surface (Q³); the other cross peaks are typical for silylated silica aerogels.

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Design of poly(N-isopropylacrylamide)-silver nanocomposites for biomedical applications

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In the last decades, polymeric materials have attracted a significant interest in the biomedical field especially in their use as implants. With the emergence of new multi-drug resistant bacteria and despite the advanced sterilization procedures, the contamination of implant surfaces by bacteria is a new challenge to overcome.¹ Then, the design of new antibacterial/bactericidal surfaces in order to prevent bacterial adhesion and biofilm formation is an important task.

Silver has already been proven to be effective against bacterial infections even at low concentration (0,1-10 ppm).³ Furthermore, it has been demonstrated that nano-sized silver could be even more efficient due to a better interaction with bacteria and a more long-term activity compared to compounds based on ionic silver.⁴

In this study, we focus on the synthesis of nanocomposites composed of silver nanoparticles and of the well-known poly(N-isopropylacrylamide) (PNiPAAm). This polymer is widely studied for biomedical applications especially in tissue engineering owing to its good biocompatibility and thermos-sensitivity with a critical solution temperature (LCST) close to 32°C. In practice, the polymer is readily soluble below this temperature, while above the LCST, it becomes insoluble and precipitates out.⁵

In the context of this work, the polymer was synthesized by RAFT polymerization in order to provide additional silver binding sites at the sulfur atoms. Nanocomposites with different ratios of silver-to-polymer have been prepared.

Ionic Conductivity and Lithium Ion Transference Number in Lithium Ion Battery Separators: Membrane Geometry versus Surface Chemistry

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¹ETH Zürich

Li-ion battery (LIB) separators are porous membranes that electronically isolate the battery's electrodes yet allow ionic transport between them. As a result, the optimal separator design is a tradeoff between high cycling performance and battery safety [1]. Up to now, separator membranes have mainly been evaluated based on geometrical considerations with high porosity thought to yield high ionic conductivity and high tortuosity thought to increase cell safety by reducing dendrite growth [2].

Here, we investigate how the surface properties of separator membranes, such as the surface charge or functional groups, influence the performance of lithium-ion batteries. For this purpose, we modified commercially available polyethylene separators with layers of selected polyelectrolytes. The polyelectrolyte coatings are thin (~1 nm) and therefore do not significantly alter the separator's geometry. This is confirmed by scanning electron microscopy and air permeability measurements. The polyelectrolyte-modified separators are electrochemically stable and show a thermal stability comparable to that of the unmodified membranes. Polyelectrolyte modifications significantly reduce the hydrophobicity of the polyethylene separators resulting in reduced contact angles with water and polar solvents like EC and PC [3], and a higher electrolyte uptake. This reduced hydrophobicity also results in notably improved electrochemical properties, namely, electrolyte conductivity and lithium-ion transference number as confirmed by electrochemical impedance measurements.

We find that the electrochemically determined electrolyte conductivity of the pristine separator is considerably lower compared to what is predicted by the separator's geometry. The polyelectrolyte modifications significantly increase this value and thereby show that surface chemistry has a strong influence on separator performance.

Testing the cycling performance of cells assembled with the modified separators, we show that polyelectrolyte-modified separators improve a battery's cell potential and C-rate capability. We demonstrate through complementary Comsol simulations that this effect is primarily caused by increased transference numbers.

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Self-Assembly of Gold Nanoparticle at Liquid-Liquid Interfaces: the Role of the Interfacial Surface Tension

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¹EPFL Valais Wallis, SB ISIC LEPA

Over the years many techniques and methods have been proposed to self-assemble nanoparticles (NPs) at liquid-liquid interfaces. However, vast majority of them are dedicated to reduce the Coulombic repulsion between nanoparticles with salts or aggregation “promoters”,^{1,2} to charge a gold core^{3,4} or to use solvent evaporation.⁵ However, self-assembly of gold nanoparticles (AuNPs) at a liquid-liquid interface can also be achieved by decreasing the interfacial surface tension rather than decreasing the Coulombic repulsion.

Here, propylene carbonate (PC) having an extremely low interfacial surface tension with water was examined towards the formation of lustrous nanofilms even without tetrathiafulvalene (TTF) molecules. Presence of TTF slightly changed wetting properties of AuNPs and allowed them to cross the interface forming new colloid of AuNPs@TTF charged particles in PC (Fig.1A). AuNPs@TTF in PC phase had a distinguishable UV-Vis extinction spectrum from a nanofilm (Fig. 1B). Qualitative calculations confirmed experimental observations. Among potential applications there are: fabrication of ultra-concentrated AuNPs suspensions for ink-jet printing, electrically-driven liquid mirrors, as well as biphasic SERS.

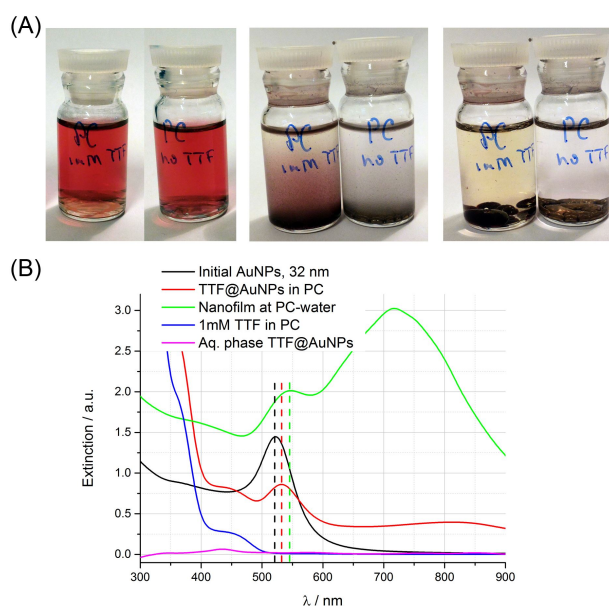


Figure 1. (A) Photographs of PC-water system. From left to right: before, right after shaking, and after complete phase separation with and without TTF in the PC phase at the bottom. **(B)** UV-Vis spectra of the initial solutions, the spectra of the aqueous and PC phases after complete phase separation and the extinction spectra of nanofilms formed at the given LLI.

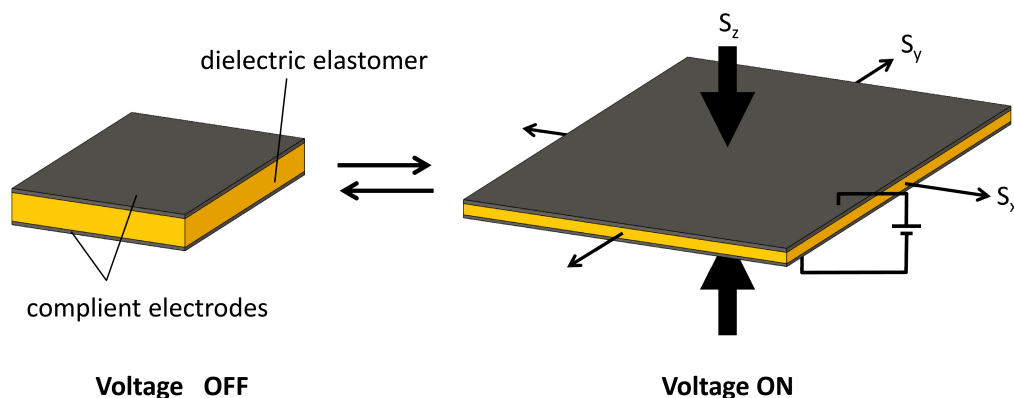
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Polar Siloxanes for Dielectric Elastomer Actuators

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Silicone elastomers are often used as dielectric in dielectric elastomer actuators (DEA) mainly due to their high flexibility and stretchability, good mechanical and insulating properties. Nevertheless, they have the disadvantage of a low permittivity, typically below 3, which inherently leads to high driving voltages to acquire useful actuation.



In the presented work, high permittivity silicone based materials were synthesized by modifying the siloxane backbone with polar side groups. The synthesis is based on the fast and quantitative conversion of the vinyl groups of high molecular weight polymethylvinylsiloxanes with thiols *via* thiol-ene reaction. A simple one-step process in which the dipole grafting and the crosslinking occurred simultaneously, allowed the formation of soft high permittivity silicone films with suitable elastic properties for DEA.

Silicone elastomer containing varying amount of polar nitrile groups were prepared. The obtained elastomers feature permittivity values up to 17, which is nearly 6 times higher than for commercial silicone. Furthermore the mechanical properties and electromechanical response of these novel materials were investigated.

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Hydrophobization of silica aerogels by mixed alkoxy silanes

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Aerogels are amorphous mesoporous materials with a diverse range of exceptional physical properties and numerous potential applications such as thermal insulation, catalysis and oil/water separation. Silica aerogels are particularly promising for commercialization due to the possibility for ambient pressure drying (APD) which significantly reduces the production costs. In order to perform APD, silica gels must be hydrophobized with organic functional groups to prevent shrinkage of the gel during drying. We performed a parametric study how modification with pure mono- (M), di- (D) and trifunctional (T) alkoxy silane compounds and their mixtures influence the shrinkage process and final aerogel characteristics such as density, surface area and pore size. Water uptake of hydrophobized samples is measured at different relative humidity and showed that even small addition of trifunctional alkoxy silane significantly improves the hydrophobicity. SEM images revealed formation of superhydrophobic microstructures in the case of pure trifunctional alkoxy silane modification. Solid state NMR is used to analyze connectivity and rearrangement of alkoxy groups after the hydrophobization of silica aerogels.

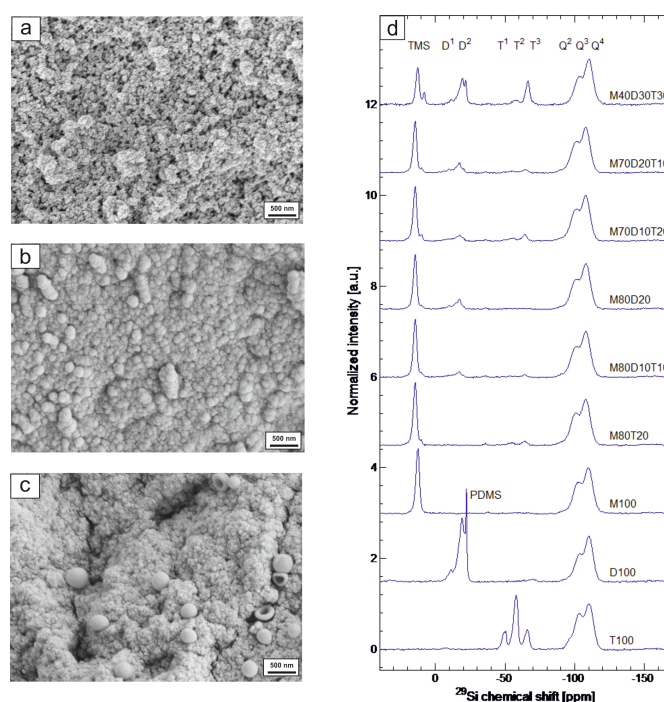


Figure 1. SEM of silica aerogel topography after modification with a) monofunctional b) difunctional c) trifunctional alkoxy silane d) ¹H-²⁹Si cross polarization NMR spectra of silica aerogels hydrophobized with various hydrophobization agents.

Water sorption behavior of physically and chemically activated monolithic nitrogen doped carbon

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¹Empa, ²IBM Research GmbH

Adsorption heat pumps (AHP) have recently gained growing interest by engineers and planners as they are considered an environmental-friendly and cost-effective alternative to compressor-based heat pumps. AHPs utilize waste heat rather than electrical energy to provide space heating and cooling. The state of the art in the field of adsorption cooling cannot be considered as wholly satisfactory because of poor adsorbent material efficiency. Ordered mesoporous silicates are appreciated for their high water uptake, but offer poor heat transport properties. To address these issues, monolithic adsorbents have been proposed to enhance heat transport.¹

In this work, resorcinol-melamine-formaldehyde (RMF) resins were synthesized, pyrolyzed and physically activated with CO₂. The influence of the activation time on the physicochemical properties and the water sorption behavior was investigated. Furthermore, a comparison between physical activation with CO₂ and chemical activation with KOH is presented. Carbon monoliths with high water sorption capacity (45wt.%) can be obtained by pyrolysis and CO₂ activation (800°C, 3hours), resulting in a significantly increased BET surface area of 1200m²/g. During the CO₂ activation treatment, O and N containing surface functional groups are better preserved than with KOH activation. Materials performance validation in an adsorption chiller test setup for a temperature step from 90°C → 50°C, reveal that CO₂ activated RMF carbons exhibit a maximal specific cooling power which is a factor of 1.7 higher in comparison to a commonly used, commercial silica gel reference material (430 W/kg compared to 255 W/kg). This is surprising considering that the CO₂ activated carbon is still comparable hydrophobic. The superior performance of carbon based sorbents is believed to originate from the superior heat transport properties and higher surface area (water uptake capacity) of monolithic carbons over commercial silica gels. At an optimum temperature swing 60°C → 30°C, the RMF derived carbon yields a specific cooling power 3.2 times greater than that of the silica gel reference.

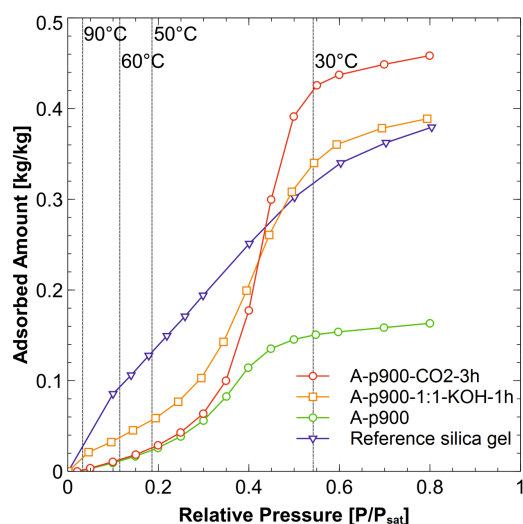


Figure 1. Water sorption isotherms of pyrolyzed and activated RMF resins and the reference silica gel

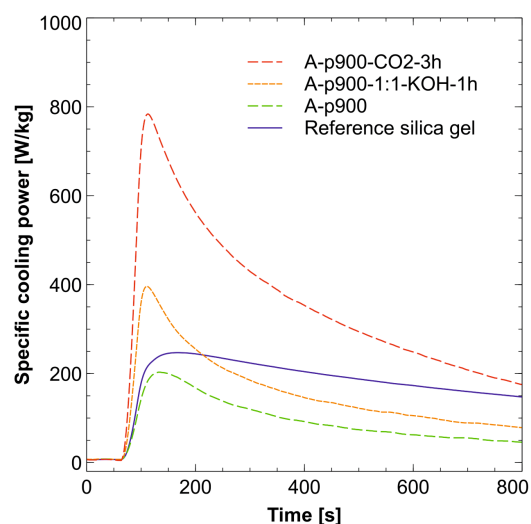


Figure 2. Specific cooling power at temperature step 60°C → 30°C. The temperature step was initiated after 60 seconds.

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Self-cleaning, reliable and accurate: new nanostructured device takes electroanalysis of neurotransmitters to the next level

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The detection and quantification of neurotransmitters in biological fluids is of paramount importance for the clinical diagnosis of behavioral diseases and even some kind of tumors (e.g. pheochromocytoma). The application of electroanalytical techniques would significantly reduce overall costs and time of analysis; nevertheless two major issues make it a challenging task: interfering species and fouling. Ascorbic acid and uric acid are the most common interferents: they are ubiquitous in biological fluids, with concentrations 1000-fold higher than that of neurotransmitters, also their electrochemical properties dramatically overlap with those of catecholamines such as dopamine and norepinephrine. These, in turn, have a strong tendency to irreversibly adsorb to electrode surfaces causing heavy fouling and premature failure of the sensing device.

To overcome these issues, we designed an innovative composite electrode based on silver nanoparticles sandwiched between a silica and a titania layer, supported on conductive glass. The fabrication process is simple and relies on sol-gel technology. The resulting electrode is transparent, mechanically robust, highly performant in terms of sensitivity and selectivity and, above all, self-cleaning.[1] This latter property allows regenerating the electrode performances simply by UV light irradiation, which removes any contamination. The cleaning step can be performed even using low-power LED UV sources and directly in solution, opening the door for *in situ* applications.[2]

This electrode has been tested in cerebrospinal fluid, plasma and urine mimics, allowing accurate and reproducible electroanalytical detection and quantification of dopamine, norepinephrine and serotonin even in mixed samples and in presence of biologically relevant concentrations of interferents.[3] Most of all, these performances were stable, *i.e.* they were not affected by repeated (> 50) cycles of cleaning.

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Efficient Anion-Exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, I)

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Postsynthetic chemical transformations of colloidal nanocrystals, such as ion-exchange reactions, provide an avenue to compositional fine-tuning or to otherwise inaccessible materials and morphologies. While cation-exchange is a facile and commonplace process for numerous colloidal semiconductor nanocrystals, anion-exchange reactions have not received substantial deployment. Here we present fast, efficient, deliberately partial, or complete anion-exchange at low-temperature in highly luminescent semiconductor nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, I). The bright photoluminescence can be easily tuned over the entire visible spectral region (410 – 700 nm) by simply adjusting the halide composition while maintaining the characteristic high quantum yields of 20-80% and narrow emission line widths of 10-40% (from blue to red). Moreover, homogeneous mixt halide compositions like CsPb(Cl/Br)₃ or CsPb(Br/I)₃ can be easily obtained via a fast internanocrystal anion-exchange simply by mixing CsPbCl₃, CsPbBr₃, and CsPbI₃ nanocrystals in appropriate ratios.

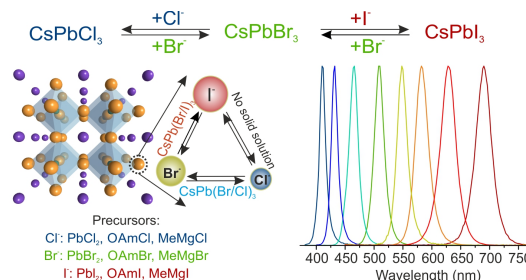


Figure 1: Anion-exchange in the colloidal semiconductor CsPbX₃ perovskite nanocrystals and the tunability of the bright emission over the entire visible spectral region via anion-exchange.

G. Nedelcu et al. *Nano Letters* **2015**, *15*, 5635-5640.

From supramolecular to covalent Polymers via disulfide crosslinkingG. Picca¹, R. Häner^{1*}

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Supramolecular polymers are macromolecules obtained by the self-assembly and self-organization of repeating, non-covalently linked units.^[1] The structural and functional properties of supramolecular polymers largely depend on the nature of the noncovalent interactions between the individual units. Therefore, the macroscopic properties of the system are strongly dependent on the supramolecular organization and not solely defined by the properties of the molecular components.^[2] Herein, we are describing a pyrene-derived trimer (**Figure 1**) for the preparation of covalent polymers from supramolecular scaffolds via S-S bond formation to evaluate the supramolecular structure. Pyrene molecules are connected each other by a phosphate group and the structure ends with a thiol group at the two extremities.

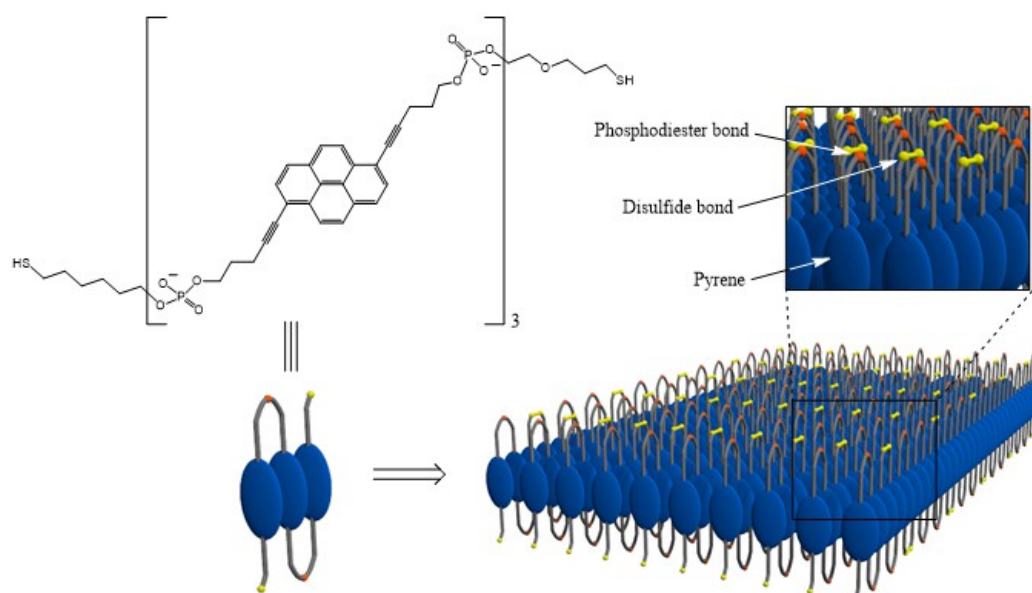


FIGURE 1: Pyrene trimer self-assembly

The aim of this project is to follow the self-assembly process in the presence of alkylthiol chains and additional phosphates, in particular if supramolecular polymers can be linked to covalent 2D polymers via disulfide formation. Spectroscopic measurements and crosslinking results will be shown.

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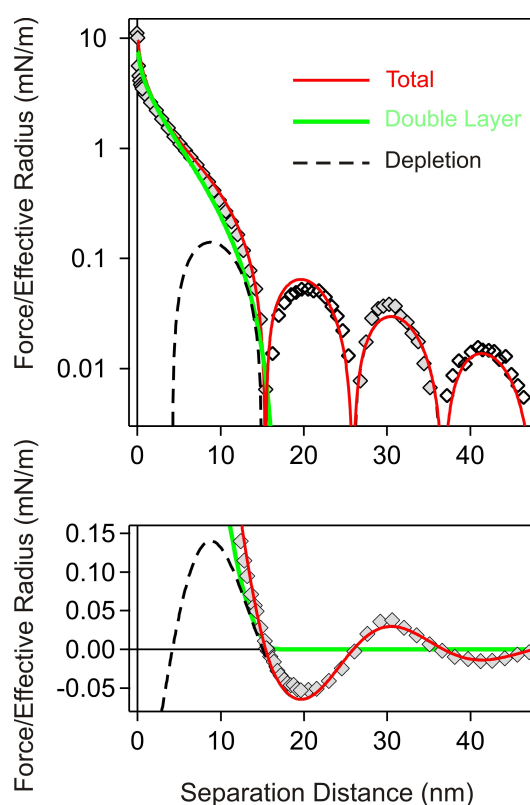
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Study of Electrical Double Layer in Solutions of Like-Charged Polyelectrolytes Using an Atomic Force Microscopy

M. M. Gudarzi¹, T. Kremer¹, V. Valmacco¹, P. Maroni¹, M. Borkovec¹, G. Trefalt¹

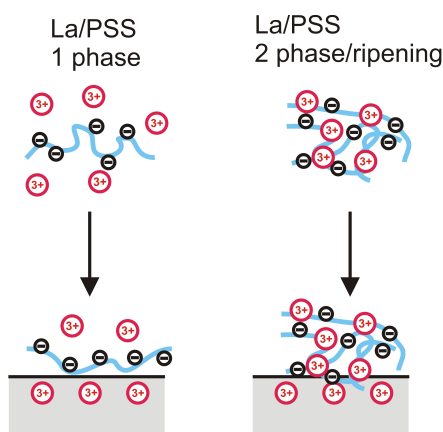
¹University of Geneva

Interactions among charged interfaces control the stability and the phase behavior of colloidal suspensions. Ionized species in solution interact with the interface in Coulombic fashion and like-charged species repelled from the interface, forming an electrical double layer (EDL). In concentrated solutions of like-charged polyelectrolytes, however, the EDL's structure is distorted from the classical picture. Here, we studied surface forces between negatively charged silica particles in the presence of a like-charged strong polyelectrolyte using a colloidal probe atomic force microscopy. We explore the low salt regime, where the number of ionic species in solutions is determined by polyelectrolyte concentration. The force profiles can be quantitatively interpreted as a superposition of depletion and EDL forces. Poisson-Boltzmann theory can quantitatively predict the EDL forces provided the polyelectrolyte molecules are treated as highly asymmetric electrolyte. Long-ranged and non-exponential EDL forces originate from large effective charges (Z_{eff}) of polyelectrolyte molecules due to their exclusion from the interface. We found that Z_{eff} is always lower the bare charge (Z) of polyelectrolytes due to counterion condensation. The ionization fraction (Z_{eff}/Z) indeed matches with experimental results and Manning theory.



Polystyrene sulfonate adsorption on silica induced by multivalent counterionsT. Kremer¹, A. Tiraferri², P. Maroni¹, M. Borkovec^{1*}¹University of Geneva, ²Polytechnic University of Turin

Polyelectrolyte adsorption on opposite charged surfaces has been extensively used in some industrial processes like water treatment, papermaking and surface coating due to possibility of formation thin films and controlling suspension stability. Alternative mechanisms involving polyelectrolyte layers formation on like-charged solid surfaces assisted by multivalent ions from diluted aqueous solutions are not elaborated topic so far, with some exceptions.[1] For these reasons we present experimental results showing that polystyrene sulfonate (PSS) adsorption on silica can be triggered by multivalent ions of high charge density (La^{3+} , Mg^{2+} , Ba^{2+}). While there is no adsorption in the presence of Na^+ , the PSS adsorbs in the presence of Ba^{2+} , Mg^{2+} and La^{3+} . PSS adsorbed mass was monitored by means of highly sensitive optical reflectometry and gravimetry techniques (QCM). To get a better insight in whole mechanism, silica zeta potential in presence of multivalent ions listed above was determined by streaming potential measurements on silicon wafers.



Main significance in this study is placed on PSS layers formation on silica interface stimulated by trivalent lanthanum ions. Considering two different phase states occurring for PSS/ La^{3+} mixture, two distinct film growth trends were noticed; so called ripening at two phase and regular trend, characteristic for monolayer formation, at one phase. It has been shown that precipitation rate increases with increasing LaCl_3 concentration. The obtained film also contains a large amount of water. According to these results, driving forces for PSS adsorption actually originate, depending on phase composition, either from La^{3+} adsorption on silica or short ranged bridging interactions. Unlike La^{3+} , some polarizable complex multivalent cations (like $\text{Co}(\text{NH}_3)_6^{3+}$) do not induce PSS adsorption on silica, although phase separation for that system was observed, probably because of different aggregation kinetics, precipitation range and silica charge in that case. Our findings contribute to better understanding not only adsorption mechanism and polyelectrolyte film structure but also the behavior of polyelectrolyte solution containing multivalent ions.

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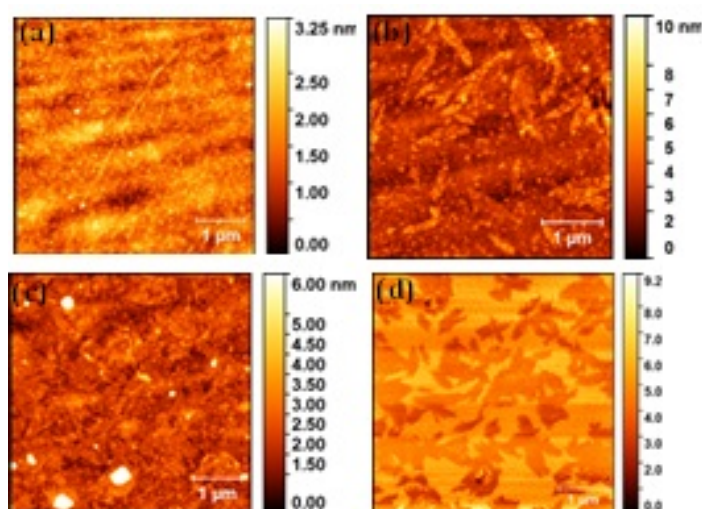
Self-Assembled Monolayer (SAM) of Cyanine Dye J-Aggregates on Surfaces for Mesoscopic Solar Cells

S. B. Anantharaman^{1,2}, F. Nüesch^{1,2}, J. Heier²

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Cyanine dyes (Cy3) which can self-assemble to form J-aggregates in solution are promising for solar cells application. Further tuning the self-assembly of these molecule on surfaces to form a crystalline monolayer on functionalized glass surface will be the focus of this study.

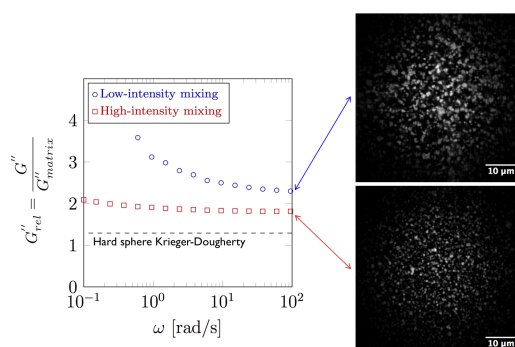
Cyanine dye (Cy3, TDBC) when dissolved in water, forms J-aggregates with molar extinction coefficient of $2.071 \times 10^5 \text{ cm}^{-1}$ and full-width half maximum (FWHM) width of 13.2 nm. Glass substrates functionalized with a monolayer of polyamidoamine (PAMAM) dendrimers (4th generation) can help to achieve plate-like J-aggregate morphology. Upon investigating an alcoholic route, with methanol as co-solvent to water in equivolume ratio, the dye monomers assemble to form a J-aggregate film. This is ascribed to the in-situ nucleation of J-aggregates on PAMAM substrates. Fluorescence spectroscopy studies of J-aggregate films when excited at 550 nm showed a Stokes' shift of 3 nm between the absorption and emission peak, a characteristic of excellent energy transport. Using this monolayer as active layer, its application in solar cells will be discussed in this work.



Topography of glass surface functionalised with PAMAM monolayer (a) covered with J-aggregates in plate-like (b) and in monolayer form (c) Phase image showing the J-aggregates in monolayer (d).

Investigating partially dispersed colloidal suspensions by high-frequency rheology.B. Schroyen^{1,2}¹ETH Zurich, ²KU Leuven

Nanoparticle based materials have substantial potential due to novel functionalities associated with the nanoscale. However, to express this functionality the particles need to be well dispersed. The actual morphology of nanodispersions is much more complex than often realized: even well-dispersed nanoparticles eventually aggregate in the formation of clusters. Typical methods for dispersion analysis such as electron microscopy or scattering methods only study the local microstructure and often provide data that are non-trivial to analyze. In some cases, classical rheological measurements can be used quantitatively to offer an integrated picture of the state of dispersion. To extend the applicability of these techniques high-frequency dynamic measurements are needed to determine the degree of dispersion. The aim of this research is the development of a general framework to assess dispersion quality. A home-built piezo-rheometer is developed to extend the dynamic frequency range of classical rheological measurements. As such, both conventional and high-frequency measurements are combined with optical methods such as confocal microscopy to offer an integrated view of the quality of a dispersion.



Dynamic rheological measurements and confocal images of fluorescent silica particles partially dispersed in PDMS by Ultra-Turrax mixing at different intensity.

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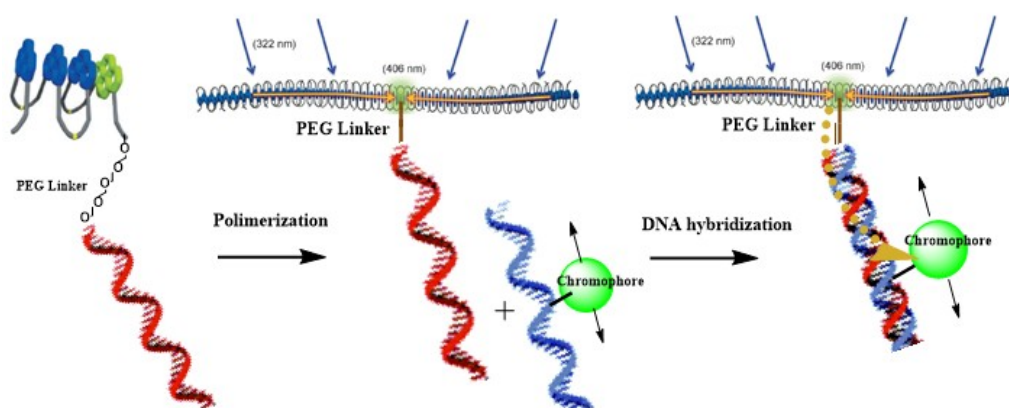
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Efficient light-harvesting Antenna through the intermediate donor-acceptor pyrene derivative

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Efficient artificial light-harvesting antennas composed of multichromophoric array in a DNA scaffold are nowadays a key aspect in the supramolecular photochemistry [1]. Recently it was reported that the phenanthrene-pyrene supramolecular polymers can efficiently absorb photons which are transferred to the pyrene collection centre [2]. To expand this idea, 3,6-dialkynylphenanthrene trimer and new pyrene related oligomers were synthesized. As the DNA scaffolds are ideal platforms to organize chromophores the interesting point due to energy transfer is to introduce another acceptors in well-defined interchromophore distance from pyrene. This approach can be done by introducing complementary strand which contains appropriate chromophore in different position. Such a supramolecular complexes were investigated with different spectroscopic methods to prove efficient harvesting and transport of energy to the acceptor core through the intermediate donor-acceptor pyrene derivative.



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Polymer brushes: new opportunities for their patterning and characterizationG. Panzarasa¹¹Empa Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland

Polymer brushes, surface-confined macromolecules, are a key topic in polymer nanotechnology and one of the most versatile tools for the engineering of surfaces and interfaces. The goal of the present talk is to review recently described and extremely promising approaches for the patterning and characterization of polymer brushes: photocatalytic lithography, electrochemical impedance spectroscopy and positron annihilation spectroscopy.

Photocatalytic lithography relies on the ability of some semiconducting oxides (especially titanium dioxide) to efficiently degrade organic compounds under near-UV irradiation. This property allows to make patterns of surface-grafted initiators, which can then be amplified into polymer brushes by grafting-from. Compared to classic photolithography, photocatalytic lithography (both direct and remote) enables the patterning of polymer brushes with unprecedented ease without the need of resists and intense UV sources. Moreover, the possibility to use conventional as well as self-assembled nanospheres as photomasks allows to obtain both micro- and nanostructures.[1,2]

Silicon wafer is the most common substrate for the production of polymer brushes. However, despite being the material of choice for microfabrication, it displays very poor electrochemical properties due to its insulating native oxide. Using state-of-the-art electrochemical techniques, namely cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), we were able to demonstrate that grafted-from polymer brushes can efficiently overcome this problem, paving the way for the development of electrochemical devices based on silicon.[3]

Probing the distribution of nanoparticles in stimuli-responsive brushes is of paramount importance to understand the properties of such complex nanocomposites. Positron Annihilation Spectroscopy (PAS) is a non-destructive technique, based on the implantation of positrons in a matrix and on the study of the resulting annihilation features. The usefulness of PAS for the study of polymer brush-nanoparticle composites arises from its sensitivity to nanometer- and subnanometer-sized holes and on the possibility to extract details on the chemical composition of the probed environment. We described for the first time [4] the application of PAS to a nanocomposite obtained by loading silver nanoparticles into poly(dimethylaminoethyl methacrylate) brushes. PAS not only allowed us to obtain a rapid and accurate discrimination between protonated and deprotonated states, but also to identify changes in the mass density of the brushes films embedded with silver nanoparticles and the introduction of new defects associated to the brushes/nanoparticles interface.

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Artificial lipid droplets covered by a monolayer of sphingomyelin and cholesterol

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Artificial lipid droplets (LD) named nanoemulsions of LD bearing a polar lipid monolayer surface may serve as a useful lipid membrane model complementary to a vesicle lipid bilayer or lipid monolayer formed at the water/air interface. Nanoemulsions of LD are thermodynamically metastable and kinetically stabilized by a surfactant. Furthermore, they share several physico-chemical characteristics in common with natural LD. These natural LD have fundamental roles in metabolism, and may also be involved in various diseases. Hence, a well-characterized and defined artificial LD system would be convenient because natural systems are usually very complex and less stable. Our study focuses on the characterization of nanoemulsions of LD composed of a trioleoylglycerol (TOG) core coated with a sphingomyelin (SM)/cholesterol (Chol) monolayer. This combination of lipids was chosen since SM and Chol are essential for formation of liquid ordered lipid domains found in both artificial lipid mono- or bilayers and biological membranes. Such domains are implicated in multiple biologically important functions. LD covered by combined SM and Chol have been poorly characterized in contrast to respective SM/Chol vesicles. Our study aimed at an improved production and characterization of artificial LD composed of TOG, SM, and Chol, suitable for the use in various research areas. A combined modified reverse-phase evaporation/ultrasonication method was developed for preparation of the LD. Structure of nanoemulsions of LD was investigated by using several methods and techniques. LD parameters such as size and shape, and lipid core and monolayer membrane characteristics were determined.

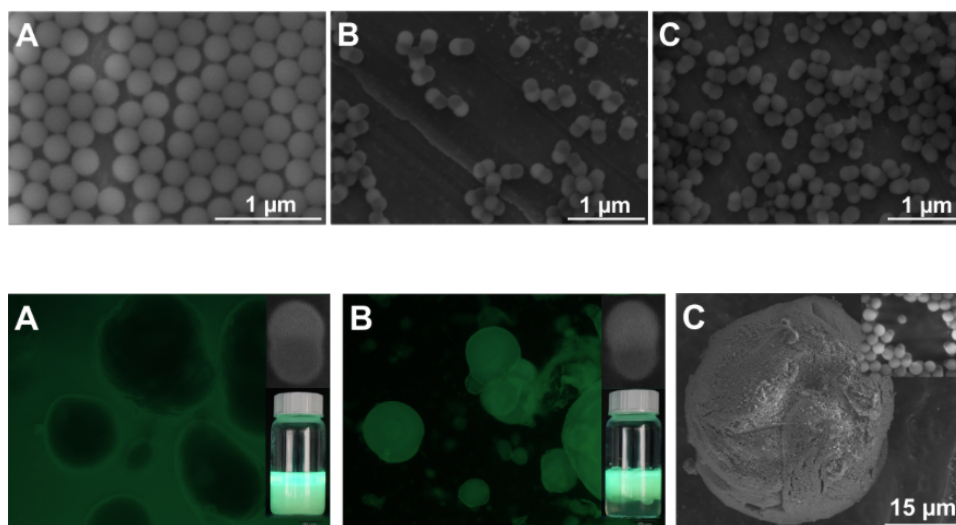
Homogeneous Synthesis of Surfactant-free Janus Nanoparticles and Its Application as Solid Amphiphiles

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The Janus nanoparticles (JNPs) initially conceptualized by Casagrande¹ followed by Paul de Gennes,² were named after the two-faced roman god Janus. Especially, the faces of JNPs processing different hydrophilicities are called amphiphilic JNPs which are similar with molecular surfactants and can be used to stabilize emulsions and forms.³

Here, we report an efficiency surfactant-free seeded polymerization method for synthesizing gram-scale snowman-like Janus nanoparticles (PS-P(3-TSPM)). SEM images clearly show the asymmetric morphologies of synthesized nanoparticles comparing PS seed nanoparticles (Figure 1). In addition, hydrophobic initiator AIBN, hydrophilic initiator APS and amount of second monomer 3-TSPM are used to control the newly appeared 3-TSPM lobe polarity. The resulting JNPs can favour formation of O/W and W/O two kinds of emulsions as solid emulsifier. The emulsion types, sizes and the transferring line of emulsion types are depending on the size of 3-TSPM lobes, types of organic solvent, ratio of water and organic solvent and used initiator (Figure 2A and 2B). Importantly, the AIBN-JNPs can stabilize the Pickering emulsions with PS lobe facing to the hydrophobic Wax and P(3-TSPM) lobe facing to the aqueous phase (Figure 2C).



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Influence of particle anisotropy on cluster rigidity and rheology of colloidal gelsG. Colombo¹, J. Vermant^{1*}¹ETH Zürich

Colloidal gels are a class of soft materials having interesting technological applications. Many of these exploit the reversible solid to liquid transition of weakly flocculated suspensions, typical of thixotropic materials. Even though such complex flow behavior is widespread in a number of consumer products and industrially relevant systems, the changes in microstructure underlying thixotropy remain poorly understood. Recent scaling arguments propose a dependence of the mechanical properties of gels under flow on subpopulations of rigid, isostatic clusters of closely packed particles. Such a scaling does not rely on fractal geometry or glassy dynamics, which only take into account ensemble averaged descriptors and are therefore insensitive to highly localized events, which may determine the rheological response.

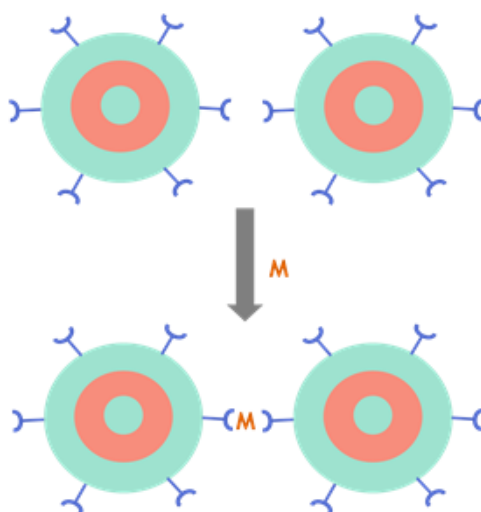
In this work, we intend to test and expand on these ideas of cluster rigidity, by varying the packing behavior in gels changing the particle aspect ratio slightly. We also aim at clarifying the role of microstructural gel anisotropy upon flow, so far neglected in current modeling efforts, whose relevance is confirmed by superposition rheometry measurements. We find mechanical anisotropy in a model colloidal system for thixotropy, with a difference between elastic moduli in axial and rotational direction of up to 2-3 orders of magnitude.

Controlled self-organisation of networks based on $\{M(2,2':6',2''\text{-terpyridine})_2\}^{2+}$ -zipped co-block polymer nanocompartments

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We show how the chelating power of bis(2,2':6',2''-terpyridine)metal(II) complexes can be applied to 'zip' together co-block polymer vesicles to give pre-organized assemblies.¹ Different approaches have been used to functionalize polymer vesicles which condense with appropriately functionalized 2,2':6',2''-terpyridine (tpy) domains; sequential reaction with metal ions e.g. Fe^{2+} leads to an organized assembly. All reactions are carried out under ambient conditions and in aqueous media. The principle of the procedure is shown in the scheme below:



Scheme. Strategy for assembly of arrays of coupled polymer vesicles.

The characteristic MLCT absorption associated with the $\{Fe(tpy)_2\}^{2+}$ chromophore is a powerful probe with which to assess the degree of vesicle aggregation. This along with AFM and TEM studies will be discussed.

The ordered structure of the polymer vesicle assembly provides a platform for an array of artificial compartments for a molecular factory. Surface modification is particularly attractive.² Future directions of the work will be discussed, e.g. encapsulation of components of the 'factory' within hollow vesicles and communication between the compartments.

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Wetting of rough particles at flat liquid-liquid InterfacesM. Zanini¹, C. Marschelke², A. Synytska², L. Isa³¹ETH, ²Leibniz Institute of Polymer Research, Dresden, ³ETH Zurich

Wetting of colloids is one of the most studied phenomena in surface science. It has fascinated researchers since the early decades of 20th century [1,2] and still nowadays presents great perspectives for further investigations. Particularly, wetting of rough colloids has recently gained increasing interest due to the potential of rough particles to stabilise more effectively emulsions and foams [3,4], as well as from a more fundamental point of view in relation to the generation of capillary forces [5,6,7]. Moreover, even if standard colloids are considered to be perfect spheres, they are not necessarily smooth and homogeneous at the nanoscale and those heterogeneities may have a strong impact on the particles' behaviour at interfaces. To date, all investigations on the effects of particle surface roughness have been limited to indirect evidence, linking particle surface properties to macroscopic behavior at interfaces, e.g. aggregation [8], viscoelasticity [9] or motion [10], and systematic microscopic studies are missing. Here, we employ Freeze-fracture Shadow-Casting (FreSCa) combined with cryo-SEM imaging [11] to investigate for the first time the wetting of micron colloids with tailored surface roughness. In this work, all-silica model rough particles with tuneable and controlled surface roughness were synthesised and imaged by FreSCa at flat liquid-liquid interfaces in order to shed light on the role of roughness for the wetting of individual particles in an exhaustive and systematic fashion. We observed that roughness strongly affects the wetting due to contact line pinning and that particles beyond a critical roughness do not even breach the interface.

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Synthesis of amphiphilic giant hollow helices

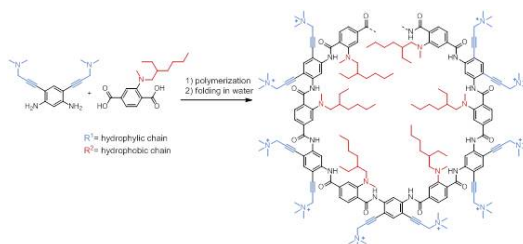
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Tubes are ones of the most present structures in nature, the different size of tube determines the function of these structures. Big tubes, for example, transport blood and nanotubes are used to transport anions and cations through the cell membrane. Over the past years many successful reports on the synthesis of tubular helices inspired by nature have been reported.

There are many different ways to synthesize a helix. Our strategy is to fold a rigid shape-persistent amphiphilic single polymeric chain. High molecular weight tube-like polymeric helices have not been reported to date. The aim of this work is to improve the hydrogen-bonded helix reported by Schulze *et al.*^[1] via polycondensation between para-linked monomer and meta-linked monomer units (Figure 1). The driving force for the folding of the final structure is the side chain amphiphilicity. The polymer obtained by polycondensation of these two monomers should fold into a helical shape if exposed to water.

The aramide backbone is composed of a para-linked terephthalic acid monomer carrying a hydrophobic side chain and a meta-linked diamino monomer carrying two hydrophilic side chains. For this work the polymerization is based on the commercial Kevlar-synthesis (A₂/B₂-monomer system) because the highest molecular weights and fewest side reactions are expected for this strategy.



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Templated polymerization using nucleobase-substituted monomers for non-covalent interactions

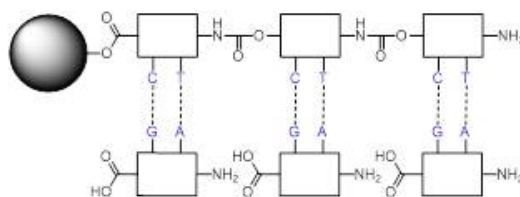
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Nature has the ability to synthesize long and precise polymers, in which each chain has the exact same length and the exact same arrangement of monomers along the chain. Macromolecules with well-defined three-dimensional structures can be created by nature using non-covalent interactions, sequence control, molecular recognition and self-assembly.

In this project, a novel synthetic pathway to macromolecules by mimicking transcription and translation found in natural protein synthesis is developed. By combining the classical solid supported synthesis and the templated synthesis, rigid rod-like oligomers carrying natural nucleobases will be obtained. Thanks to the complementarity of nucleobases, monomers carrying the opposite nucleobases will self-assemble and become pre-arrange for polymerization (Figure 1). Previous studies have been done on aromatic peptide nucleic acids (APNA).^[1] However, shape persistent rigid rod-like aramid nucleic acids have never been reported.

An advantage of this approach is the possibility to recover the template once the polymerization has been performed and re-use it for many other synthetic cycles.



The development of this templated synthesis requires different steps such as the synthesis of monomers carrying solubilizing side chains, coupling of modified nucleobases to monomers via Sonogashira reaction (Figure 2), analyses of the templation patterns and polymerization.



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The counter-intuitive destabilizing effect of surfactant addition in a dispersion of polymer-brushed particles

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The starting point of the here presented work is the counter-intuitive destabilization of an aqueous dispersion of polymethyl methacrylate (PMMA) microparticles grafted with polyacrylic acid (PAA) brushes after the addition of sodium dodecyl sulfate (SDS) as surfactant. Experimental data, indeed, showed that SDS induces particles aggregation with a pH-dependent behavior.

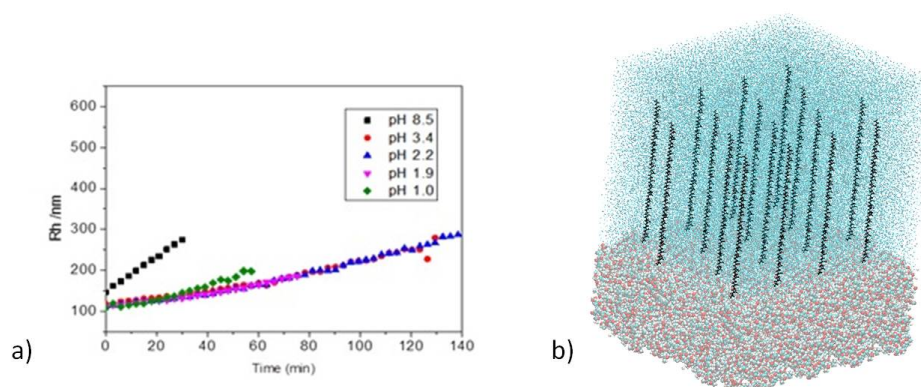


Figure 1. Hydrodynamic radius of dispersed particles as a function of time for different pH value, after addition of 0.2 % of SDS (a); molecular model of PMMA surface (transparent VdW spheres) grafted with PAA chains (black residues) in explicit water (blue dots) (b). Explicit ions are here omitted for the sake of clarity.

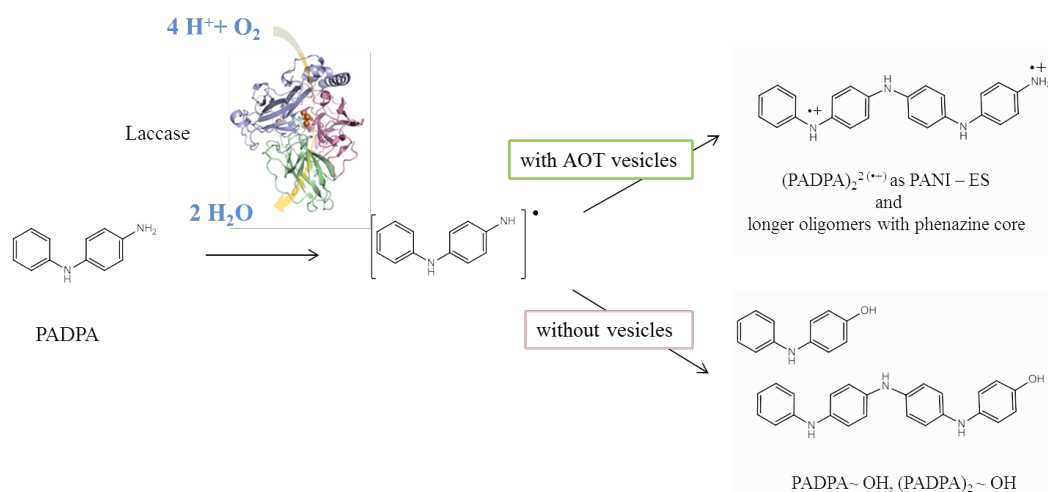
Molecular dynamics simulations (MD) were performed in order to investigate such curious experimental evidence. Since the interactions with the surfactant occur at the particle/solvent interface, the primary particle was modeled as a flat surface made of PMMA, where PAA chains are grafted assuming a regular hexagonal packing. The system was built so that the length of polymer brushes and acrylic acid density per unit of PMMA surface are consistent with experimental data. In particular, two different systems were created, representative of high pH (where carboxyl moieties are dissociated) and low pH (where carboxyl moieties are fully protonated) environments. Simulations were carried out at fully atomistic level, with explicit solvent molecules, explicit ions and explicit SDS molecules. Simulations showed that the pH-dependent interactions between polyacrylic acid brushes and surfactant play a key role on system behavior. In order to highlight and verify the fundamental role of PAA and its protonation state, additional experiments were performed adding SDS to water solutions of PAA at different pH values. The obtained results were in agreement with the mechanism proposed through MD simulations, thus confirming the reliability of the analysis.

Enzymatic oligomerization in AOT vesicle membranes

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The oxidation of the aniline dimer, *p*-aminodiphenylamine (PADPA), with *Trametes versicolor* laccase and molecular oxygen in aqueous solution of pH = 3.5 is strongly influenced in a positive manner by the presence of negatively charged AOT (= sodium bis(2-ethylhexyl) sulfosuccinate) vesicles with a diameter of \approx 100 nm. In the presence of vesicles, a product which resembles conductive polyaniline in its emeraldine salt form (PANI-ES) is obtained (unpaired electrons), whereas in the absence of vesicles this type of product does not form.¹ In order to understand the role of the vesicles in this reaction, the product distribution, the product structures, and the reaction mechanisms in the presence and absence of AOT vesicles were determined by analyzing reactions carried out with selectively deuterated PADPA using HPLC-MS, complemented with time-dependent density function simulations.² It was found that in the presence of vesicles, one main product is obtained in about 50 % yield, which is the linear aniline tetramer in its half-oxidized form (Scheme 1). It displays the spectroscopic properties of PANI-ES. A secondary reaction route yields longer oligomeric PADPA molecules which must contain phenazine structural units. Without vesicles, all of the intermediate products were found to have undergone partial hydrolysis.² Molecular dynamics simulations show that PADPA and its main oxidation product are embedded within the AOT membrane, leading to a significantly lower radial distribution of water around the molecules than when they are dissolved only in water. In this way, the vesicle membranes provide a microenvironment with a low water activity for PADPA and its oxidation products, which suppresses hydrolysis and enables the coupling reaction. Furthermore, cryo-TEM images show that AOT vesicles undergo fusion after PADPA is added to the suspension; a complex process which can be followed using a stopped-flow apparatus.



Scheme 1: Illustration of the laccase-catalyzed oxidation and oligomerization of PADPA at pH = 3.5. At the top, the main product of the reaction the presence of AOT vesicles is shown: The green PADPA dimer in its half-oxidized, half-reduced state with spectroscopic similarities to PANI-ES. At the bottom, two hydrolysis products formed in the absence of vesicles are shown (not obtained with vesicles).

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Quantification of lipid vesicle-entrapped peroxidase with *p*-phenylenediamine

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A new sensitive spectrophotometric assay for the quantification of phospholipid vesicle-entrapped horseradish peroxidase (HRP) in the presence of hydrogen peroxide (H_2O_2) as oxidant was developed. The method is based on the enzymatic oxidation of the colorless substrate *p*-phenylenediamine (PPD) at $\text{pH} = 7.0$, which yields Bandrowski's base (3,6-bis[(4-aminophenyl)imino]cyclohexa-1,4-diene-1,4-diamine) with an absorption maximum at 520 nm. Since PPD permeates across phospholipid bilayers, the assay can be used for the quantification of HRP inside phospholipid vesicles without permeabilizing or destroying the vesicles. Using a mixture of PPD and a phospholipid bilayer-impermeable HRP substrate, ABTS²⁻ (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate)), it is possible to selectively oxidize PPD and to distinguish HRP molecules present inside the vesicles from HRP molecules which are present in the bulk solution (Figure 1). Compared to *o*-phenylenediamine (OPD), another well-known phospholipid bilayer permeable substrate of HRP which yields 2,3-diaminophenazine (DAP) with maximal absorption at 417 nm [1], the spectrophotometric HRP quantification with PPD can be carried out at higher wavelength (520 nm).

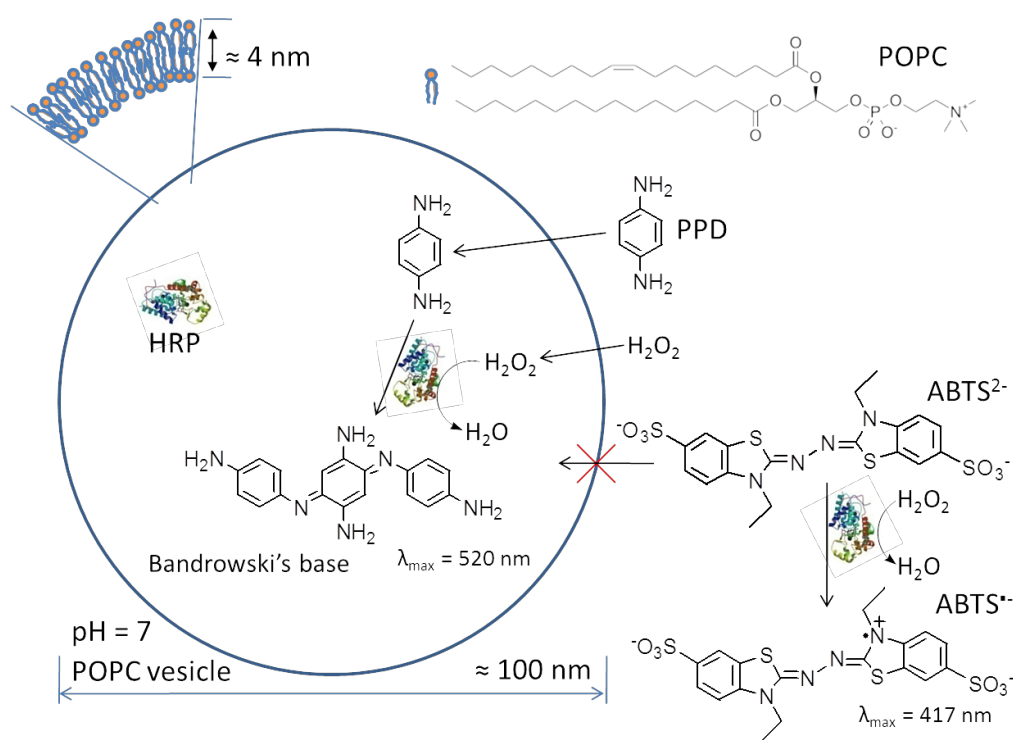


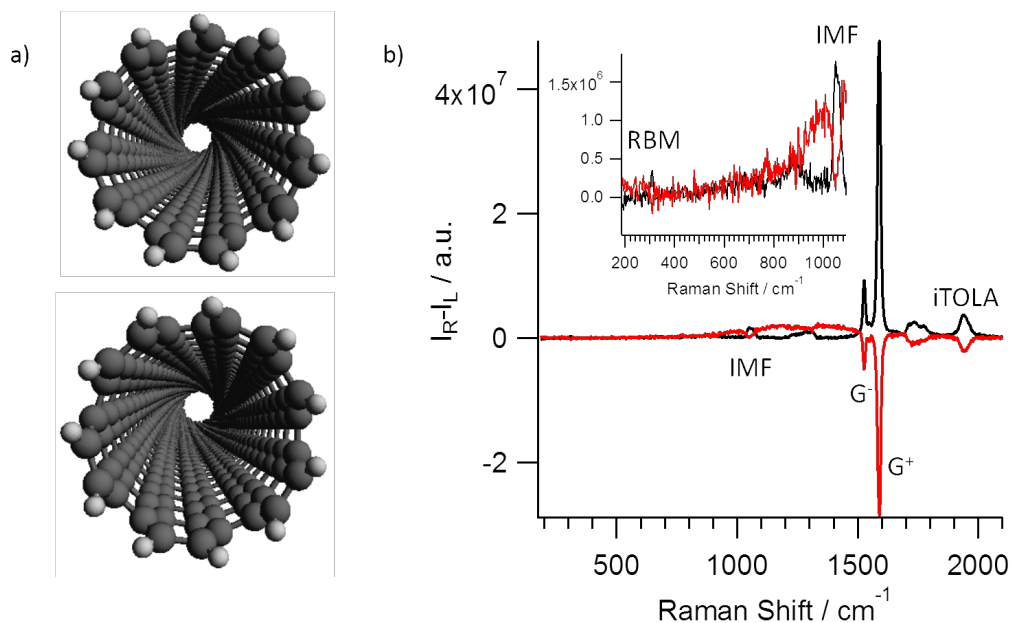
Figure 1: Illustration of the assay system for the spectrophotometric determination of the activity of phospholipid vesicle-entrapped HRP with PPD as substrate and H_2O_2 as oxidant. ABTS²⁻ can not permeate the phospholipid bilayer and is only oxidized by non-entrapped HRP. POPC: 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine.

Acknowledgment: Ya Zhang acknowledges financial support by the China Scholarship Council.

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Resonance Raman Optical Activity of Single Walled Carbon Nanotube EnantiomersM. Magg¹, P. Oulevey¹, T. Bürgi^{1*}¹University of Geneva

Single Walled Carbon Nanotubes (SWCNTs) are, except for zigzag and armchair configurations, helically chiral nanostructures. As such, they exist in two enantiomeric forms which may be denoted as *P* and *M* according to the sense of their helix. Little attention has been paid so far to investigate the properties of SWCNT enantiomers owing to the difficulty to prepare enantio-enriched SWCNT samples.^[1]



We present continuous work on Raman Optical Activity (ROA) as a new technique to characterize the structure and handedness of SWCNTs.^[2] Experimental spectra at 532 nm on highly purified (6,5)-SWCNTs were recorded. Spectra are found to be in agreement with the single-excited-state theory (SES). Strong enhancement of the G-band is found which is in line with strong resonance between the Stokes-shifted photon and the electronic E_{22}^S transition. As calculation of resonance ROA for SWCNTs is not practical, predicted resonance ROA spectra on smaller conjugated chiral carbon systems are performed. In general, Raman spectroscopy is not limited to solution based measurements, but also provides the opportunity to characterize chiral films of SWCNTs.

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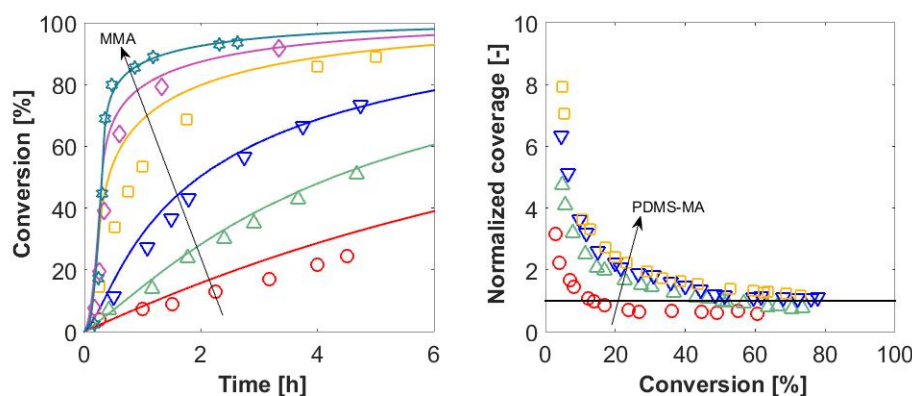
Kinetic and Particle Size Considerations in Dispersion Polymerization of Methyl Methacrylate in Hexane

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By dispersion polymerization, particles of a size ranging between the sizes produced by emulsion and suspension polymerization can be produced.^[1] Along the reaction, the growing chains precipitate, so that the originally homogeneous organic phase becomes heterogeneous^[2]. Through the addition of a steric stabilizer, the particle size can be controlled and low size polydispersity is obtained.^[3] The monomer is soluble in both the continuous and dispersed phase, so that both phases contribute to the overall reaction and polymer buildup. This contribution focuses on the experimental analysis of the dispersion homo-polymerization of methyl methacrylate in hexane, using a reactive stabilizer (methacrylate terminated PDMS). The effect of initial monomer and stabilizer concentrations on conversion, molecular weight and particle size is explored. A simplified kinetic model is finally developed to elucidate the reaction mechanisms and evaluate some model parameters.

Experiments show that the reaction rate increases with monomer concentration. Due to the significant Trommsdorff effect in the particles, the reaction rate is much faster in this phase than in the solvent. This results in the apparent auto-acceleration at increasing monomer content.



The number of particles remains practically constant all along the reaction. As confirmed by model results, if the initial monomer weight fraction exceeds 10%, the amount of polymer produced in the dispersed phase becomes larger than that produced in the continuous phase. The stability of the polymer dispersion is not good enough at low stabilizer contents, where particle aggregation takes place thus reducing the surface area of the dispersed phase. When the actual area exceeds the maximally stabilizable interphase area, aggregation takes place in order to keep constant the area. This behavior is confirmed by the experimental results: particles start to aggregate until they reach a size of ca. 50 μm . This behavior can be observed for many concentrations of monomer and stabilizer, so that a criterion can be determined: if the polymer particle surface coverage falls below a certain value – which is a constant for this monomer/stabilizer system independent of their relative concentration (Figure 1) – aggregation occurs and the distribution turns bimodal.

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Cu-In-Te and Ag-In-Te colloidal nanocrystals with tunable composition and size

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Semiconductor telluride materials find an application niches in e.g. thermoelectrics, photovoltaics, infrared detectors or phase change memory devices. Many of these are based on precise composition control of ternary and quaternary tellurides. Colloidal nanocrystals of multicomponent tellurides provide additional device engineering tool - size tunability of their optical and electronic properties.

Synthesis of ternary telluride colloidal nanocrystals, however, has not been extensively developed. Here we report a simple and reliable protocol towards ternary Cu-In-Te and Ag-In-Te colloidal nanocrystals. (1) Notably, our synthesis provides both composition and size tunability, narrow size distributions for the growth times between 1 and 10 min (Figure 1a, inset). Figure 1c and 1d show examples of size- and composition-dependent properties, i.e. absorbance as a function of Cu-In-Te size (Figure 1c) and X-ray diffraction for different compositions of Cu-In-Te nanocrystals (Figure 1d).

Figure 1 shows results for the case of Cu-In-Te materials. The size of Cu-In-Te nanocrystals can be controlled by growth time (Figure 1a) and composition can be controlled by amounts of respective chloride salts in the reaction mixture (Figure 1b). The synthesis provides very narrow size distributions for the growth times between 1 and 10 min (Figure 1a, inset). Figure 1c and 1d show examples of size- and composition-dependent properties, i.e. absorbance as a function of Cu-In-Te size (Figure 1c) and X-ray diffraction for different compositions of Cu-In-Te nanocrystals (Figure 1d).

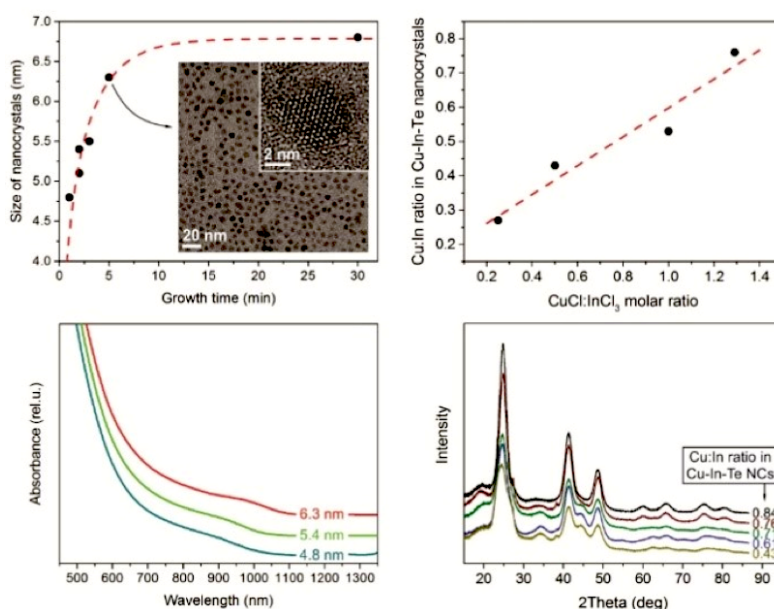


Figure 1. (a) Size of Cu-In-Te nanocrystals for different growth times at 260°C; (b) composition tunability for Cu-In-Te nanocrystals at growth time of 3 min; (c) absorbance of differently sized Cu-In-Te nanocrystals; (d) X-ray diffractograms of Cu-In-Te nanocrystals with different compositions. Inset (a): exemplar TEM and high-resolution TEM image of Cu-In-Te nanocrystals

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Colloidal Chemistry to Advance Solar-to-Chemicals Conversion StudiesR. Buonsanti¹¹EPF Lausanne

Design of electrochemically stable visible-light absorbers and catalysts for solar fuels applications poses new challenges for chemists and material scientists. When aiming at maximizing energy conversion performance, the ability to tailor-make material platforms with tunable morphological characteristics in an unrestricted compositional range is critical for achieving optimal design specifications, as well as for providing understanding of the sensitivities of performance parameters to different compositional and structural parameters.

Our work highlights how colloidal chemistry can aid to construct materials for storing energy in chemical bonds. An overview on our recent studies on complex semiconductor metal oxide light absorbers (Sb-BiVO₄ and BiVO₄/metal oxide heterostructures) to drive water oxidation and on copper nanocrystals to carry out electrochemical CO₂ reduction will be given.¹⁻⁴

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Smart Photonic Crystals of Stimuli-responsive Microgels

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Keywords: Stimuli-responsive, Microgels, Color change

Smart microgels have attracted great attention in soft matter studies for various applications, such as drug delivery vehicles and sensors, owing to their ability to respond to a variety of physical and chemical stimuli, e.g. temperature and pH. Poly (N-isopropylacrylamide) (PNIPAM) with a thermoreversible volume phase transition (VPT) temperature of $\sim 32\text{ }^{\circ}\text{C}$ - $34\text{ }^{\circ}\text{C}$ and poly (vinylpyridine) (PVP) with $pK_a \sim 4$ are among the most studied polymers with temperature and pH responsive behavior, respectively. Colloidal crystals of monodisperse microgels made of these polymers can show iridescent colors. The stimuli responsiveness, on top of this, provides them the ability of changing their size and therefore their spacing in colloidal crystals assembly, which results in a color change. Incorporating organic or inorganic dyes in the microgels combine with the structural color further allows one to enhance/tune the color-changing pattern within the system. The objective of this work is to prepare monodisperse pH and temperature-reponsive microgels by means of water-based free radical polymerization methods with modification of previous works [1,2], which can undergo strong change in their size in response to a stimulus. The self-assembly of these microgels into ordered crystalline structures, as well as their ability to either alter their structural order to reversibly move towards a disordered state in response to a stimulus has been investigated (Fig.1 -3).

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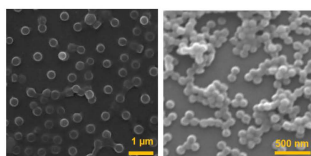


Fig. 1: Microgels morphology- Left: PNIPAM, Right: PVP

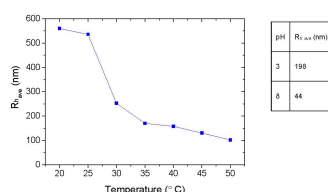


Fig. 2: Average hydrodynamic radius change with Left: temperature- PNIPAM, Right: pH- PVP

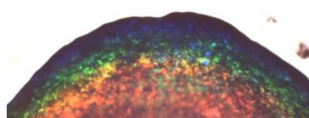


Fig. 3: Drop of liquid PVP microgels on Silicon

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Ultra light nanofiber based 3D scaffolds with tunable porosity and air permeabilityF. Deuber¹, S. Mousavi^{1,2}, C. Adlhart^{1*}¹Zurich University of Applied Sciences, ZHAW, ²University of Sistan & Baluchestan of Iran, USB

Electrospinning became an established technology for the fabrication of nanofibers. Despite their spectacular properties such as interconnected porous structure, huge available surface area, low density, high porosity and high flexibility in surface functionality, nanofiber based materials are limited to 2D materials by their lamellar anisotropic deposition character during electrospinning. To overcome these limitations, 3D structures such as tubes, yarns and sponges are of particular interest.

Alternatively, nanofibers can be turned into 3D nanofiber sponges – novel bulk aerogels with a hierarchical cellular fibrous network and well-bonded nanofibers [1,2]. This post-treatment augments all the nanofibers properties with tunable density, porosity, additional mechanical stability, and flexible macroscopic shape.

3D sponges are obtained through the technique of freezing-casting [3] from mechanically cut nanofibers. The well dispersed nanofiber suspension is frozen at a controlled rate. While freezing the growing solvent crystals push the nanofibers away and thus unidirectional channel are created. After removing the solvent crystals by sublimation the new porous structure can be cross-linked to obtain a highly mechanical stable aerogel (see Fig. 1).

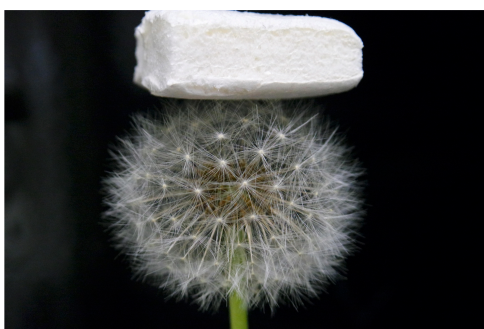


Fig.1 : Ultra light 3D nanofiber based aerogels

We found that by controlling the the freezing parameters such as initial slurry density and freezing temperature one can tune the pore size and porosity of the nanofiber based aerogels. Thus enabling a customized approach for different applications such as air filtration, tissue engineering, water treatment and sound absorption.

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Reversible Thermoresponsive Dispersion / Aggregation of Inorganic Nanoparticles embedded in Polymer Matrix

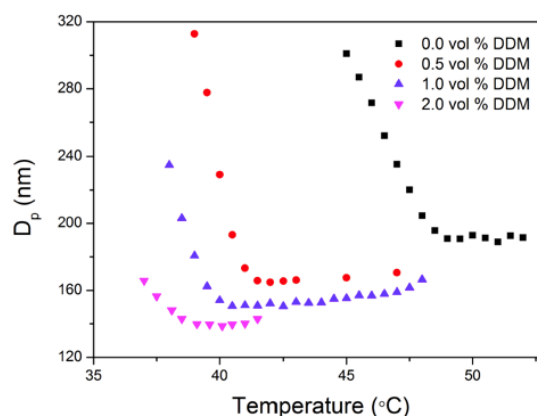
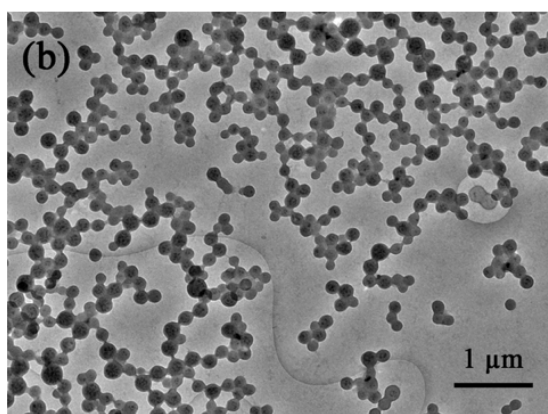
Lu Jin¹

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Hybrid materials, commonly referring to inorganic-organic composites, have found wide applications in various fields due to their complementary physiochemical properties. In the practical case, the inorganic nanoparticles are usually required to be homogeneously blended with a continuous organic media. It is essential to achieve stable dispersion and avoid agglomeration in order to retain the optimized properties. Traditional method is to tune the surface physiochemical properties of inorganic cores through grafting or modification with polymers (dendrite or linear) or organic molecules. Inspired by this, we propose a hybrid system of polymeric matrix embedded with inorganic nanoparticles. By adjusting the chain length in outermost polymer layer, we not only achieve the fast and homogeneous dispersion of hybrid nanoparticles, but also verify the aggregation and re-dispersion behaviors could be flexibly and reversibly induced by changing temperature.

In our experiment, TiO₂ nanoparticles are selected as inorganic component to be confined in cross-linked polystyrene matrix through mini-emulsion polymerization, and further encapsulated within additional shell composed of linear poly (methyl methacrylate) chains through emulsion polymerization. In this design, the outermost linear polymer chains provide dynamic force to flexibly promote the separation or aggregation triggered by temperature, while the inner cross-linked polymer matrix can sterically impede the complete aggregation of nanoparticle, thus guarantee the reversible re-dispersion.

Particularly, hybrid nanoparticles with different chain-length in outermost polymer layer are prepared through introducing chain-transfer agent, and dispersed in binary solvents composed of butyl acetate and ethanol. The results highlight the essential impact of chain-length on facilitating solubility, colloidal stability and reversible thermoresponsive behavior of hybrid nanoparticles. The shorter chain-length polymers show the relatively lower critical temperature at which aggregation or dispersion occurs upon continuously decreasing or increasing temperature. This temperature-induced property could be utilized to controllably manipulate the dynamic behavior of nanoparticles, potentially facilitating the recycling of inorganic fillers in painting, food or cosmetic industries.

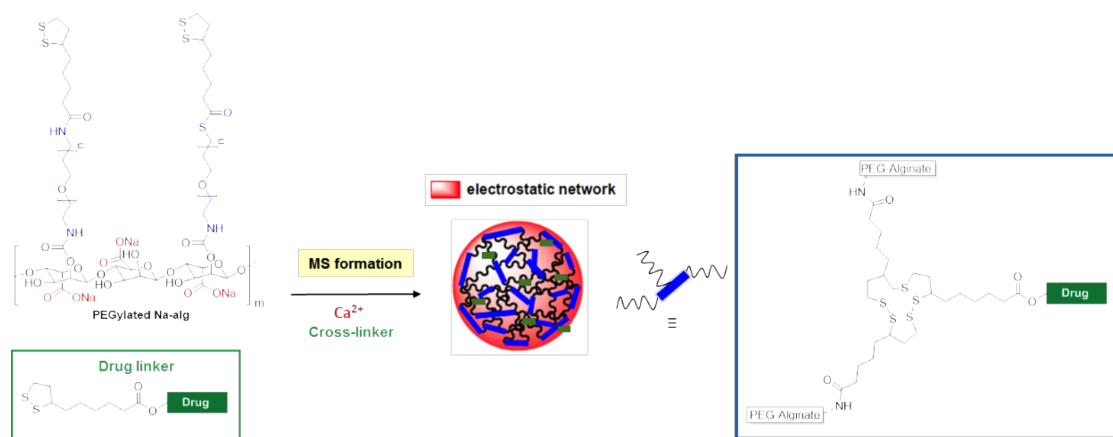


Development of functionalized hybrid hydrogels

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¹EPF Lausanne, ²Geneva University Hospital

The progress of medical therapies, which rely on the transplantation of microencapsulated cells, depends on the quality of the encapsulating material. Such material has to be biocompatible, its physical characteristics have to be adjustable, and the microencapsulation process must be simple and not harm the cells. Although great progresses were done concerning the resistance of microspheres [1-4] inevitable inflammation response and fibrosis formation leading to cell asphyxiation is observed for long term experiments [5]. Therefore improving lifetime of microspheres in living organisms by tuning the composition of the polymeric components of the hydrogels is necessary. The strategy used for this purpose relies on the conjugation of anti-inflammatory agents on the polymeric components or cross-linkers involved in hydrogel formation to obtain microspheres with surface functionalization that might be released in a controlled manner 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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Challenges in determining the rate capability of battery materials

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The specific charge of battery materials can be easily calculated based on Faraday's law. On the other hand, there is no theoretical limit for the rate capability as one could nanosize the battery materials further and further. However, testing the true rate capability of a battery material is challenging since a setup with at least two electrodes has to be used for electrochemical cells. Thus, mass transfer in the electrolyte and kinetics of the lithium metal counter electrode contribute to the overall tested cell performance. This leads to strong variations in the measured rate capabilities for the same active material depending on loading, particle size, porosity of the electrode, and cell set-up (total geometric area, used separator, etc.). Two typical materials, graphite and LiFePO₄, will be discussed.

Graphite shows delithiation rates of up to 600C based on 80% specific charge in thin layer electrodes of 2 μm, 0.2 mg/cm² [1], but only 6C for 5 mg/cm² [2]. Usually, this difference of two orders of magnitude is attributed to tortuosity effects in the active material electrode [3]. However, other effects like the current density through the separator and on the Li-metal counter electrode do not scale with the used C-rates. The total current density differs by a factor of 3.5 (37 mA/cm² vs. 11 mA/cm²) between the two electrodes and not by a factor of 100 as one would assume from the C-rates.

The same can be observed for other battery materials with diluted or standard active material contents [4, 5]. Experiments in half-cells of graphite and LiFePO₄ are compared to Li-Li symmetrical cells. A deconvolution of the different effects is performed by Comsol multiphysics extracting the specific influences on the overpotentials of the electrodes.

In our contribution, we show that if the active materials become fast due to high solid-state diffusion coefficients such as for graphite [6] or nanosizing as for LiFePO₄ or LiMn₂O₄ [4, 7], the other cell components become important for rate capability tests. Techniques of electrode dilution [4], thin layer fabrication [1] or single-particle experiments [8] have to be applied in order to determine the active material properties correctly. The actual improvement to a real battery with electrodes of ≥ 80 μm is usually significantly less than the researchers intend, and the 3D microstructure [9] and mass transfer in the electrolyte [10] need to be improved before further nanosizing is needed.

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Dendrimer decorated nylon 6 electrospun nanofibrous membranes for the efficient dye removal from waste water

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Nowadays, water pollution is an important issue all over the world due to growth of population, urbanization, and industrialization. Textile industry effluent is one kind of environmental pollution full of various non-biodegradable and carcinogenic dyes.

Among various techniques which are investigated for dye removal, membrane filtration is an economic, environmental friendly and easy to use method without any additional chemical agents required for wastewater treatment [1]. Nowadays, electrospun nanofibrous membranes have been widely used due to their outstanding properties such huge available surface area, low density, high porosity and high flexibility in surface functionality. Filtration efficiency or membrane performance may further be improved by surface modification [2, 3].

Lately, dendrimers as highly branched, globular and nanoscopic macromolecules with many functional end-groups, empty internal cavities and high local density of active groups have been studied as potential adsorbents. They provide spectacular adsorption capacity but their separation from aqueous solutions in the dye removal process is difficult.

By decorating electrospun polyamide 6 nanofibrous membranes with polyamidoamine dendrimer (PAMAM), an easily manageable biodegradable filtration membrane with high anionic dye adsorption capacities is obtained.

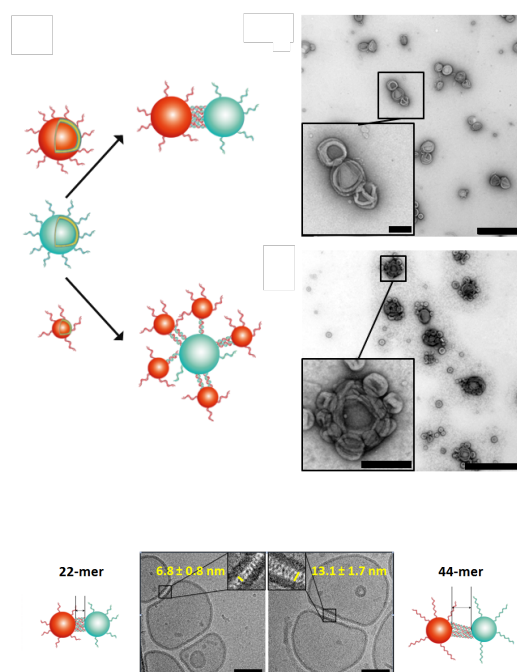
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Self-organization of polymeric nano-compartments or nano-reactor-origamiS. Lörcher¹, J. Liu¹, V. Postupalenko¹, D. Wu², M. Chami¹, W. Meier^{1*}, C. G. Palivan^{1*}¹University of Basel, ²Zurich University of Applied Sciences, ZHAW

Polymeric nano-reactors are composed of a self-assembled polymeric membrane, an encapsulated catalytic entity and a component enabling molecular transport across the membrane. By controlled clustering of such nano-reactors molecular systems can be engineered. Here we report a simple way to cluster polymeric nano-reactors, assembled from PMOXA-PDMS-PMOXA in aqueous conditions, to yield distinct geometrical configurations of polymeric vesicles as depicted in figure 1. Furthermore, the distance between the respective polymersomes can be fine tuned in the order of 1 nm as illustrated in figure 2.



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Radicals in the Life of Industrial Polymer

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¹BASF Schweiz AG, Basel

Radicals play a fundamental role in the life cycle of synthetic polymers. Of the 300 million tons of industrial polymers produced worldwide every year about 50% are made by *radical polymerization* of monomers that are often stabilized against undesired premature polymerization by addition of *polymerization inhibitors*. Stabilizers are necessary to protect the majority of polymeric materials during their service life from *radical degradation processes* triggered by oxygen, heat or light. Modification of the polymeric architecture can be easily achieved via *radical polymer analogous reactions*. One of the most important developments in polymer science in the last 25 years is *controlled radical polymerization*. *Radical bearing redox-active polymers* are emerging as promising materials for example in energy storage application like organic radical batteries.

Our contributions to the above mentioned fields will be illustrated on the following examples:

- a) Novel benzofuranone stabilizers^[1-2] and related serendipity discovery of novel dyes^[3-5]
- b) Eco-friendly polymerization inhibitors^[6-7]
- c) First industrial realization of controlled radical polymerization^[8-11]
- d) Radicals bearing polymers for electrochemical applications^[12-14]
- e) Novel and safe radical initiators^[15-17]

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Selective attachment of Gold Nanoparticles on Asymmetrically Functionalized Janus Nanoparticles

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In recent years, the research in the field of nanoparticle has devoted much attention to the synthesis of anisotropic nanoparticles, also called Janus Nanoparticles. Their anisotropy may have different origins, such as having non-homogeneously functionalized surface or complex internal nanostructure. These special features render the nanoparticles much more interesting than their isotropic counterparts, especially regarding their self-assembling properties. Here, we describe the synthesis and the characterization of Janus Dumbbells asymmetrically coated with gold nanoparticles. This peculiar type of nanoparticles is prepared to be used as a template for catalytic Janus nanomotors, self-propelling in appropriate conditions.

We start by synthesizing polystyrene dumbbell-shaped nanoparticles in a three-step process, as has already been reported [1]. We then performed silane chemistry to selectively bring amino groups on the surface of one hemisphere of the dumbbells only. This is possible thanks to presence of silanol groups on the surface of the first hemisphere [2].

To selectively cover one hemisphere of the dumbbells with gold nanoparticles, two different approaches were tested. In the first case, we prepared negatively-charged gold nanoparticles (coated with citric acid) by a Turkevick-like method. In proper conditions, we then mixed the two types of nanoparticles. Due to electrostatic interactions between the amino groups on the polystyrene dumbbells and the citrate groups on the gold nanoparticles, the latter selectively attached on one hemisphere, while the other remains naked.

Another synthetic approach is to reduce the gold salt directly in the presence of the functionalized polystyrene dumbbells. In a similar way as in the first method, the asymmetric distribution of amino groups on the dumbbells will lead to the selective nucleation and growth of small gold nanoparticles only on one hemisphere.

On top of interesting plasmonic properties, gold nanoparticles are also known to act as “seeds” for the growth of platinum nanoparticles (or shells). An asymmetric distribution of such catalytic nanoparticles can lead to self-propulsion of the dumbbells in appropriate conditions (i.e. with H₂O₂ fuel). Evaluation of the drawback and advantages of the different method used for the synthesis of gold-coated dumbbells will be discussed.

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Multi-stimuli responsive films designed through layer-by-layer assembly of PAA-b-PNIPAM block copolymers for biomedical applications

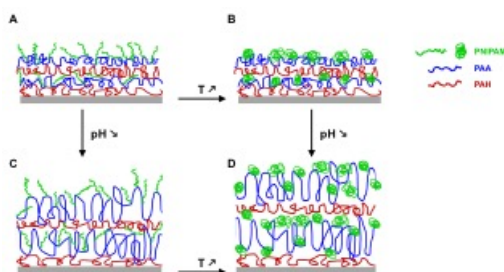
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Smart or so-called stimuli-sensitive materials that reversibly respond to the environmental changes have opened numerous routes in biomedical fields, such as protein separation, surface properties control, medical diagnostic etc [1]. In regard to bioanalytical tools development, pH and temperature responsive macromolecules are the most profoundly studied systems [2,3]. Immobilization of this kind of smart macromolecules is the key step in the fabrication of biosensing elements.

In the present work, we report on the design and elaboration of multi stimuli-responsive thin films. For this goal, we employed the robust and versatile layer-by-layer (LbL) assembly approach to incorporate block copolymers made of poly(acrylic acid) PAA and poly(N-isopropylacrylamide) PNIPAM with tunable and well-defined block lengths. The combination of ellipsometry, quartz crystal microbalance (QCM-D) and infrared data revealed the possibility to build up (PAH/PAA-PNIPAM)_n multilayers. The responsive properties towards application of different stimuli were evaluated by monitoring the adsorption of proteins (ovalbumin, bovine serum albumin) by means of QCM-D while varying (i) temperature, (ii) pH, (iii) ionic strength or a combination of all these stimuli. It emerges that temperature has a strong impact on the amount of adsorbed proteins, in accordance with the expected behavior of PNIPAM. In addition, the adsorbed amount of protein estimated by QCM-D measurements indicates that basic pH (~8) and/or low ionic strength (10⁻⁵M) conditions are not favorable for protein adsorption while low pH (~4) and/or high ionic strength (10⁻¹M) changes the surface to protein attractive state. In short, these new PNIPAM block copolymer-based LbL coatings are easy to build on substrates of various nature such as gold or silica and present highly tunable features [4]. This makes therefore them ideal candidates to be employed for applications requiring the control of protein adsorption, such as protein separation or cell culture.

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Developing New Strategies to study colloidal Nanocrystals using Dynamic Nuclear Polarization NMR Spectroscopy

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Nuclear magnetic resonance (NMR) is one of the most powerful analytical techniques to characterize molecules (solution NMR) and materials (solid-state NMR), including colloidal or powdered nanocrystals (NCs). However, NMR is suffering of inherently poor sensitivity, especially when it comes to isotopes other than ¹H, ¹³C, ¹⁹F and ³¹P, which makes most of the NCs difficult to study or not accessible by NMR.

We showed in earlier work that dynamic nuclear polarization (DNP) NMR represented a practicable solution to the sensitivity problem described above.¹ However, few NC solutions yielded mentionable signal due to aggregation at the experimental conditions of 100 K required for DNP NMR. Insertion of the NCs into meso-silica hindered them from precipitating and maintained all the NCs within reach of the radicals for efficient polarization transfer leading to significant NMR signal enhancement. This novel, universally applicable, extremely simple and inexpensive methodology for sample formulation makes use of commercially available materials (meso-silica) and pristine colloidal NC solutions in their native environment avoiding the adverse effects of the isolation of NCs, such as powdering or re-dispersion.² Eventually, the combination of conventional and DNP NMR permits the selective study of the NC core, NC surface or capping ligands, should they be of organic or inorganic nature.

Nevertheless, new insights into chemical bonding (coordination, connectivity, interatomic distances, etc.) and composition (oxidation state, distribution in and on the NC, etc.) of NCs are restricted to systems with high symmetry and little site disorder. Else, the broad signals from different species overlap and make the spectrum interpretation superficial if not impossible. 2D-spectroscopy turned out to be an elegant tool to overcome this difficulty, by visualizing interactions or by increasing resolution through the isolation of line broadening effects.^{2,3}

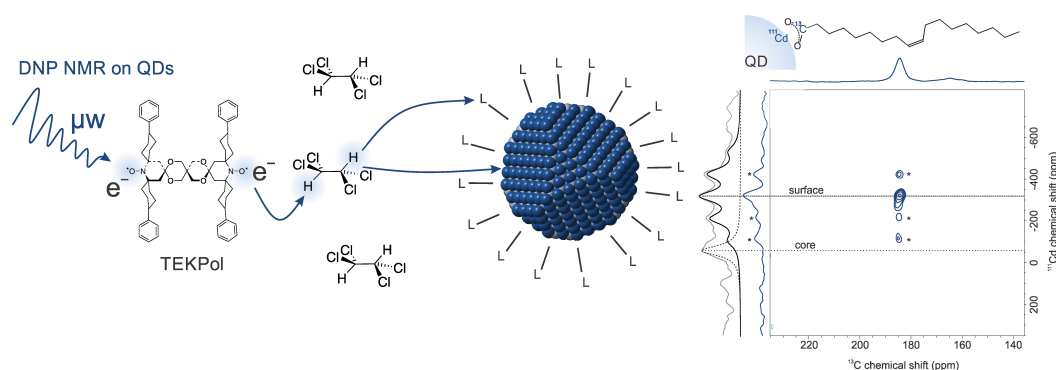
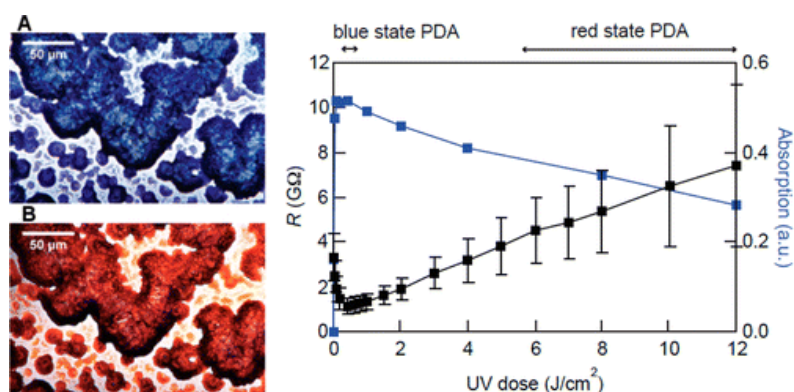


Figure: (left) Polarization transfer mechanism of DNP NMR leading to enhanced signal intensity of atoms of the ligand, at the surface or inside the NC. (right) D-HMQC-R³ spectrum displaying connectivity of the oleate ligand to the surface cadmium species, which can easily be distinguished from the core (chemical shift, CSA).

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Combined Electrical and Optical Characterization of PolydiacetyleneC. Girard-Reydet¹, R. D. Ortuso¹, M. Tsemperouli¹, K. Sugihara^{1*}¹Department of Physical Chemistry, University of Geneva, Quai Ernest Ansermet 30, 1211 Geneva 4, Switzerland

Polydiacetylene (PDA) is a conductive polymer that has mechanochromism. When the polymer is exposed to mechanical stresses, change in temperature (thermochromism), pH (ionochromism), and so forth, the structural perturbation can be seen by the change in its color. Although it presents interesting electrical and optical properties, the relationship between these signals has rarely been investigated. We studied the correlation between the electrical conductivity and the absorption spectra of PDA. Upon UV irradiation, PDA absorption spectra presented a blue shift, which coincided with the decrease in the electrical conductivity.



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Retort tie-layer: the development of a solution for barrier retort structuresE. Kupsch¹¹Dow Europe GmbH, Bachtobelstrasse 3, 8810 Horgen, Switzerland

The presented work aims at the development of adhesive resins for steam sterilizable film applications in food and medical packaging that promote the adhesion between polypropylene and oxygen / carbon dioxide gas barrier polymers like polyethylene vinyl alcohol (EVOH) and polyamide (PA). Generally the adhesive resin design is based on maleic anhydride grafted polymers. The different challenges between polyethylene and polypropylene grafting are discussed. To overcome these deficiencies for the adhesive resin design, a Dow developed compatibiliser for polypropylene/polyethylene blends was used in the adhesive resin formulation. The concept of the compatibilising polymer is demonstrated with an electron microscopy analysis of blends containing different ratios of polypropylene, polyethylene and compatibiliser. Finally it could be demonstrated that in multi-layer extruded film the resulting adhesive resin formulation proves to be high in adhesion strength to polypropylene, polyethylene vinyl alcohol and polyamide without performance loss after the steam sterilization process.

Phosphorescent oxygen sensors produced by spot-crazing of polyphenylenesulfide films

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Detection of molecular oxygen (O₂) by a non-chemical, reversible, contactless optical method is of high utility for many areas including industrial process control, environmental monitoring, biological detection, medicine and food packaging [1]. Conventional O₂ sensors are usually produced by making a polymeric cocktail in an organic solvent, applying it on a substrate and drying, polymerizing or curing liquid precursors. These processes usually involve toxic solvents or monomers (e.g. styrene), in significant amount and with considerable wastage [2]. Recently, solvent crazing of polymers in physically active liquid environments (PALEs) have shown an attractive alternative for the encapsulation of optical transducers in semi-crystalline polymer matrix [3]. The creation of a nanoporous structure (5–15 nm pores with a narrow size distribution and volume porosity up to 55–60%) is achieved by tensile drawing in a suitable solvent which, in the presence of the additive, allows the encapsulation of the dye by diffusion forces in one-pot approach.

In the present work, phosphorescent oxygen sensors based on platinum benzoporphyrin and palladium benzoporphyrin dyes encapsulated in polyphenylenesulfide (PPS) films by the spot-crazing method are described. The new polymer matrix enables simple, one-step production of discrete, high-performance O₂ sensors using a low toxicity solvent 2-butanone, low overall strain (8%), low amounts of solvent and precise spatial control. The resulting nano-structured sensor materials display markedly enhanced brightness, high photo-, mechanical and chemical stability.

Their structural and physico-chemical properties were characterized by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), optical microscopy and phosphorescence lifetime imaging microscopy (PLIM). The PPS sensors show a high degree of lateral and in-depth homogeneity on the micro- and macro-scale, as revealed by confocal microscopy, linear Stern-Volmer plots and single exponential decays. Operating in phosphorescence lifetime mode, optimised sensors show stable O₂ calibrations in the range of 0.1–100 kPa O₂, low temperature dependence (linear in the range 10–50 °C), low cross-sensitivity to humidity and high reproducibility (RSD 1.5% at 21 kPa and 0.5% at zero O₂). This technology facilitates the production of low-cost disposable O₂ sensors and their integration in large scale industrial applications such as packaging.

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100% Renewables-Based Polyethylene Furanoate (PEF) for the "Green Bottle" Via Ring-Opening Polymerization

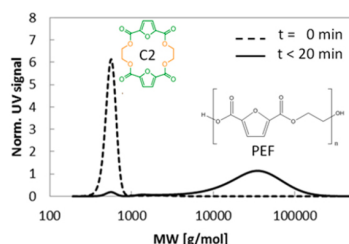
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¹ETH Zurich

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 post-polymerization (PC-SSP), 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^[1,2]. 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.^[3].

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. Within 4 hours, cyOEF are formed with a selectivity of 80% towards cyOEF. The 20% unconverted linears 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) sufficiently high molecular weights, 2) reproducible reaction control and 3) colorless products. cyOEF were subjected to catalytic ROP at temperatures up to 280°C using tin catalysts such as FDA-approved tin octoate, the application of which could simplify the entry to regulated food packaging market, to form PEF chains in yields of >95% and molecular weights equivalent to a PET bottle (~60'000 g/mol). Absolute molecular weight measurement is essential for process development, which we perform with laser scattering (MALS) and diffusion (DOSY) NMR^[4]. Cyclic monomers do not have end-groups and thus render byproduct removal unnecessary, allowing for complete conversion to high molecular weight PEF within less than 20 min. Combined with cyOEF synthesis time, ROP outperforms commonly applied PC-SSP by about a factor of 10. Compared with PET, the higher glass transition temperature (85°C vs. 73°C) and lower melting point compared (215°C vs. 260°C) of PEF indicate higher thermal stability and easier processing of the final bottles. An at least 5x higher oxygen diffusion barrier complements the 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 PC-SSP.



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Force-Induced *Cis-to-Trans* Isomerization of Carbon-Carbon Double Bond Using Atomic Force Microscopy

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Numerous examples of carbon-carbon double bond containing molecules exist in chemistry and biology. An attribute of these molecules is that their *cis* and *trans* isomers normally present different physical and chemical properties. Thus isomerization of double bond is a necessary process that naturally occurs or is artificially induced via irradiation, thermally or by catalysts to deliver specific function. So far the effect of mechanical force on isomerization of double bond has not been investigated. We present our results on force-induced *cis-to-trans* isomerization of double bond at the level of single polymer molecules containing *cis* double bond. Three double bond containing polymers, namely **P1**, ***cis*-PB** and **PB**, were used. The structures of these polymers are shown in figure 1(a).

Upon stretching *cis* double bond containing polymers to elevated forces using atomic force microscopy, a sudden relaxation in force and increase in elongation of polymer was observed in the force versus extension profile. The transition is attributed to isomerization. An example of force-induced isomerization in **P1** is shown in figure 1(b). Investigation of exclusively single bond containing polymers did not show any trace of isomerization. Our results reveal an isomerization force of 800 ± 60 pN as shown in figure 1(c). This force is slightly lower than the force associated with breaking of covalent bonds and rings $\sim 1-2$ nN [1,2]. Our results show that the mechanical force can be used to trigger isomerization of double bond. Our results also open the possibility of a new class of force-responsive polymers based on mechano-isomerization of double bond.

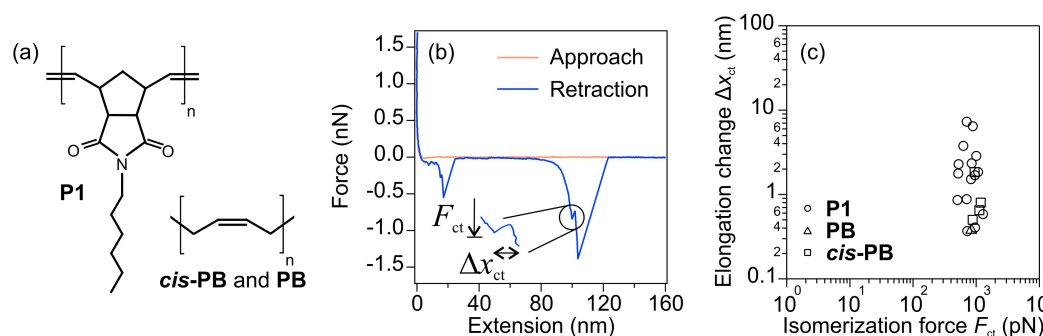


Figure 1: (a) Structural formulas of the *cis* double bond containing polymers used in this study: newly synthesized polymer **P1**, *cis*-1,4-polybutadiene (***cis*-PB**, 98% *cis* double bonds) and *cis/trans*-1,4-polybutadiene (**PB**, 36% *cis* double bonds). (b) Force versus extension of **P1** showing an isomerization event. The onset of *cis-to-trans* isomerization is denoted by force F_{ct} that accompanies an elongation change Δx_{ct} . (c) The elongation change Δx_{ct} of **P1**, **PB**, and ***cis*-PB** as a function of the *cis-to-trans* isomerization force F_{ct} .

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Biomimetic Polymersomes through a Symbiosis of Organic and Polymer Chemistry

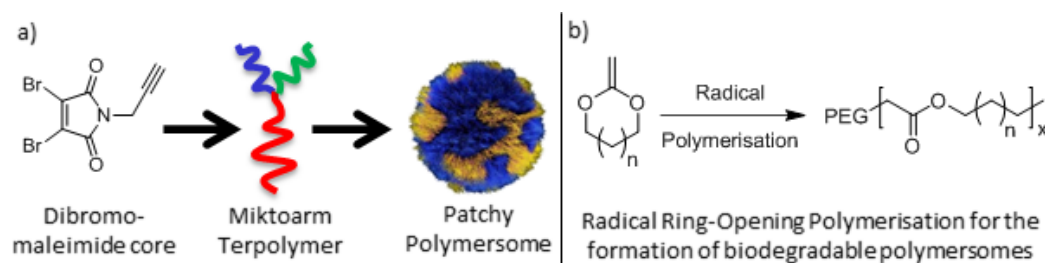
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The chemical versatility polymers is one of the major benefits of polymersomes.¹ However, even more potential can be unlocked if polymer chemistry is combined with organic chemistry to obtain the polymer.

Polymersomes usually have a surface without any domains, which represents a major drawback with respect to natural vesicles. We accomplished stable domains by synthesising a miktoarm star terpolymer based on dibromomaleimide (see figure).² Translated from organic chemistry it proved to serve as a highly stable linker to form a miktoarm star terpolymer, which enabled the formation of polymersomes with stable domains (see figure). In order to make the patches visible, we translated the TAD chemistry, recently translated from organic chemistry, towards a method for polymer conjugation.³

One gap however, the development of smart and degradable polymersomes is only filling slowly. This is mainly due to the fact that ring-opening polymerisation does not tolerate the unprotected amines or alcohols necessary. By using controlled radical ring opening polymerisation (CoRROP) from cyclic ketene acetals (CKAs), this issue can be overcome.⁴ The first key for this polymerisation is the monomer synthesis, hence the organic chemistry required. In very recent studies and ongoing research we aim at showing that CKAs are well accessible and how well CoRROP from cyclic ketene acetals can be used to create biodegradable polyesters unavailable from other polymerisation techniques.



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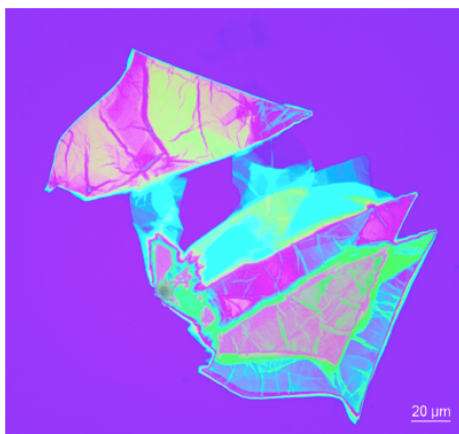
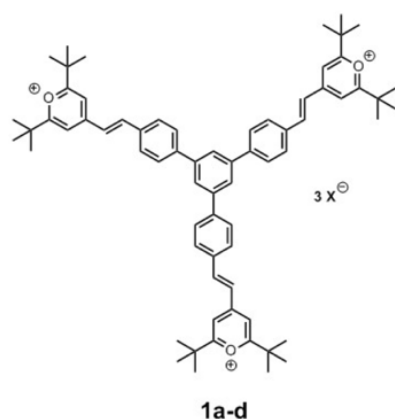
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A novel two-dimensional polymer synthesized by [2+2]-cycloaddition on the multigram scale

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Building on the results in topochemistry by Enkelmann, Novak, Wagener and Wegner¹⁻² and inspired by the advances made by Hasegawa in the 1970s on linear polymers synthesized via [2+2]-cycloadditions in the single crystalline state³, we introduce a new 2DP employing a styryl pyrylium dimerization reaction.⁴



We here report the effortless, inexpensive and large scale (up to 28 g) synthesis of the pyrylium based triolefinic monomers 1a - d (a: X = $\frac{1}{2}$ SnCl₆²⁻, b: X = TfO⁻, c: X = BF₄⁻, d: X = ClO₄⁻), their crystallization into layered single crystals and their light induced polymerization into a novel 2D polymer. The process of polymerization leaves the single crystal largely intact and the molecular structure of the 2D polymer obtained can therefore be proven by X-ray diffraction.

Single layers of 2DPs can be isolated by immersing the crystals in a suitable solvent at 20 - 80 °C. The crystal elongates in an accordion-like manner so that sharp edges of thinner sheet-packages emerge. As the exfoliation proceeds, sheet-packages as thin as just a few layers or even monolayers of 2DP detach. Atomic force microscopy (AFM) of such a dispersion deposited on a SiO₂/Si-wafer reveals that the thinnest features have an overall approximate thickness of 1.5 - 2.5 nm, which likely corresponds to one monolayer.

Compared to existing anthracene-based 2DPs, the presented system has several advantages:

- Facile monomer synthesis from inexpensive starting materials
- Access to large crystals
- Rapid exfoliation into thin sheets

Because of the ionic nature of this polymer, intrinsic properties (electrical conductivity, porosity, non-linear optical behavior) are expected that differ from the known 2DPs. The evaluation and tuning of these properties (e.g. by altering the counter ion) is part of ongoing research.

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