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Oral Presentation Abstracts

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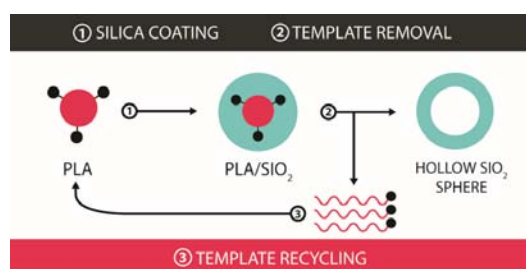
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## Efficient recycling of polylactic acid nanoparticle templates for the synthesis of hollow silica spheres

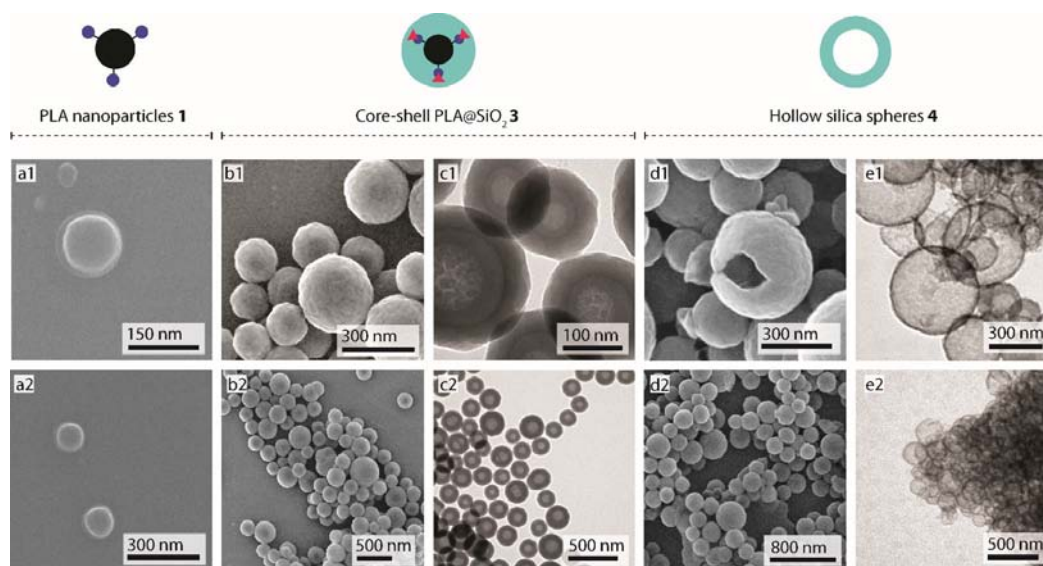
E. Schneider<sup>1</sup>

<sup>1</sup>ETH Zurich

Hollow silica spheres can be obtained in a recycling process using bio-derived polylactic acid as a template, thus avoiding CO<sub>2</sub> emissions compared to standard processes using calcination for template removal.<sup>[1]</sup>



Herein, we present the first successful silica coating of polylactic acid nanoparticles, resulting in fully coated polylactic acid-silica core-shell nanoparticles. Subsequent dissolution treatment efficiently dissolved the polylactic acid core template and exclusively yielded hollow silica spheres with a shell thickness of  $16 \pm 1$  nm. The collected polylactic acid could then be directly recycled from the template removal solution and re-used to synthesize polylactic acid nanoparticles for a next batch of hollow silica nanospheres. Such hollow particles are of interest in next generation insulation materials and as light weight fillers in polymers for fuel efficient mobility.



[1] Manuscript accepted and under revision at ACS Sustainable Chemistry and Engineering

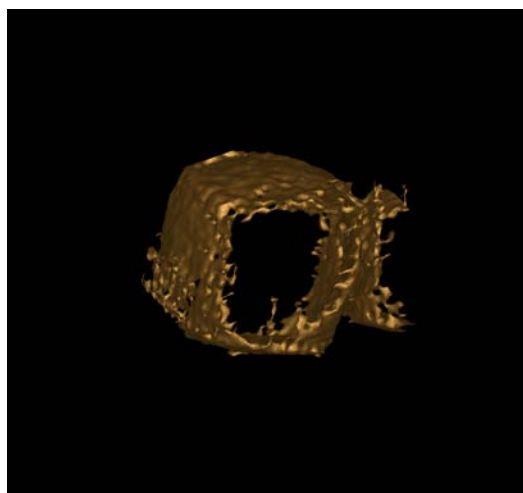
## Vesicle Origami: Cuboid Phospholipid Vesicles Formed by Template-Free Self-Assembly<sup>[1]</sup>

F. Neuhaus<sup>1</sup>, A. Zumbühl<sup>1\*</sup>

<sup>1</sup>University of Fribourg, Department of Chemistry

Phospholipid vesicles are typical self-assembled structures. Typically these vesicles take spherical shape to minimize the energy. Deciphering the bilayer code, the basic physical interactions between phospholipids, would allow to utilize these molecules as building blocks for novel, non-spherical structures.

Here, we present a 1,2-diamidophospholipid that self-assembles into a cuboid vesicle structure in a template-free manner. Due to intermolecular hydrogen bonding, the bilayer membranes form an exceptionally tight subgel packing leading to a maximization of flat membrane shapes and a minimization of any edges. These conditions result in the geometrical structure of a cube. Surprisingly, the lateral surface pressure in the membrane is only one third of the value typically assumed for a bilayer membrane, questioning a long-standing rule of thumbs.



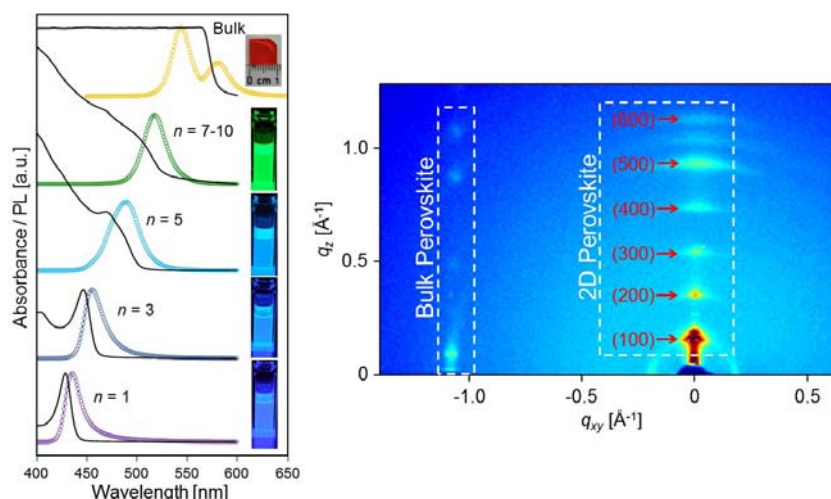
[1] Frederik Neuhaus, Dennis Mueller, Radu Tanasescu, Sandor Balog, Takashi Ishikawa, Gerald Brezesinski, Andreas Zumbuehl, *Angewandte Chemie*, **2017**, *in press*.

## Colloidal quantum-confined perovskites for ultrapure green optoelectronics: synthesis and applications

J. Jagielski<sup>1</sup>, S. Kumar<sup>1</sup>, C. Shih<sup>1\*</sup>

<sup>1</sup>Institute for Chemical and Bioengineering, D-CHAB, ETH Zürich, Zürich, Switzerland

Hybrid lead halide perovskites, described by a formula  $ABX_3$ , recently emerged as a new class of semiconducting materials for various optoelectronic devices.<sup>[1]</sup> In particular, in form of colloidal nanocrystals they exhibit properties like high photoluminescence quantum yield (PLQY), tunable bandgap, defect tolerance, efficient carrier recombination, outstanding color purity (FWHM less than 25 nm) or low cost of production, which are all a prerequisite for a material used in fabrication of efficient, solution-processed light-emitting diodes (LEDs).<sup>[2]</sup> Analogously to conventional, inorganic quantum dots (QDs), quantum confinement effects could be observed upon forming colloidal perovskite nanoplatelets (NPLs) with thicknesses below  $\sim 10$  unit cells.<sup>[3]</sup> In our work, on the example of  $\text{MAPbBr}_3$  we demonstrate how the number of layers comprising the nanoplatelet can be precisely controlled.<sup>[4]</sup> As a consequence not only is the emission wavelength varied without altering the chemical composition, but also an increase in exciton binding energy within these structures can be observed, which is crucial for efficient radiative carrier recombination within these structures.



Furthermore, it can be proven that high PLQY values obtained in solution (50-90%) are also retained after depositing the colloidal dispersions on solid substrates, a phenomenon that could not be achieved till now and clearly distinguishes perovskite NPLs from inorganic QDs.<sup>[5]</sup> With the aid of computational methods we indicate the changes in the crystal lattice depending on the NPL surrounding, which are responsible for such great performance of perovskite NPLs in solid form. In order to exploit the exceptionally high PLQY in solid films, both active matrix, as well as passive (down-converted) green LEDs using quantum confined perovskites are prepared. The former exhibits maximum power efficacy of 7.7 lm/W – one of the highest values achieved among colloidal perovskite nanocrystals-based active matrix LEDs. On the other hand, the latter can reach values exceeding the performance of commercial monochromatic InGaN devices. This opens an avenue towards low-cost and high-throughput production of solution-processed light-emitting devices.

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[3] J. A. Sichert *et al.*, *Nano Letters*, **2015**, 15, 6521.

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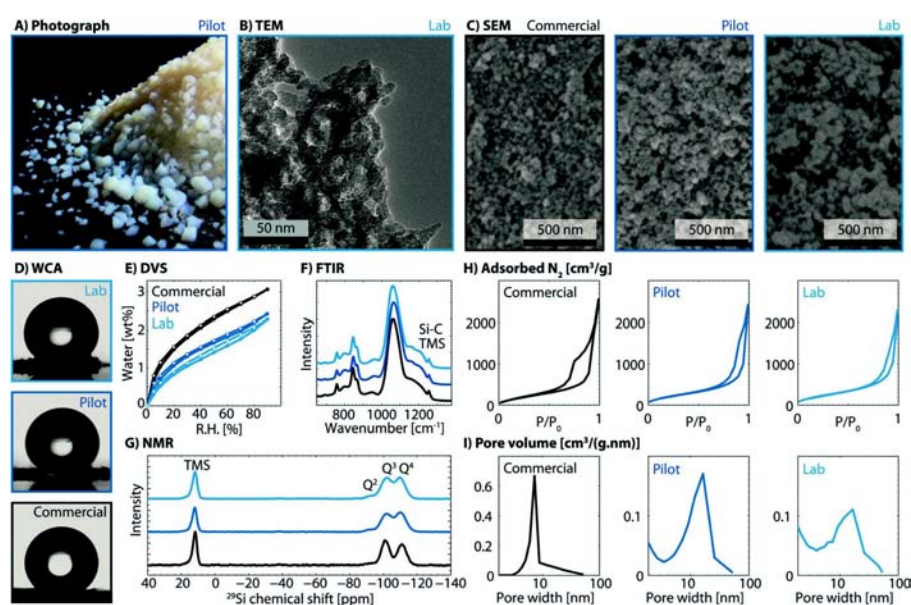
[5] B. G. Jeong *et al.*, *ACS Nano*, **2016**, 10, 9297.

## Fast and Minimal-Solvent Production of Superinsulating Silica Aerogel Granulate

L. Huber<sup>1</sup>, Z. F. Fei<sup>1</sup>, W. J. Malfait<sup>1</sup>, S. Vares<sup>2</sup>, M. M. Koebel<sup>1\*</sup>

<sup>1</sup>Empa, Laboratory for Building Energy Materials and Components, Überlandstrasse 129, 8600 Dübendorf, <sup>2</sup>VTT Technical Research Center of Finland, Vuorimiehentie 5, Espoo, Finland

Silica aerogel superinsulation products have a tremendous growth potential, mainly for industrial and pipe insulation. However, the high production cost prevent the adoption of silica aerogel products outside of their established niche markets. A one-pot synthesis for silica aerogel granulate is presented that significantly decreases solvent use, production time, and global warming potential. The inclusion of the hydrophobization agent prior to gelation with a postgelation activation step, enables a complete production cycle of less than four hours at the lab scale for a solvent use close to the theoretical minimum. The one-pot aerogel granulate retains the exceptional properties associated with silica aerogel, mostly the thermal conductivity of  $14.4 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  for the pilot scale materials, about half that of standing air ( $26 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ).



**Figure 1.** Structure, properties, and surface chemistry of one-pot and commercial aerogel. A) Photograph, B) TEM image, C) SEM images, D) water contact angle (WCA), E) dynamic vapor sorption (DVS), F) FTIR spectra, G)  $^{29}\text{Si}$  CP MAS NMR spectra, H) nitrogen sorption isotherms, I) pore size distributions.

[1] Lukas Huber, Shanyu Zhao, Wim J. Malfait *et al.*, *Angew. Chemie - Int. Ed.*, **2017**, 56, 1-5

**Probing the 3D Lipid Monolayers at the Surface of Adiposome Organelle Models**H. I. Okur<sup>1</sup>, Y. Chen<sup>1</sup>, N. Smolentsev<sup>1</sup>, S. Roke<sup>1\*</sup><sup>1</sup>Laboratory for Fundamental BioPhotonics(LBP), IBI, IMX, STI, LACUS, EPFL, CH-1015 Lausanne, Switzerland

Three-dimensional (3D) phospholipid monolayers at hydrophobic surfaces are omnipresent in nature as adiposome organelle, also known as lipid droplets, or in man-made materials such as drug delivery systems. Nevertheless, the molecular level understanding of such monolayers remains elusive. We investigate the molecular structure of phosphatidylcholine (PC) lipids forming 3D monolayers on the surface of hexadecane nanodroplets. The influences of acyl chain length, saturation, and number of acyl tails per lipid were studied with vibrational sum frequency, and second harmonic scattering, interface sensitive non-linear optical techniques. We find that 1,2-dihexadecanoyl-sn-glycero-3-phosphocholine (DPPC; 16:0) lipids form tightly packed, liquid-condensed-like monolayers.[1] Upon shortening the tail length to 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC; 14:0) and 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC; 12:0), more gauche defects in the lipid tails are observed. Monolayers of unsaturated 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC; 18:1) and single acyl tailed 1-palmitoyl-2-hydroxy-sn-glycero-3-phosphocholine (lyso-PC; 16:0) contain more disorder. Despite these variations in the packing of the tail region, the headgroup orientation remains approximately parallel to the nanodroplet interface. Remarkably, the lyso-PC lipids uniquely form more diluted and “patchy” 3D monolayers.[2] These results are supported by zeta-potential measurements and fluorometric analysis of Nile-red dye adsorption to these 3D phospholipid monolayers. Our findings suggest a vital role for the presence of single-tailed lipids on the lipid droplet organelles. Specifically, these lipids enhance the accessibility of the hydrophobic non-polar core by the water soluble enzymes; i.e. lipase, present in the cytosol.

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[2] Halil I. Okur, Yixing Chen, Nikolay Smolentsev, Evangelia Zdrali, and Sylvie Roke, J. Phys. Chem. B 2017, 121, 2808-2813.

## The PHA toolbox

N. Hanik<sup>1</sup>, M. Bassas<sup>1</sup>, A. Gonzalez<sup>1</sup>, E. Carreño-Morelli<sup>2</sup>, M. Zinn<sup>1\*</sup>

<sup>1</sup>HES-SO Valais, Institute of Life Technologies - Route du Rawyl 64, 1950 Sion, Switzerland, <sup>2</sup>HES-SO Valais, Institute of Systems Engineering - Route du Rawyl 47, 1950 Sion, Switzerland

For the sake of energy storage, the majority of organisms produce polymers from high-energy monomers and recycle them during starvation conditions. Starch as a prominent example has been utilized already by the ancient Greek in the classical antiquity and remains an important component in today's industrial products (e.g. thickener and stabilizer in food industry, internal sizing and surface sizing in papermaking, corrugated board adhesives, clothing starch for laundry).

Polyhydroxyalkanoates (PHAs) comprise a large class of polyesters synthesized by many bacteria as storage polymers. Depending on the specific bacteria strain as well as the substrate feed, the properties of the isotactic polyesters range from highly crystalline to completely amorphous dictated by the type and composition of side chains of the monomeric units. Thus, a wide range of mechanical properties is available when it comes to choosing the right polymer for a given application. Apart from their mechanical properties and the fact that PHA synthesis is independent from fossil resources, these polyesters offer a class of sustainable material revealing further interesting properties such as biodegradability and biocompatibility.

A large number of scientists make effort on the optimization of the fermentation procedures and down-stream processing to increase the productivity as well as the number of different available polymers within the two subclasses of polyhydroxyalkanoates, namely short- and medium-chain-length PHAs (e.g. different monomeric composition, molecular weight and molecular weight distribution). On the other hand, researchers use chemical modifications of available polymers to tailor the material properties of the polyhydroxyalkanoates produced by the bacteria. (e.g. changing the solubility by the introduction of functional groups in the side-chains).

In the Institute of Life Technologies at the University of Applied Sciences in Valais, Switzerland, we bring together fermentation expertise with the molecular design of the biogenic polymers by chemical modification, creating an integrated approach to provide advanced materials to a variety of highly demanding applications (e.g. medical devices and implants, drug carriers and coatings, metal injection molding). This synergy provides a fast and complete continuous feedback loop with less risk of design failure due to mismatched processes between fermentation optimization and chemical modification, lowering the barrier to create new tailor-made materials for highly demanding applications.

**Understanding the Nanoscale Structure, Mechanics, Hydration, and Organic Interfaces of Calcium Sulfate Phases Using an Accurate Force Field**

R. K. Mishra<sup>1</sup>, R. J. Flatt<sup>1</sup>, H. Heinz<sup>2</sup>

<sup>1</sup>Department of Civil, Environmental and Geomatic Engineering, ETH Zurich, Zurich, Switzerland, <sup>2</sup> Department of Chemical and Biological Engineering, University of Colorado at Boulder, USA

Calcium sulfates are major components in materials for construction, casts, implants, and tissue healing. Despite their broad usage, the relationship between nanoscale properties and functions delivered by these minerals has remained largely unknown. This study reports insight into the structure and dynamics of calcium sulfate minerals and organic interfaces in atomic-detail using a novel force field and molecular dynamics simulations. Data from X-ray diffraction, interfacial, and mechanical measurements are reproduced in high accuracy, one to two orders of magnitude better than generic atomistic force fields. Nanoscale origins of hydration, solubility, and modification of crystal growth by polymers are described. Thereby, structures of the minerals and their hydrated phases, (h k l) cleavage planes, hydration reactions and energies, anisotropic mechanical and thermal properties, as well as facet-specific adsorption of organic modifiers are explained. Using our validated atomistic model of calcium sulfate minerals, we have also verified the transition temperature for the gypsum to anhydrite conversion and the thermal stability of these phases at a given temperature range. The force field matches available experimental measurements, exceeds the accuracy of common DFT methods, and can be applied to systems as large as 100 million atoms. The models can be used with multiple force fields (INTERFACE FF, CHARMM, AMBER, GROMACS, PCFF, OPLS-AA) and for similar sulfate/sulfonate nanomaterials.



**Two component polyurethane adhesives for advanced automotive manufacturing**S. Grunder<sup>1</sup>, S. Schmatloch<sup>1</sup><sup>1</sup>Dow Europe GmbH, Bachtobelstrasse 3, 8810 Horgen, Switzerland - sgrunder@dow.com

The automotive industry has seen a trend to reduce the weight of vehicles. In order to follow the light-weight strategies, a variety of different metals, reinforced plastics, and other materials have been implemented. This multi-material mix is requiring new joining methods.<sup>[1]</sup> Adhesives have been established as an important joining method both to facilitate the assembly process of cars but also to enable new joining capabilities of a variety of materials as well as to improve the performance of the vehicles.<sup>[2]</sup> Two part (2K) polyurethane (PU) adhesives are selected as a process of choice to assemble parts in the trim shop since they show i) a good stress distribution in bonded parts in comparison with locally mechanically fixed assemblies, ii) the ability to bond complex shapes, iii) the ability to bond dissimilar materials as well as iv) the capability to offer tailorable curing kinetics. We report the development and implementation of latent 2K PU adhesives which show a long open time followed by a fast cure at room temperature. The open time offers assembly flexibility and improved material consumption, the rapid cure at room temperature allows advanced assembly processes. Further the adhesives are designed such that they can be cured fast by heat allowing cycle times down to less than one minutes. The combination of modulus and elongation offers superior crash management and long term durable assemblies also for dissimilar materials.

The presentation will shows the DOW Automotive Systems latest developments in two part polyurethane adhesive technology, it lists applications in the area of composite bonding and provides an insight into structure - property relationships that are the basis for above outlined requirements.

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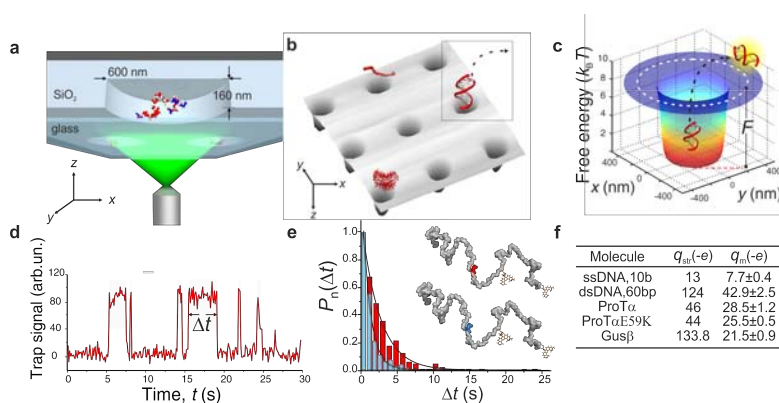
[2] S. Grunder, S. Schmatloch, A. Lutz, *Adhäsion Kleben + Dichten*, **2017**, 3, 34 - 37.

## Single-molecule electrometry

E. Ruggeri<sup>1</sup>, F. Zosel<sup>1</sup>, B. Schuler<sup>1</sup>, M. Krishnan<sup>1</sup>

<sup>1</sup>University of Zurich

Electrical charge is a fundamental property of biomolecules, strongly influencing their function [1] and stability. We demonstrate for the first time a high-precision ( $<1e$ ), measurement of the electrical charge of biomolecules in solution. The method is based on parallel, external field-free trapping [2] at an unprecedentedly low estimated sensitivity of yoctomoles (1-10 molecules). Our single molecule trap is created in a fluid-filled gap between two charged walls. Nanoscale patterning of one of the surfaces leads to a modulation of the local electrostatic potential, creating a deep thermodynamic potential well for a like-charged entity (Fig.a-b). In our new method "Escape Time Electrometry" (ETe) [3] we show for the first time stable trapping of biomolecules in solution, for tunable timescales ranging from hours to milliseconds. The depth of the well,  $F$ , experienced by a charged molecule is linearly proportional to its effective charge  $q_m$  (Fig.c). A molecule undergoing Brownian motion will reside in a trap for a time ( $t_{esc}$ ) given by Kramer's analytical expression,  $t_{esc} = t_r \exp(F/k_B T)$ , where  $t_r$  is a relaxation time that depends on the diffusion coefficient of the molecule. When occupied by a fluorescently-labelled molecule the optical intensity of the trap region is high (Fig.d). The duration of the intensity bursts ( $\Delta t$ ) follows an exponentially decaying probability distribution  $P_n(\Delta t)$ , which is fitted to extract  $t_{esc}$ , yielding information on the well depth and thus directly giving the effective charge  $q_m$ . Finally,  $q_m$  can be theoretically modelled and related to the molecule's known structural charge ( $q_{str}$ ); the table in Fig.f summarizes a few representative results.



The measured charge of DNA molecules is in remarkable agreement with existing theoretical predictions [4] and suggest that ETe can serve to readout the inter-nucleotides spacing of a nucleic acid molecule or polyelectrolyte. The study of the enzyme Gusβ suggests substantial regulation of the structural charge in a globular molecule [5], while our measurements on ProTa, a disordered one-dimensional polypeptide, provides unique insight into the charge renormalizing behavior of short, strongly charged segments within the molecule. Crucially, the exponential dependence of  $t_{esc}$  on the charge of the molecule permits us to distinguish between two ProTa variants that differ by a mutation of a single amino acid (E59K, 4% of the structural charge) (Fig.e). The Electrometry measurement can also be performed on a single molecule in real time, with the potential of detecting charge fluctuations, making ETe a new tool for ultrasensitive, rapid structural studies on biological macromolecules in the fluid phase.

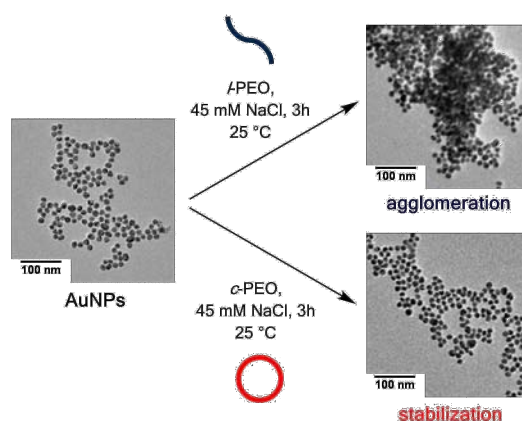
[1] Perutz, *Science*, **1978**, 201:1187-1191. [2] Krishnan et al., *Nature*, **2010**, 467:692-695. [3] Ruggeri et al., 2017; *Nature Nanotechnology*, **2017**, 12:488-495 [4] Manning, *Journal of Chemical Physics*, **1969**, 51:924-& 492. [5] Ninham, Parsegian, *Journal of Theoretical Biology*, **1971**, 31:405-428

## Surface Functionalization of Metal Nanoparticles and the Effect of the Polymer Topology on the Colloidal Stability

J. O. Quinsaats<sup>1,3</sup>, F. A. Nüesch<sup>1,4</sup>, D. M. Opris<sup>1\*</sup>, T. Yamamoto<sup>2\*</sup>

<sup>1</sup>Swiss Federal Laboratories for Materials Science and Technology, <sup>2</sup>Hokkaido University, <sup>3</sup>Japan Society for the Promotion of Science, <sup>4</sup>École Polytechnique Fédérale de Lausanne

Metal nanoparticles exhibit an array of properties which have enabled their use in various scientific disciplines. However, the preservation of the nanoparticle stability towards agglomeration or dissolution remains a major drawback since those phenomena alter the size- and shape-dependent properties of the nanostructures. The key to the enhancement of the stability is the tuning of the surface properties of the nanoparticles, and various approaches have already been conducted in order to achieve this goal. For instance, the surface of metal nanoparticles has already been functionalized with various inorganic, organic or hybrid inorganic-organic shells in order to tailor them for their specific target applications. This strategy enabled the preparation of non-conducting metal nanoparticles suitable as dielectric materials [1] or core-shell particles rendered hydrophobic through surface-initiated radical polymerization beneficial for their dispersion in different organic solvents [2]. Although a variety of polymers have already been grown or attached onto the nanoparticle surface or have simply been applied as additional stabilizer into the colloidal dispersion, the effect of the polymer topology on the enhancement of the nanoparticle stability has not yet been subjected to thorough investigation. Previous work featured that micelles composed of cyclic ABA triblock copolymers exhibit enhanced stabilities towards salt-induced agglomeration compared to the micelles of their corresponding linear counterparts.[3] Hence, a key highlight of this work features the synthesis and stabilization of metal nanoparticles (gold and silver) by polyethylene oxide (PEO) where substantial changes in the average nanoparticle size and stability under saline conditions were observed through the variation of the polymer topology. Overall, the average particle size of the metal nanoparticles is reduced in the presence of cyclic PEO (*c*-PEO) and the resistance of the nanoparticles towards agglomeration is extended over a larger concentration of NaCl ( $\leq 180$  mM) which is in direct contrast to the nanoparticles stabilized by linear PEO (*l*-PEO) where agglomeration occurs at NaCl concentrations as low as 45 mM.



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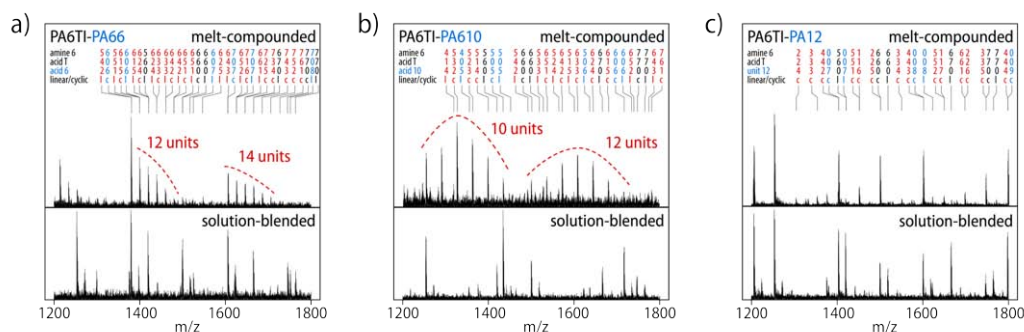
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## High Temperature Copolyamides by Efficient Transamidation of Crystalline-Crystalline Polyamide Blends

J. Cretenoud<sup>1</sup>, S. Galland<sup>1</sup>, C. J. Plummer<sup>1</sup>, H. Frauenrath<sup>1\*</sup>

<sup>1</sup>EPF Lausanne

High performance thermoplastic composites based on semiaromatic polyamides are prime candidates for metal replacement in lightweight structural applications. However, the low ductility and toughness of semiaromatic polyamides remain major obstacles to their wider industrial application. Here, we show that novel random copolymers are formed by the unexpectedly efficient transamidation during the melt compounding of semicrystalline semiaromatic with semicrystalline aliphatic polyamides. To this end, we melt-blended poly(hexamethylene terephthalamide-co-isophthalamide) (PA6TI) with different proportions of poly(hexamethylene adipamide) (PA66), poly(hexamethylene sebacamide) (PA610) and poly(lauro lactam) (PA12). In the case of the even-even polyamides PA66 and PA610, MALDI-TOF spectrometry confirmed random copolymers with PA6TI to be formed during melt compounding (Figure 1), resulting in homogeneous materials with single melting temperatures as well as glass transitions. A high degree of crystalline order was observed in these blends, as evidenced by differential scanning calorimetry and wide angle X-ray diffraction. By contrast, blends of PA6TI with the more hydrophobic and less hydrogen-bonded polyamide PA12 showed phase separation and a less efficient transamidation process. We propose that semicrystalline polyamides with compatible crystal structures, a high degree of hydrogen bonding and similar hydrogen-bonding show good initial compatibility and, therefore, undergo extensive transamidation. This opens the way to the systematic design and preparation of novel high performance thermoplastic polyamides by simple melt compounding.



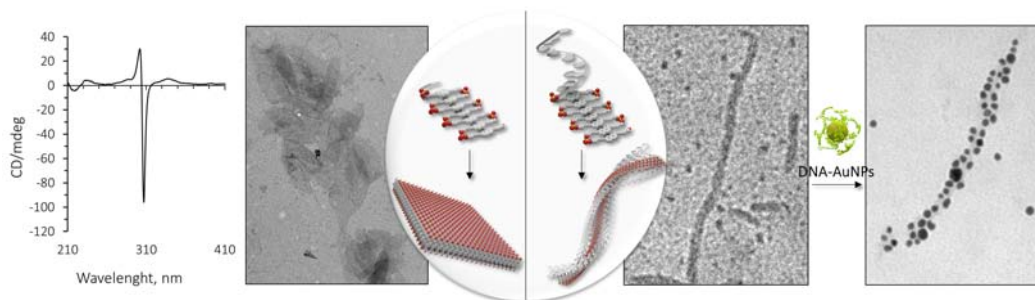
**Figure 1.** MALDI-TOF spectra of semiaromatic PA6TI melt compounded with 50 wt% of aliphatic (a) PA66, (b) PA610 or (c) PA12, together with the corresponding reference spectra of the polymers solution-blended at room temperature. Peaks are assigned to the pure PA6TI (black), the pure aliphatic segments (blue), and copolymer segments consisting of a mixture of the two components (red). The observed distribution of mass peaks is hence consistent with extensive transamidation and randomization of the polymer sequence in the copolymers PA6TI-PA610 and PA6TI-PA66 resulting from melt compounding.

## Introducing supramolecular polymers to DNA nanotechnology

Y. Vyborna<sup>1</sup>, R. Häner<sup>1\*</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of Bern Freiestrasse 3, CH-3012 Bern, Switzerland

Self-assembly of DNA-containing molecules into biocompatible functional materials has attracted considerable attention over the last years. In this contribution, we present our recent findings in the field of self-assembled DNA conjugates and their potential applications as stimuli-responsive materials, cargo binding vehicles, and energy transfer platforms.<sup>1</sup> The DNA conjugates consist of a short oligonucleotide strand covalently bound to an array of phosphodiester-linked pyrenes. Depending on the strand composition and conditions, the self-assembly governed by the stacking and hydrophobic interactions between pyrenes leads to a variety of shapes: micelles, one-dimensional ribbons and two-dimensional nanosheets. In the case of 1D structures (DNA-grafted supramolecular polymers), the polymer core is formed by the stacked pyrenes, whereas the oligonucleotides are arranged at the edges of the ribbons in a comb-like fashion.



The ability to design interactions between oligonucleotides is central in mastering the properties of DNA-grafted supramolecular polymers.<sup>2</sup> For example, a helical array of AuNPs is created on the ribbons via sequence-specific DNA binding.<sup>3</sup> Additionally, hybridization of the single-stranded DNAs from the ribbons with a complementary non-modified DNA strand leads to the formation of hierarchically organized networks.<sup>4</sup> The transformation occurs in a highly cooperative manner, resembling certain biological processes. In the case of 2D structures, the assemblies exhibit unique chiroptical properties. Finally, our results suggest great opportunities towards potential applications in biosensing, complex carrier systems and functional nanoarchitectures. Our current attempts aim at integrating these oligonucleotide-based assemblies in the field of DNA nanotechnology.

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[4] Vyborna, Y.; Vybornyi, M.; Häner, R. *J. Am. Chem. Soc.* **2015**, 137, 14051-14054.

**Mechanically triggered fluorescent changes in polymers**M. Karman<sup>1</sup>, E. Verde-Sesto<sup>2,1</sup>, Y. C. Simon<sup>3,1</sup>, C. Weder<sup>1\*</sup>

<sup>1</sup>Adolphe Merkle Institute, University of Fribourg, 1700 Fribourg, Switzerland, <sup>2</sup>POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, 20018 Donostia/San Sebastian, Spain, <sup>3</sup>School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg 39406 MS, USA

Despite an increasing number of studies that have investigated mechanochemical effects in polymers, the number of polymers whose fluorescence characteristics change upon exposure to mechanical stress is still limited. Here, we report on two families of mechanoresponsive polymers whose fluorescence can be mechanically turned on or off, respectively. The fluorescent dithiomaleimide (DTM) motif was used as a mechanically responsive moiety whose fluorescence can be turned off upon mechanically induced chain cleavage. This mechanophore was incorporated into poly( $\epsilon$ -caprolactone)s (PCL) of different molecular weights through ring opening polymerization initiated from a DTM dihydroxy derivative. This strategy allows us to position the DTM in the middle of a PCL chain and further study its response to ultrasound-induced mechanical stress. Indeed, when solutions of high molecular-weight PCL-DTM were exposed to ultrasound, the fluorescence intensity and molecular weight decreased according to first-order kinetics with comparable rate constants. A substantial decrease of the fluorescence intensity was also observed when solid samples of the high molecular-weight PCL-DTM were grinded. The data thus demonstrate the usefulness of the DTM motif as mechanophore that displays fluorescence turn-off upon mechanochemically induced scission. On the other hand, a hydroxy-benzoxazole derivative was used in a similar manner to achieve mechanically induced fluorescence turn-on. On account of an excited state intramolecular proton transfer (ESIPT), the hydroxy-benzoxazole is photoluminescent, but esterification affords to a 'caged' molecule, in which the ESIPT is suppressed. Thus, a benzoxazole ester was used to initiate the polymerization of methyl acrylate through an atom transfer radical polymerization, affording poly(methyl acrylate) comprising a chain-centered caged luminophore. Ultrasonication experiments were used to induce mechanochemical chain cleavage of the benzoxazole ester, which in turn restores the photoluminescence of the parent hydroxy-benzoxazole.

