

SSD

# **Invited Speakers**

Prof. Thomas Schäfer, (University of the Basque Country, Spain) Dr. Robert Style, (ETHZ, Switzerland)

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# Support







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# How to get there

# **Conferene Venue**

University of Geneva Building Sciences II

Quai Ernest-Ansermet 30 1205 Geneva, Switzerland Location: N 46.198036, E 6.132405



The 20th edition of the Swiss Soft Days will take place in the **Sciences II** building at the University of Geneva. The building is easily reachable by public transport (**TPG**) from the main train station (**Gare Cornavin**), there you take **Tram 14** direction **Bernex P + R** and get off at the stop **Jonction**. From there it is a few minutes walk to the venue.







Talks: Room A100



# Program 20th SSD Geneva

- **9:00-10:10** *Registration/Coffee*
- **10:10-10:15** *Welcome*
- **10:15-11:00** DNA-Gating in Nanopores (Thomas Schäfer, Uni Basque Country)
- Session 1 Colloids and Surfaces (Chair: Eric Dufresne, ETH Zurich)
- **11:00-11:15** Mass Flow through Individual Nanotubes Measured Using Landau-Squire Jet (E. Secchi, ETH Zurich)
- **11:15-11:30** Determination of Surface Potential and Electrical Double-Layer Structure at the Aqueous Electrolyte-Nanoparticle Interface (M.A. Brown, ETH Zurich)
- **11:30-11:45** Polyelectrolyte Functionalization of Nanostructures: A Way to Improve Their Stability (P. Rouster, Uni Geneva)
- **11:45-12:00** Self-Propelled Colloidal Bead Chains: From Rotators to Flagella (H. R. Vutukuri, ETH Zurich)
- **12:00-13:30** Lunch + Poster Session
- **13:30-14:00** The Surface Tension of Soft Solids (Robert Style, ETH Zurich)

Session 2 - Bio-Inspired and Bio-Relevant Materials (Chair: Kitty van Gruijthuijsen, Firmenich)

- **14:00-14:15** Effects of Archaea-Inspired Lipid Structure on H<sup>+</sup>/OH<sup>-</sup> Permeation Across Liposome Membranes (T. Schroeder, AMI Fribourg)
- **14:15-14:30** Smart Surfaces or How to Reversibly Switch Enzymatic Activity on Polymer Brushes with Light (M. Dübner, ETH Zurich)
- **14:30-14:45** Exploiting the Enhanced Magnetic Susceptibility of Phospholipid Bicelles doped with Cholesterylamine and Complexed Lanthanide Ions (S. Isabettini, ETH Zurich)
- **14:45-15:00** [4-]Helicene Squalene Nanoassemblies with Mitochondrial Targeting Properties (A. Babic, Uni Geneva)
- **15:00-15:15** Monolayer and Bilayer Properties of a 1,2-Diamidophospholipid (F. Neuhaus, AMI Fribourg)
- **15:15-16:00** Afternoon Coffee + Poster Session
- Session 3 Soft Materials (Chair: Istvan Szilagyi, Uni Geneva)
- **16:00-16:15** Gold Nanowire Rabrication with Lipid Nanotubes
  - (K. Jajcevic, Uni Geneva)
- **16:15-16:30** Continuous Network Solid Polymer Electrolytes for Lithium Batteries (P. Sutton, AMI Fribourg)
- **16:30-16:45** Microgel Monolayers for Soft-Colloidal Templating: Particle Size Effects on Nanolitography (M.A. Fernandez-Rodriguez, ETH Zurich)
- **16:45-17:00** Rapid and Directed Assembly of Nanoparticles into Periodic Arrays (C. Kinnear, Uni Melbourne)
- 17:00-17:05 Concluding Remarks
- **17:05-** ... Drinks at Halles de l'Ile (at own expense)

# List of Posters

- 01 Colloidal Switches by Electric and Magnetic Fields (A.F. Demiroers, ETH Zurich)
- **02** Janus Microswimmers at Oil-Water Interfaces (K. Dietrich, ETH Zurich)
- **03** Mechanism of the Cooperativity in Antimicrobial Peptides (E. Drab, Uni Geneva)
- 04 Biomimetic Engineering of Polymersome Membranes for Stimuli Triggered Activity of Nanoreactors (T. Einfalt)
- **05** Symmetry Control in Gyroid-Forming Terpolymers by Solvent Vapour Annealing (K. Korzeb, AMI Fribourg)
- 06 Anionic and Anionic Amphiphilic Silver Nanocubes Interfacing with Lipid Vesicles and Ligand Exchange Evolution By SERS (A. Lapresta-Fernández, EPFL)
- 07 Force Spectroscopy of Unfolding Metal-Ligand Single Chain Polymer Nanoparticles (L. Neumann, Uni Fribourg)
- 08 Decode Polydiacetylene-Peptide Interaction Mechanism at Raft Boundaries (J. Nuck, Uni Geneva)
- 09 Mechanosensitivity of Polydiacetylene with a Phosphocholine Headgroup (R.D. Ortuso, Uni Geneva)
- 10 Hybrid Materials Based On Layered Double Hydroxides (M. Pavlovic, Uni Geneva)
- 11 Interaction of Organic Ions with Proteins (L. Pérez-Fuentes, Uni Granada)
- 12 Soil-on-a-Chip: Probing the Interplay between Fungi, Nematodes, Bacteria and Plant Roots Using Microfluidic Platforms (C.E. Stanley, Agroscope)
- **13** Spray Drying Amorphous Salt Nanoparticles (M. Steinacher, EPFL)
- 14 Effect of Shear Strength on Shear Aggregation Rates in the presence of Repulsive Electrical Double Layer Forces (T. Sugimoto, Uni Tsukuba)
- **15** Optical and Electrical Characterization of Voltage Sensitive Dyes in Lipid Bilayers (M. Tsemperouli, Uni Geneva)
- **16** Forces between Silica Particles in Presence of Monovalent and Multivalent Coions (B. Uzelac, Uni Geneva)
- 17 Production of Mechanically Robust Capsules with Ultrathin Shells (A. Vian, EPFL)

# **DNA-Gating in Nanopores**

Thomas Schäfer

#### POLYMAT, University of the Basque Country, San Sebastián, Spain

DNA-aptamers are oligonucleic acids that can be selected to specifically interact with in principle any kind of target molecule. An important asset of aptamer conjugates is the fact that upon specific binding, their spatial conformation may change drastically. Recently, if has been shown that this specific conformational change can be exploited for creating biomimicking gating membranes, where aptamers serve as a "nanovalve" which selectively triggers the opening or closing of a nanopore depending on the presence of a target molecule. Such systems add an important degree of freedom in the design of stimuli-responsive systems which conventionally respond to bulk stimuli such as pH, temperature, light or electrical and magnetic fields.

In this presentation a short overview will first be given of how DNA can be used as a gating element in nanodevices and membranes with particular emphasis on how to quantify target-DNA interactions and respective conformational changes by advanced surface sensitive characterization techniques. Subsequently, an outlook will be presented on how far this versatility can be pushed while maintaining the function of such DNA-building blocks in membranes, such as their use in non-conventional media.

The examples given will illustrate that DNA is indeed a highly versatile building block for creating biomimicking membranes of different responsive functions.

## Mass Flow through Individual Nanotubes Measured Using Landau-Squire Jet

E. Secchi<sup>1</sup>, S. Marbach<sup>2</sup>, A. Niguès<sup>2</sup>, A. Siria<sup>2</sup>, L. Bocquet<sup>2</sup>

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**INTRODUCTION:** Carbon nanotubes are hollow cylinders formed from carbon atoms arranged in a graphite-like structure and have nanometre-scale diameters<sup>1</sup>. Over the last decade, a few experimental works and simulations<sup>2</sup> demonstrated that water transport through carbon nanotubes is almost frictionless, and that the flow rate exceeds predictions made using classical theories by many orders of magnitude. Thanks to this peculiarity, carbon nanotubes might be the answer to the need of better water-purification, desalination technology and energy harvesting. However, due to the challenge of performing ultra-sensitive reliable experiments and given the huge difference in reported results, claims of rapid water transport have been strongly questioned and debated. In this work we develop experiments of flow transport across individual nanotube under pressure driven flow<sup>3</sup>, thanks to the development of a new velocimetry technique with an unprecedented sensitivity down to femto-liters per second.

**METHODS:** We fabricate a nanofluidic system consisting of a single nanotube inserted at the end of nanopipette, using nanomanipulation techniques performed inside a Scanning Electron Microscope (SEM, Nova Nanosem)<sup>4</sup>. The cell is composed of two macroscopic reservoirs bridged by the nanocapillary with the nanotube located at the tip. The rear reservoir allows pressure control, while the one in the front permit the visualization of the region in front of the nanocapillary tip with an optical microscope. We use two different types of nanotubes, Carbon (CNT) and Boron-Nitride (BNNT) nanotubes.

**RESULTS:** Under a pressure drop, our nanodevice generates a fluid jet in a reservoir, which far from the nanotube can be described by the classical Landau-Squire solution. Due to the peculiarity of this flow, it can be used as a very efficient probe to characterize the permeability of nanochannels.

Thanks to the unprecedented sensitivity of our technique, we revealed unexpectedly large and radius-dependent flow enhancement in carbon nanotubes, determined by the surface slippage. Surprisingly, no slippage was detected in boron nitride nanotubes that are crystallographically similar to carbon nanotubes, but electronically different.



Fig. 1: a, Sketch of the fluidic cell used to image the Landau–Squire flow; b, SEM image of a CNT inserted into a nanocapillary; c, Trajectories of individual colloidal tracers in a Landau– Squire flow field in the outer reservoir.

**DISCUSSION & CONCLUSIONS:** The pronounced contrast between CNT and BNNT originates from subtle differences in the atomic-scale details of their solid–liquid interfaces. By providing a deeper understanding of well-defined aqueous interfaces, these measurements might aid the design of improved membranes and nanofluidic devices.

**REFERENCES:** <sup>1</sup>E. Secchi, A. Niguès, L. Jubin, A. Siria, & L. Bocquet; **2016**; *Phys. Rev. Lett.*; 116: 154501. <sup>2</sup>K. Falk, F. Sedlmeier, L. Joly, R. Netz & L. Bocquet; **2010**; *Nano Lett.*; 10, 4067– 4073. <sup>3</sup>E. Secchi, S. Marbach, A. Niguès, D. Stein, A. Siria & L. Bocquet; **2016**; *Nature*; 537: 210. <sup>4</sup>A. Siria *et al.*; 2013; *Nature*; **494**: 455.

**ACKNOWLEDGEMENTS:** We acknowledge funding from the European Union's H2020 Framework Programme/ERC Starting Grant agreement number 637748 — NanoSOFT and funding from ANR project BlueEnergy.

# DETERMINATION OF SURFACE POTENTIAL AND ELECTRICAL DOUBLE-LAYER STRUCTURE AT THE AQUEOUS ELECTROLYTE-NANOPARTICLE INTERFACE [1]

M.A. Brown<sup>1</sup>, Z. Abbas<sup>2</sup>, A. Kleibert<sup>3</sup>, R.G. Green<sup>4</sup>, A. Goel<sup>1</sup>, S. May<sup>5</sup>, T.M. Squires<sup>6</sup>

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**SUMMARY:** The structure of the electrical double layer has been debated for well over a century, since it mediates colloidal interactions, regulates surface structure, controls reactivity, sets capacitance, and represents the central element of electrochemical supercapacitors. The surface potential of such surfaces generally exceeds the electrokinetic potential, often substantially. Traditionally, a Stern layer of nonspecifically adsorbed ions has been invoked to rationalize the difference between these two potentials; however, the inability to directly measure the surface potential of dispersed systems has rendered quantitative measurements of the Stern laver potential, and other quantities associated with the outer Helmholtz plane, impossible. Here, we use x-ray photoelectron spectroscopy from a liquid microjet to measure the absolute surface potentials of silica nanoparticles dispersed in aqueous electrolytes. We quantitatively determine the impact of specific cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>) in chloride electrolytes on the surface potential, the location of the shear plane, and the capacitance of the Stern layer. We find that the magnitude of the surface potential increases linearly with the hydrated-cation radius. Interpreting our data using the simplest assumptions and most straightforward understanding of Gouy-Chapman-Stern theory reveals a Stern layer whose thickness corresponds to a single layer of water molecules hydrating the silica surface, plus the radius of the hydrated cation. These results subject electrical double-layer theories to direct and falsifiable tests to reveal a physically intuitive and quantitatively verified picture of the Stern layer that is consistent across multiple electrolytes and solution conditions.

**METHODS:** Combining XPS with a liquid microjet has allowed us to perform the very first measurement of the absolute surface potential of a NP suspended in an aqueous electrolyte. XPS experiments are performed at the SIM beam line [2] of the Swiss Light Source using a 0.032-mm liquid microjet operating at 279 K and a flow rate of 0.45 mL/min to continuously drive silica NPs in aqueous suspension through the beam, while maintaining an evacuated environment for the photoelectrons to traverse and be collected. A complete description of in situ XPS at the three-way interface of air-water-

colloid is given elsewhere [3]. The Swiss Light Source near ambient pressure photoemission end station is used [4].



Fig. 1: XPS at the water-silica nanoparticle interface. (a) A liquid microjet delivers a stable free-flowing suspension of colloidal silica inside the measurement chamber of an XPS spectrometer. (b) O 1s and Si 2p spectra for 5.0 wt % SiO2 in 50-mM LiCl, NaCl, KCl, and CsCl electrolytes at pH 10. (c) Measured Si 2p BE, relative to the vacuum level, as a function of hydrated cation radius [37]. The change in surface potential relative to that in NaCl electrolyte is shown on the right- hand axis. Error bars represent the standard deviation of four repeat measurements.

**REFERENCES:** <sup>1</sup>M.A. Brown *et al.*; **2016**; *Phys. Rev. X*; 6:011007. <sup>2</sup> U. Flechsig *et al.*; **2010**; *AIP Conf. Pro.*; 1234:319. <sup>3</sup>M.A. Brown *et al.*; **2013**; *Surf. Sci.*; 610:1. <sup>4</sup>M.A. Brown *et al.*; **2013**; *Rev. Sci. Instrum.*; 84:073904.

ACKNOWLEDGEMENTS: SNSF grant no. 153578 and 162320.

# Polyelectrolyte functionalization of nanostructures: a way to improve their stability

P. Rouster, M. Pavlovic, I. Szilagyi

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**INTRODUCTION:** In present days, titania nanosheets (TNS) are gaining more and more interest as their properties tend to overcome the ones of spherical nanoparticles, e.g., in photocatalysis[1]. However in solution, these bare particles can easily aggregate depending on the properties (e.g. pH, ionic strength, temperature etc.) of the medium. Therefore, a convenient method to tune the stability of the particles is to functionalize them with some polyelectrolytes.

**METHODS:** Titania nanosheets of anatase phase were synthesized by hydrothermal treatment in hydrofluoric acid followed by sodium hydroxide washing steps in order to exchange the surface fluoride anions with hydroxide ions[2]. The composition and structure of the obtained TNS were investigated by X-ray diffraction experiments, transmission electron microscopy and atomic force microscopy. Polyelectrolyte functionalized TNS were obtained by adding TNS into a polyelectrolyte solution. The colloidal behaviour of the bare and/or coated particles was studied as a function of the polyelectrolyte dose applied and ionic strength by electrophoresis and dynamic light scattering measurements.

**RESULTS:** Bare TNS possess a limited colloidal stability in NaCl solutions where particles aggregate at salt concentrations above 19 mM. As a result, in order to improve the stability of the TNS. they were functionalized with some polyelectrolytes namely poly(diallydimethylammonium chloride) (PDADMAC) and poly(acrylamide-co-DADMAC) (PAAm-co-DADMAC). Electrophoretic mobility and aggregation rate measurements in both systems showed that charge neutralization and charge reversal could be observed at appropriate polvelectrolvte doses (Fig. 1a). Charge neutralization occurred at the isoelectric point (IEP) resulting in unstable suspensions whereas charge overcompensation led to a restabilization of the system (Fig 1b). The effect of the polyelectrolyte coating was studied and revealed an enhancement of the nanosheets stability in the salt medium due to electrostatic and steric repulsion between the particles.



Fig. 1: Electrophoretic mobility (a) and stability ratio (b) of the TNS as a function of the polyelectrolyte dose. Note that a stability ratio close to unity indicate fast aggregating systems and above one more stable samples.

DISCUSSION & **CONCLUSIONS:** The colloidal behaviour of the bare TNS can be explained by the DLVO theory. At low salt levels, the TNS repeal each other due to the overlap of their electric double layer which overcomes the attractive van der Waals forces whereas at high salt levels, the electric double layer vanishes due to charge screening of the particles by the salt ions. In addition, the colloidal stability upon polyelectrolyte adsorption is due to DLVO forces and to non-DLVO interactions namely patch-charge attractive and repulsive steric interactions. forces Furthermore, during aggregation, it appeared that the nanosheets would adopt a face-to-face orientation in the clusters while primary particles could be observed in stable suspensions.

To summarize, the colloidal stability of bare particles can be significantly improved by functionalizing them with polyelectrolytes. These coated particles could then be used in further applications, where the bare particles were initially inadequate.

**REFERENCES:** <sup>1</sup> Y. L. Yu et al.; **2014**; J. Phys. Chem. C; 118:12727-12733. <sup>2</sup> P. Rouster et al.; **2016**; *RCS Adv.*; 6:97322-97330.

**ACKNOWLEDGEMENTS:** This work was supported by the Swiss Secretariat for Education, Research and Innovation, COST Action CM1303, University of Geneva and Swiss National Science Foundation.

# Self-propelled colloidal bead chains: from rotators to flagella

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Active systems exhibit a plethora of exotic phenomena such as clustering, segregation, swarming, vortex formation, and anomalous density fluctuations. Many systems with such behavior can be found in nature, for instance, schools of fish, flocks of birds, and swarms of bacteria. Self-propelled colloidal particles or artificial microswimmers have been identified as a new class of matter with great potential, owing to their ability to mimic the collective motion of complex living systems. Self-propelled colloidal particle systems are currently a subject of great interest in soft condensed matter, owing to their ability to mimic the collective behavior of complex living systems, but also serve as model systems to study intrinsically out-of-equilibrium systems. The quest for designing new self-propelled colloidal model systems is fueled by the demand for more realistic model systems to study the behavior of their more complex natural counterparts. Here, we introduce a new type of self-propelled colloids, namely self-propelled colloidal bead chains with tunable flexibility between the beads, created from self-propelled spherical particles. Our assembly process relies on a combination of dipolar interactions induced by external AC electric fields to assemble the Janus particles into staggered linear chains and a bonding step to keep the chains intact even after the field is removed. In the presence of fuel, self-propelled particle chains spontaneously rotate or spin (Figure 1a) when the spherical swimmers are connected rigidly, while they show flagellum-like propulsion (Figure 1b) when the connections between the spherical swimmers are semi-flexible<sup>1</sup>. Moreover, our method also enables us to make complex selfpropelled chains composed of two parts: one semiflexible and one rigid. Our method is general and opens a new way to design novel complex selfpropelled objects using different complex particles as starting building blocks in combination with the flexibility between the building blocks. Finally, we show preliminary results on collective behaviour of circular swimmers.



Figure 1. Time-lapse optical microscopy images show the circular motion of self-propelled 'ridgid' bead chain (**a**), and Flagellum-like motion of selfpropelled semiflexible bead chain(**b**) in the presence of the fuel. The arrow depicts the direction of the motion.

**REFERENCES:** <sup>1</sup> H. R. Vutukuri and W.T.S. Huck, underreview.

**ACKNOWLEDGEMENTS:** H.R.V. was partially supported by a Marie Skłodowska-Curie Intra European Fellowship (G.A. No. 708349-SPCOLPS) within Horizon 2020.

## The surface tension of soft solids

Rob Style ETH Zürich, Zürich, Switzerland.

Just like liquids, solids can also have a surface tension. Typically it is too weak to significantly deform a solid. However in soft gels and elastomers it starts to play an important role. For example, I will present experiments showing how soft composites, soft wetting, and soft adhesion behave very differently from what would be normally expected. I'll explain why these novel effects typically arise at length scales smaller than a critical, material-dependent elastocapillary length.

#### **REFERENCES:**

- 1. R. Style, et al., PRL 110, 066103 (2013).
- 2. R. Style, et al., PNAS 110, 12541 (2013).
- 3. R. Style, et al., Nature Commun. 4 (2013).
- 4. R. Style, et al., Nature Phys. 11, 82 (2015).



Figure 1: Droplets of water condensing on a soft, flat, silicone gel surface. The surface has gradients in thickness, with the deepest parts being given by the dark lines. Droplets spontaneously move to deeper parts of the surface, causing aligned patterns like the one shown in the figure.



Figure 2: The behavior of simple liquid/soft solid composites. a) Individual liquid inclusions imaged as the surrounding solid is stretched. Smaller inclusions stretch less than larger inclusions due to the effect of surface tension. b) The change in Young's modulus of a piece of silicone elastomer as an increasing volume fraction of small liquid droplets are added. The black diamonds show a relatively stiff solid, that gets softer as liquid is added. The blue circles show a soft solid (Young's modulus of 3kPa) that actually stiffens as liquid is added. The curves are theoretical predictions.

# EFFECTS OF ARCHAEA-INSPIRED LIPID STRUCTURE ON H<sup>+</sup>/OH<sup>-</sup> PERMEATION ACROSS LIPOSOME MEMBRANES

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**INTRODUCTION:** Acidophilic archaea have evolved to survive in environments with pH values as low as 0.7 despite needing to maintain a nearneutral internal pH. These archaea often express lipids with unique characteristics thought to aid in maintaining a steep proton gradient across their cell membranes, including ether linkages, branched fatty acid chains, and transmembrane tethers linking two hydrophilic head groups across the membrane [1]. We have measured  $H^+/OH^-$  permeation across homogeneous liposome membranes composed of a class of archaea-inspired synthetic lipids containing these motifs in order to systematically test the relationships between various structural and simulated parameters of a membrane and its permeability [2].

**METHODS:** We collected H<sup>+</sup>/OH<sup>-</sup> permeability values using a fluorescence-based permeation assay with an internal calibration adapted from Paula et *al.* [3] at room temperature. Briefly, we synthesized unilamellar liposomes approximately 80 nm in diameter containing the pH-sensitive ratiometric dye pyranine via the hydration of a lipid film followed by freeze/thaw and extrusion. We measured the liposomes' size distributions using DLS, then measured the exponential decay of their fluorescence signals following the addition of pH jumps. We included K<sub>2</sub>SO<sub>4</sub> and valinomycin in the system to prevent the buildup of an electrical gradient. Lateral diffusion coefficients were determined using FRAP and membrane thicknesses were determined using AFM. MD simulations were performed for 50 ns on model membranes containing 1458 lipid head groups.

**RESULTS:** We found that  $H^+/OH^-$  permeability increased with tether length, decreased with the inclusion of isoprenoid methyl branches, and was independent of tethering at room temperature. The average  $H^+/OH^-$  permeability values correlated well with both (a) the number of instances that three water molecules occupied the membrane simultaneously and (b) the number of instances that two water molecules appeared in the membrane within 5 Å of one another during a 50 ns simulated period (Fig. 2).



Fig. 1: Examples of archaea-inspired lipids.



*Fig. 2: A snapshot of six water molecules in a simulated bolaamphiphilic lipid monolayer.* 

**DISCUSSION & CONCLUSIONS:** We found the positive correlation between permeability and membrane thickness in tethered lipids to be counterintuitive at first; it could possibly be attributed to changes in the mismatch between the ends of the dangling phytanyl chains (Fig. 1). We hypothesize that transmembrane tethering dampens the positive correlation between a membrane's permeability and temperature rather than lowering its permeability at RT. Simulated instances of water penetration into lipid membranes may be useful as a predictor of permeability.

**REFERENCES:** <sup>1</sup> N. P. Ulrih, D. Gmajner, P. Raspor; **2009**; *Appl Microbiol Biotechnol*; 84:249-260. <sup>2</sup> T. B. H. Schroeder, G. Leriche, T. Koyanagi, M. A. Johnson, K. N. Haengel, O. M. Eggenberger, C. L. Wang, Y. H. Kim, K. Diraviyam, D. Sept, J. Yang, M. Mayer; **2016**; *Biophys J*; 110:2430-2440. <sup>3</sup> S. Paula, A.G. Volkov, A. N. Van Hoek, T. H. Haines, D. W. Deamer; **1996**; *Biophys J*; 70:339-348.

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# Smart Surfaces *or* How to Reversibly Switch Enzymatic Activity on Polymer Brushes with Light

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**INTRODUCTION:** Smart surfaces are of great interest, as they allow the switching of properties or functionalities on demand, based on their responsiveness to a certain trigger, such as temperature, pH or light. Polymeric surfaces with reactive groups that can be modified under mild, metal-free conditions open up a broad field of applications, including diagnostic-microarray fabrication utilizing bioconjugation processes.

**RESULTS:** Here we report the grafting of polymeric copolymer-brush structures on substrates, which provide both amine- and thiolreactive units suitable for post-polymerization orthogonal modification. Radicals serving as initiators were created by exposure of ETFE films to extreme ultraviolet light using the x-ray interference lithography beamline at the Swiss Light Source<sup>[1,2]</sup>. Free-radical polymerization was used to graft orthogonally functionalizable copolymers containing epoxide (glycidyl methacrylate, GMA) and furan-protected maleimide (FuMaMA) groups as side chains. The removal of the furan protecting group after polymerization via a retro Diels-Alder reaction yields chemoselective thiol-reactive maleimide groups. Multifunctional smart surfaces (Figure 1a) were fabricated in a two-step postpolymerization modification using, firstly, the amine-epoxide reaction for bioconjugation of microperoxidase-11 (MP-11) chemoselectively to GMA and, secondly, the nucleophilic thiol-ene reaction to covalently attach photochromic spiropyran (SP) moieties to activated maleimides. A light-induced switch in enzymatic activity of P(GMA-MP-11-co-MaMA-SP) copolymer brushes demonstrated via the MP-11-catalyzed was oxidation of colorless 3,3'5,5'-tetramethylbenzidine (TMB) diamine to deep-blue colored TMB diimine. The drastic change in enzymatic activity was interpreted as a consequence of a switch in the wetting and swelling behavior of the grafted brushes from a non-charged, collapsed state under visible light to a zwitterionic, elongated state (upon UV-light exposure). Furthermore, integration of the smart surfaces into an optofluidic lab-on-a-chip device (Figure 1b) enabled the reversible *in-situ* activation of the biochemical response under a

controlled light stimulus in a dynamic, remotely-controlled fashion.<sup>[3]</sup>

Fig. 1: (a) Grafted photochromic bioconjugated polymeric P(GMA-MP-11-*co*-MaMA-SP) copolymer brushes orthogonally functionalized using chemoselective amine-epoxide and thiol-ene



post-polymerization modifications. (b) Schematic cross-section of the fabricated optofluidic device integrated with the modified smart substrate showing the two possible states of the grafted polymer brushes: i) non-charged, collapsed state under visible light (left) and ii) their zwitterionic, elongated state after UV-light activation (right).

**DISCUSSION & CONCLUSIONS:** The results represent a major milestone in responsive bioconjugated polymeric surfaces, as they combine chemospecific highly efficient PPM in an orthogonal fashion to implement multifunctionality on a single brush. The well-controlled brush structures open up a broad variety of applications for responsive bio-conjugated polymer brushes in, for example, all-polymeric smart diagnostic systems.

**REFERENCES:** <sup>[1]</sup> M. Dübner, T.N. Gevrek, A. Sanyal, N.D. Spencer, C. Padeste, *ACS Applied Materials & Interfaces* **2015**, *7*, 11337-11345; <sup>[2]</sup> M. Dübner, N.D. Spencer, C. Padeste, *Langmuir* **2014**, *30*, 14971-14981. <sup>[3]</sup> M. Dübner, V.J. Cadarso, T.N. Gevrek, A. Sanyal, N.D. Spencer, C. Padeste, submitted.

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# Exploiting the Enhanced Magnetic Susceptibility of Phospholipid Bicelles doped with Cholesterylamine and Complexed Lanthanide Ions

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**INTRODUCTION:** Bicelles composed of DMPC, cholesterol and the lanthanide-chelating  $(Ln^{3+})$ phospholipids DMPE-DTPA are highly tunable magnetic-responsive systems.<sup>1</sup> Although it is known that the bicelle's magnetic response may by enhanced with their size, little has been done to tune their intrinsic magnetic susceptibility. We address this gap by enhancing the magnetic susceptibility by replacing cholesterol with  $3\beta$ -cholest-5-en-3-amine (Chol-NH<sub>2</sub>). The chemical modification of the hydroxyl head group with a primary amine resulted in unprecedented bicelle alignment in an external magnetic field. Chelation of different lanthanide ions permits fine-tuning of the magnitude and direction of alignment. These systems may be valuable tools for biomolecular research and as building blocks for the development of magnetically responsive soft materials.

**METHODS:** Bicelles were prepared as described previously<sup>1</sup>. The bicelles were characterised by birefringence, Cryo-TEM, DLS and SANS. The importance of the sterol dopant's molecular structure was evaluated by comparison with a cholesteryl amine conjugate (Chol-C<sub>2</sub>OC<sub>2</sub>-NH<sub>2</sub>), which has an aliphatic chain between the sterol backbone and the primary amine head group. A more profound understanding of the reasons behind the enhanced magnetic-response of Chol-NH<sub>2</sub> doped bicelles was achieved by molecular dynamics simulation. Finally, the potential of these bicelles for the development of magnetically-responsive optical gels was investigated by imbedding them into a gelatin network.<sup>2</sup>

#### **RESULTS:**



Fig. 1: Cryo-TEM micrographs of A) DMPC/Chol-NH<sub>2</sub>/DMPE-DTPA/Tm<sup>3+</sup> and B) DMPC/Chol-C<sub>2</sub>OC<sub>2</sub>-NH<sub>2</sub>/DMPE-DTPA/Tm<sup>3+</sup> flash frozen at 5 °C. Each scale bar represents 200 nm.

Fig. 2: Alignment factor as a function of magnetic field strength for DMPC/Chol-NH<sub>2</sub>/DMPE-DTPA/Ln<sup>3+</sup> bicelles at 5 °C. The lanthanide ion  $(Ln^{3+})$  is either Tm<sup>3+</sup>, Dy<sup>3+</sup> or Yb<sup>3+</sup>. The SANS 2D



scattering patterns were measured at 8 T. The magnetic field B is directed upwards as indicated with an arrow.

**DISCUSSION & CONCLUSIONS:** Introducing a primary amine as polar head group of the sterol moiety allows for selective tuning DMPC/Chol-NH<sub>2</sub>/DMPE-DTPA/Ln<sup>3+</sup> (16:4:5:5, molar ratio) bicelle's magnetic susceptibility without changing their size. Full alignment is reached at reasonable field strengths. Therefore, chemical tuning of the polar region of lanthanide-containing polymolecular assemblies offers a strong possibility for enhancing their magnetic response. Furthermore, the bicelles were successfully aligned and fixed in a gelatin network in a thermos-reversible manner.

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**ACKNOWLEDGEMENTS:** We warmly thank the SNF for funding (project n° 200021\_150088/1)

# [4-]HELICENE SQUALENE NANOASSEMBLIES WITH MITOCHONDRIAL TARGETING PROPERTIES

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**INTRODUCTION:** Squalene based nanoassemblies have arisen as a robust platform in nanomedicine. Squalenoylation has been found to improve pharmacokinetics, enhance drug stability, lower toxicity, and increase the solubility of poorly water-soluble molecules to allow their use in biomedicine.<sup>1</sup> Helicenes have been rarely used for biomedical applications. This is due to their poor solubility and their blue-green spectral properties. Recently, several derivatization possibilities have allowed fine-tuning of chiro-optical properties of [4]helicenes<sup>2</sup> making them suitable as a building block for nanoconstructs.

We present the synthesis of diaza[4]helicenesqualene conjugates using functionalized [4]helicenes and squalene as nanoassembly scaffold. The new far-red fluorescent biomaterials were comprehensively characterised in racemic and enantiopure series and tested on cancer cell lines *in vitro*.

**METHODS:** Diaza[4]helicene-squalene building blocks were synthesized from carboxy-[4]helicene and derivatized functionalized squalene. These building blocks were used to build nanoassemblies by controlled nanoprecipitation in water. The building blocks and nanoassembly systems were characterized by dynamic light scattering, nanoparticle tracking analysis, (cryo)transmission electron microscopy and <sup>1</sup>H nuclear magnetic resonance. Chiro-optical properties of were also investigated.

**RESULTS:** Nanoprecipitation of all synthesized building blocks yielded nanoassemblies in water.

They were perfectly spherical, monodisperse and generally around 100-200 nm in diameter.



Fig. 1: [4]helicene-squalene building block and nanoassemblies (top); optical properties of nanoassemblies and mitochondrial labelling in PC3 cancer cells (bottom).

PDI values were below 0.10 with positive zeta potentials. They showed impressive stability over several months. When incubated with PC3, U87MG and HeLa cell lines *in vitro* their cytotoxicity was low and they accumulated specifically within mitochondria.

**DISCUSSION & CONCLUSIONS:** The [4]helicene-squalene nanoassemblies demonstrate excellent stability, good far-red optical properties and unprecedented subcellular mitochondrial accumulation in several cancer cell lines with great potential as new targeted theranostic nanoplatform.

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#### Monolayer and Bilayer Properties of a 1,2-Diamidophospholipid

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Phospholipid monolayer experiments are versatile and powerful tools to gain insight into the membrane organization at the air/water interface. Combined with bilayer experiments, a holistic view of the membrane organization of a particular phospholipid is possible. We synthesize new phospholipids and study their biophysical properties in order to learn more about the forces at play in lipid self-assembly and to ultimately guide the self-assembly process.

Herein, we analyze the self-assembly process of 1,2-diamidophospholipid Pad-Pad-PC (1, see Figure 1), which surprisingly results in distorted phospholipid vesicle cubes [1].



**Figure 1.** Molecular structure of the 1,2-diamidophospholipid Pad-Pad-PC (1).

The Pad-Pad-PC was synthesized by optimizing a literature procedure [2]. With this lipid we formulated bilayer vesicles as well as prepared monolayers. The lipid monolayer was studied using high-brilliance grazing incidence-angle Xray diffraction at PETRAIII (DESY) and the bilayer vesicles were analyzed by in house small- and wide-angle X-ray scattering as well

as cryo transmission electron microscopy tomography.

At low subphase temperature and low surface pressures the lipid monolayer organized in a perfect  $L_2$ ' packing at the air/water interface. Upon further compression, the amide-amide hydrogen bonding network was destroyed and a  $L_2$ , Ov, and finally an LS phase was found. In the bilayer experiments a subgel phase was visible. Overall an extremely tightly packed membrane was formed, which showed neither intrinsic nor extrinsic curvature, resulting in the formation of the very first soft phospholipid vesicle cubes. Interestingly, the area per lipid chain found in the bilayer (19.2 Å<sup>2</sup>) corresponds to the area found at low monolayer surface pressures of 5-10 mNm<sup>-1</sup>. This suggests that the lateral surface pressure of the bilayer itself is also 5-10 mNm<sup>-1</sup>, contradicting the rule of thumb that all bilayers have a surface pressure of approx. 30 mNm<sup>-1</sup> [3].

The herein presented results show new information concerning the self-assembly of lipid-membranes and are the next evolutional steps towards guided self-assembly.

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# Gold nanowire fabrication with lipid nanotubes

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**INTRODUCTION:** The fabrication of con-ductive nanostructures is the key technology in semiconductor industry and has gained importance in biology for applications such as biosensors and drug delivery.

We have demonstrated a high-throughput approach to fabricate gold nanowires on surfaces with a lipid nanotube template<sup>1</sup>.

**METHODS:** Biotin-tagged lipid nanotubes are formed from lipid blocks in inverted hexagonal phase adsorbed on polymer-coated surfaces upon application of shear force. Streptavidin-coated gold nanoparticles were attached to the biotin-tagged lipid nanotubes and gold nanoparticle-encapsulated LNTs were cross-linked by chemical fixation. Samples were dried and treated with oxygen plasma to remove the organic template and connect the particles.

**RESULTS:** Figure 1 shows the strategy of attaching gold nanoparticles to lipid nanotubes. Gold nanoparticles were found both inside and outside lipid nanotubes.



Fig. 1: (A) An illustration showing the strategy of attaching gold nanoparticles to lipid nanotubes. (B) A cryo-TEM image of gold nanoparticles attached to a lipid nanotube.

The presented work also clarifi ed the advantages (high

throughput, cheep) and the challenge (pearling effect of liquid gold) of the method. The approach can be used to align different particles, proteins, and peptides by replacing GNPs with other molecules. It can also be combined with the single LNT patterning with a micromanipulator [30] to create defi ned objects instead of random networks

**DISCUSSION & CONCLUSIONS:** An approach to surface-assemble nanoparticles with a lipid nanotube template was demonstrated. The method is advantageous because the small size of lipid nanotubes enables the fabrication of solid nanostructures with a higher throughput without using expensive electron beam lithography. The approach can further be combined with single lipid nanotube patterning with a micromanipulator<sup>2</sup> to create distinct patterns instead of random networks.

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# CONTINUOUS NETWORK SOLID POLYMER ELECTROLYTES FOR LITHIUM BATTERIES

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**INTRODUCTION:** One major branch of lithium (Li) battery research is focused on replacing conventional liquid electrolytes with more stable solid polymer electrolytes (SPEs). The benefits of a workable SPE include improved safety through the elimination of the flammable liquid, easier manufacturing, and enhanced energy density by allowing the use of lithium metal over Li-ion hosts. Currently, the major challenge with SPEs is the inherent sluggish ionic conductivity at room temperature, typically orders of magnitude below the required minimum of  $10^{-3}$  S/cm [1,2]. While the mechanical strength of a solid provides advantages for batteries, conductivity is inversely related to viscosity, explaining the current popularity of liquid electrolytes. This research aims to exploit block copolymers and their nano-scale self-assembly to combine desirable individual polymer properties network into continues structures that simultaneously satisfy the mechanical and conductivity requirements for a commercial cell. Through chemical design and various annealing techniques, unique blocks are oriented to maximize SPE performance.

METHODS: Samples are prepared by mixing copolymers different block (BCPs) and/or homopolymers with an appropriate solvent, plus varying Li-salt concentrations. These solutions are spin-coated onto silicon wafers, or drop casted for characterization; electron microscopy (SEM, TEM), atomic force microscopy (AFM), and x-ray scattering (GISAXS, SAXS). Samples are temperature and solvent annealed to achieve different morphologies. Additionally, drop cast samples are assembled in symmetrical cells for impedance measurements (EIS), and added to electrode slurries for electrochemical testing.



Fig. 1: AFM image of PS-b-PEO polymer selfassembled into a network of cylinders and spheres (annealed at 190°C,  $Li^+/EO = 0.05$ )

**DISCUSSION & CONCLUSIONS:** Currently, spin-coated thin-film processing protocols have been extended to thicker micron scale samples appropriate for application in commercial cells. Resulting morphologies seem to be independent of film thickness, a detail that is in the process of being confirmed by TEM, SAXS, and GISAXS. Moving forward, it will be essential to include electrochemical cell testing to confirm the effects of achievable network structure on practical battery function.

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# MICROGEL MONOLAYERS FOR SOFT-COLLOIDAL TEMPLATING: PARTICLE SIZE EFFECTS ON NANOLITOGRAPHY.

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Germany.

**INTRODUCTION:** Microgels are soft colloidal particles that can arrange in highly ordered hexagonal monolayers at water/oil interfaces due to steric interactions [1]. These monolayers can be transferred to silicon substrates to act as masks for the etching of Vertically Aligned Nanowires (VA-NWs) [2]. Thus, controlling the microstructure of the monolayers confined at a water/oil interface is the key to their successful application as nanolithography masks.

METHODS: P(Nipam-co-MAA) microgels with bulk sizes of 1.45 µm, 426 nm and 210 nm were [1,3]. The microgels synthesized were characterized in situ at water-decane interfaces by Freeze Fracture Shadow Casting Cryo-SEM [3]. interfacial activity was studied The at water/hexane interfaces in a Langmuir trough and the microgel monolayers were transferred to sillicon substrates. These substrates were further treated with photoresist and O<sub>2</sub> plasma and etched by metal assisted chemical etching [2,3] to obtain VA-NWs. The substrates were characterized by AFM and SEM.

**RESULTS, DISCUSSION & CONCLUSIONS:** The compression of the monolayer can be used to tune the microgel arrangement and to explore the full two-dimensional area-pressure phase diagram of the particles trapped at the interface. The larger microgels behave similarly to colloids with a hard core and a soft polymeric shell, exhibiting capillarity-driven clustering at large specific area and a solid-solid phase transition between two hexagonal lattices at higher compressions [4]. The medium size microgels present the same behaviour but without capillarity-driven clustering at low surface pressures. The smaller particles also show no capillary forces and a smooth transition from an hexagonal lattice to a dense disordered monolayer. We demonstrate that the larger and medium size microgels can be effectively turned into masks for the fabrication of vertically aligned silicon nanowires by means of metal-assisted chemical etching after post-treatment with photoresist and O<sub>2</sub> plasma. These findings highlight the subtle interplay between particle architecture, adsorption

and interactions at the interface, whose understating and control are at the basis of their successful use as nanopatterning tools.



Fig. 1: AFM images taken on different substrates at different surface pressures for the 210 nm (top) and the 1.45 µm microgels (bottom).

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# **Rapid and Directed Assembly of Nanoparticles into Periodic Arrays**

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**INTRODUCTION:** The assembly of individual nanoparticles into patterns on 2D surfaces holds great promise for the generation of novel functional materials and devices. These arryas can be fabricated via conventional top-down lithographic approaches such as e-beam evaporation; however, they lack scalability and cannot generate complex materials or shapes.

Recently, several inspired approaches to place single nanoparticles on a surface from suspension have been investigated such as capillary force assembly (CFA)<sup>1</sup> or via optical printing.<sup>2</sup> We have previously found that CFA can suffer from issues of reproducibility due to surface variations. Other topdown approaches, would struggle to place billions of nanoparticles with nanoscale precision at any sort of production scale.

Our goal was to rapidly, and reproducibly, place a massive number of nanoparticles directly from suspension into a predefined pattern.

**METHODS:** To generate the desired pattern, electron beam, or nanoimprint, lithography was used to etch a resist. If the underlying substrate had a oxide passivating layer, then it was functionalized with a charged layer of amino-silane via an aqueous silanization route. Single nanoparticles in solution were then functionalized with positive, or negatively, charged ligands to generate attractive interactions between the pattern and the particles.

In the case of a chemically direct assembly (CDA) where a silane was used, a simple dip-coating approach was sufficient over extended times to allow the diffusion and adhesion of the particles. For conductive substrates, upon applying a potential the particles assembled via electrophoretic deposition (EPD) into the e-beam etched wells.

**RESULTS:** Regarding CDA, a multi-amine silane and an aqueous silanization method was found to optimize pattern generation. In tuning the size of the etched well, either single gold nanoparticles from 15 to 200 nm could be adsorbed, or clusters of nanoparticles. In addition, the ionic strength of the solute controlled the number of particles observed to diffuse and adhere within each well, thus indicating the barrier to cluster formation is interparticle repulsion.

Alternatively, if the substrate is conducting then a silane is not necessary. Using an EPD cell and a substrate patterned with an insulating polymer, single gold nanospheres or nanorods could be

assembled. The nanorods were aligned, depending on the template, over cm scales enabling polarization dependent plasmonic image generation that can be observed by the naked eye.



Fig. 1: Single and clusters of gold nanoparticles in an array (left) and arranged in pixels of arrays to generate an image of the atomic symbol for gold (right).

**DISCUSSION & CONCLUSIONS:** Currently, there is no silver-bullet method that can assemble any nanomaterial into any pattern on any surface. However, with an aim towards a scalable one, we have developed two substrate dependent routes that attempt to do this. The key variables such as salt concentration, well-dimension, time, and surface charge were studied. These arrays can now not only be leveraged in applications such as biosensors, but also used to study fundamental surface chemical reactions on a single nanoparticle level.

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# Abstracts - Posters

# **Colloidal Switches by Electric and Magnetic Fields**

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**INTRODUCTION:** External electric and magnetic fields have been proven to be a versatile tool to control particle assembly, however, almost always they were used separately. It is predictable that an array of micromagnets<sup>1</sup> can be used to assemble superparamagnetic particles. However,

disassembling or re-assembling such an assembly is not trivial due to remanence and coercivity of

metals used in such applications. An interdigitated design of micromagnet and micro-fabricated electrode enables to shuttle the colloids between the magnetic and electric potential minima. Here, we use a micro-fabricated electrode to control the local electric field gradients<sup>2</sup> and thus move the superparamagnetic particles away from their magnetic potential minima. Controlling colloids between two such adjacent potential minima enable a fast on/off mechanism, which is potentially important for optical switches or display technologies. Moreover, we demonstrate that the response time of the colloids between the states is on the order of tens of milli seconds, which is compatible with the current state of art. However, our design provides a switch with shutter sizes of micrometers, tens of square desirable for downscaling the parts of micro-electronic equipments. Our work on precise dynamic control over the particle position would open new avenues to find potential applications in optical switches and display technologies.

#### **RESULTS:**



Electric Field ON Magnetic Field ON **Figure 1**: Particle types and their self-assembly directed by either external electric or magnetic fields: a) Experimental setup used to apply electric and magnetic fields, with a microfabricated bottom electrode, in the following panels only the bottom electrode is shown to highlight the differences. b) When the gold electrode is patterned, the field strength within the sample cell is modulated and particles with a negative dielectric contrast ( $\varepsilon_p < \varepsilon_m$ ) are driven to the field minima, i.e. the voids in the patterned electrode. c) When an array of ferromagnetic nickel domains are plated over the gold micro-patterned electrode, field modulation in case of an electric field will be effectively unchanged. However, these ferromagnetic micro-domains will enable magnetical manipulations by providing field modulations over the space when a magnetic field is applied. Magnetic particles, under the influence of such modulating magnetic fields, are directed to the high magnetic field regions,

on top of nickel micro-domains. i.e. d) Superparamagnetic polystyrene particles have а dielectric constant contrast, when suspended in dimethyl sulfoxide (DMSO). These particles will be responsive to both electric and magnetic fields, simultaneously, with micro-fabricated electrodes that have nickel patches. Applying an electric field to such particles will direct them into electric field minima. e) Application of a magnetic field will direct these superparamagnetic particles on the nickel microdomains. Switching the applied field between magnetic and electric fields will switch the assembly of the colloidal particles.

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# JANUS MICROSWIMMERS AT OIL-WATER INTERFACES

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**INTRODUCTION:** Artificial microswimmers. such as self-propelling colloidal particles, are promising candidates to address transport issues in many nano- and microtechnological applications<sup>1</sup>. Propulsion can be either triggered by external uniform magnetic or electric fields or by an internal conversion of fuel into a driving force, all coupled to a broken symmetry in the particle shape or surface properties<sup>2</sup>. In spite of the growing interest around these novel man-made active materials, experimental results on self-propelling particles are often limited to systems of swimmers in media. homogeneous However, complex environments, including porous media, fluids under flow and liquid interfaces are ubiquitous in nature.

**METHODS:** As model microswimmers, we have used Pt-coated Janus particles that undergo active motion due to the catalytic decomposition of  $H_2O_2$ across the Pt-cap<sup>3,4</sup>. We systematically compare the motion of these swimmers at a liquid-liquid interface with their motion close to a solid substrate. In order to elucidate the differences between the two cases, we show the details of the particle position and orientation relative to the interface using a range of complementary techniques. The behavior of the same swimmers moving through colloidal lattices of same-size particles assembled at the interface was also investigated, as a step towards a tunable complex environment.

#### **RESULTS, DISCUSSION & CONCLUSIONS:**

We find, that the rotational diffusion of the particles at the interface is slowed down significantly which results in trajectories with enhanced persistency. Particle speed, however, is linked to the individual particle orientation, whereas two main configurations are predominant. We also demonstrate that interaction between "active" particles and "passive" colloids, that self-assemble in a lattice structure, makes it possible to tune the persistency of the active trajectories, from straight persistent walks into effective run and tumble trajectories. The tumbling frequency is directly controlled by the lattice packing. In all cases, numerical simulations were performed to confirm the validity of our interpretations. With our results we will improve the understanding of the motion of microswimmers in liquid

environments and extend the possibilities of their motion control.



Fig. 1: Run-and-tumble trajectories of catalytic microswimmers. (a) Experimental and (b) numerical trajectories of an active particle inside a lattice of passive PS-beads. Lattice spacing a = 10R. The color map shows the relative speed of the swimmer.  $V_{max} = 20 \mu m/s$ . This value corresponds to the swimming speed away from the obstacles and is used as input for the simulation. (c) Experimental absolute angular velocity between the swimming velocity vectors in sequential frames for the experimental condition shown in (a). Tumbling events are registered as the angular velocity exceeds a threshold.

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### Mechanism of the cooperativity in antimicrobial peptides

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**INTRODUCTION:** In this study we aim to elucidate the fundamental mode of action of antimicrobial cooperativity.

To investigate the cooperativity between two different human peptides defensin and cathelicidin we synthesized artificial lipid bilayer onto highly doped p-type silicon electrode covered by naturally formed silicon dioxide as a clean platform to separate peptide-peptide and peptides-bilayer interactions from influence of other components within cell.

Lipid bilayer was obtained by fusion of unilamellar vesicles from buffer solution and investigated mainly by impedance spectroscopy which is nondestructive and sensitive technique.

In addition we performed Fluorescence Recovery After Photobleaching (FRAP) measurements as a complementary technique to confirm the bilayer formation by its recovery in photobleached region.

To elucidate how peptides influence on the lipid bilayer we injected LL37 and  $\alpha$ -defensin in micro molar concentration.

Next step in our investigation is to inject mixture of cathelicidins and defensins and elucidate what is the mechanism of cooperativity of two different peptides.

**METHODS:** In this project we use POPC lipids for bilayer formation by vesicles fusion and NBDPE as a fluorescent agent. The bilayer is formed on highly doped p-type silicon/silicon dioxide wafer with activated surface. For electrochemical properties we use impedance spectroscopy with 3-electrodes set up and fluorescent microscopy to confirm and measure bilayer recovery after photobleaching.

**RESULTS:** *Figure 1* shows impedance spectra before (blue line) and after (red line at highest frequency) adding the vesicle solution. This small shift in impedance indicates bilayer formation as it acts as a very good natural insulator. Two red lines at lower frequencies correspond to changes in electrical properties of bilayer after peptide injection. The obtained spectra were interpreted in terms of equivalent R(RCRC) circuit consisting of simple electrical elements such as interface and bilayer resistance and capacitance, given as an inset to the figure.



Fig. 1: Impedance spectra of the supported lipid bilayer. Blue line represents Si wafer with HEPES buffer before adding vesicle solution and red lines correspond to changes in electrical properties of bilayer after LL37 peptides injection.



Fig. 2: FRAP images of photobleached region and its recovery after 10min.

**DISCUSSION & CONCLUSIONS:** After LL37 peptide injection we observed drop in resistance and capacitance as bilayer's permanence is disturbed. Similar changes in bilayer resistance were observed for  $\alpha$ -defensin, nevertheless no significant changes in capacitance were observed in this case. In next step we will incorporate mixture of these two peptides to lipid membrane and we expect to observe decrease in resistance at lower peptides concentration. The milestone goal is to quantify the antimicrobial peptides cooperativity effect on the bilayer resistance and capacitance.

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## Biomimetic engineering of polymersome membranes for stimuli triggered activity of nanoreactors

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**INTRODUCTION:** The development of advanced stimuli-responsive systems for medicine, catalysis or technology requires compartmentalized reaction spaces with triggered functionality. An elegant nanoscience-based strategy is to engineer such compartments with triggered activity bv encapsulation/insertion of active compounds in compartments with stimuli-responsive permeability. Here, we introduce nanoreactors with reduction triggered activity based on polymersomes with encapsulated enzymes and a membrane equipped with modified channel proteins, acting as "gates" (Fig. 1). By insertion of a chemically modified porin with a reduction sensitive molecular cap we obtained a selective permeability of the membrane. The substrate can penetrate inside the cavity and the enzymatic reaction takes place only when the gate is open (by releasing its molecular cap) [1]. Then the products are released from the nanoreactor. Such a functionality is vital for *in vivo* and *in vitro mimicking* of natural cell organelles.



Fig. 1. Concept of a nanoreactor with triggered activity by a chemically engineered protein "gate" inserted in a polymersome membrane. A change in reduction potential induces the release of the sensitive molecular cap (green dots) from the protein "gate" allowing the entrance of substrates (red dots), and the release of the products of the enzymatic reaction (yellow dots).

METHODS: OmpF Modification. First, cysteine residues were introduced to the OmpF wild type porin. coupled SAMSA-Residues were with disulphide bonds, Carboxyfluoresceine bv and unreacted fluorophore was removed by filtration and dialysis. This step introduced a molecular cap that blocked the OmpF pore and introduced a stimuli responsiveness to the pore. Responsive nanoreactors were prepared from PMOXA<sub>6</sub>-PDMS<sub>44</sub>-PMOXA<sub>6</sub> copolymer, and a subset of modified or native OmpFs and horseradish peroxidase in PBS buffer pH=7.4. We used the film rehydration technique as being suited for

enzymes and channel porins (films were rehydrated to a final polymer concentration of 2.5 mg/ml). All samples were extruded through a polycarbonate membrane in order to obtain size homogeneity. Nonencapsulated enzyme was removed from the nanoreactors by dialysis against PBS.

**RESULTS:** To assess how the nanoreactor activity was affected by the chemical modification of the porin, we used the Amplex Red enzymatic substrate. The enzymatic turnover of the Amplex Red substrate (predicted polar surface area 72 A2, MW = 257 g mol-1, Log P = 0.89, charge = -0.1 at pH 7.4) was drastically reduced (down to 33%), compared to unmodified OmpF nanoreactors acting in similar conditions at pH = 7.4. The blockage of Amplex Red influx through the pore is considered to be due to a combination of effects: (i) closing of the pore by the molecular cap, and (ii) electrostatic interaction of Amplex Red with the molecular cap (Fig 2).



Fig.2: Amplex red conversion kinetics of nanoreactors equipped with different OmpFs: (1) unpermeabilised nanoreactors (blue), (2) OmpF-S-S-CF nanoreactors and (3) Ompf-WT (black), before addition of 30mM GSH (left) and after 1 hour after addition of 30mM GSH(right).

**CONCLUSION:** We designed a nanoreactor with a reduction responsive enzymatic activity, based on a cheimically modified channel porin OmpF, which was inserted in the membrane of polymersomes, and acted as a "responsive gate". The system was tested *in vivo* and *in vitro*, where the nanoreactor functionality and responsiveness was preserved.

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#### Symmetry control in gyroid-forming terpolymers by solvent vapour annealing.

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**INTRODUCTION:** The gyroid morphology<sup>1</sup> is a cubic network phase that can be created by block copolymer self-assembly. In block copolymers consisting of three different blocks, so called triblock terpolymers, the gyroid can exhibit two different symmetries<sup>2</sup>: the alternating gyroid  $Q^{214}$  and the core-shell double gyroid  $Q^{230}$ . So far, these two different gyroid symmetries could only be obtained by controlling the volume fraction of the blocks by means of polymer synthesis<sup>3</sup>. Here we demonstrate that both symmetries can be generated from the same terpolymer by controlled solvent vapour annealing.

**METHODS:** <u>Solvent Vapor Annealing (SVA):</u> Films of polyisoprene-*b*-polysytrene-*b*poly(glycidyl methacrylate) (ISG) triblock terpolymers were exposed to controlled amounts of solvent vapour using a custom-designed chamber and experimental set-up.

<u>Grazing Incidence Small-Angle X-ray Scattering</u> (<u>GISAXS</u>): *In situ* GISAXS during solvent annealing of ISG films was performed at the cSAXS beamline of the Swiss Light Source (SLS), Paul Scherrer Institut, Villigen. *Ex situ* GISAXS of ISG films after solvent annealing was carried at beamline I22 of the Diamond Light Source (UK).

Atomic Force Microscopy (AFM): Tapping mode AFM (JPK instruments, NanoWizard 2) was used to characterize the surface morphology as well as the grain size (Moiré patterns) in ISG films.

**RESULTS:** Figure 1 shows in-plane GISAXS profiles for ISG films prepared using different solvent annealing protocols. Based on the characteristic ratios between the observed scattering peaks, the morphologies of the films can be assigned to the alternating gyroid symmetry<sup>2-3</sup>  $(Q^{214})$ , and the core-shell double gyroid symmetry<sup>2-</sup>  $(Q^{230})$ , respectively. Interestingly, these two different gyroid morphologies exhibit significantly different unit cell sizes of 59 nm  $(Q^{214})$  and 118 nm ( $Q^{230}$ ), respectively. By slowly removing the solvent, gyroid grains of about 5-7 µm in size could be generated for both symmetries.



Fig. 1: In-plane GISAXS profiles for two solvent annealed films of an ISG terpolymer. The peak ratios of the observed reflections match the alternating gyroid ( $Q^{214}$ ) and core-shell double gyroid ( $Q^{230}$ ) symmetries.

#### **DISCUSSION & CONCLUSIONS:**

Controlled solvent vapour annealing of a single terpolymer film allows for the fabrication of gyroid morphologies with different symmetries (alternating or core-shell double gyroids). Furthermore, these films showed grain sizes of several microns, which makes them very promising templates for the fabrication of various inorganic nanostructures.

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# Anionic and anionic amphiphilic silver nanocubes interfacing with lipid vesicles and ligand exchange evolution by SERS

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**INTRODUCTION:** We developed a synthetic method for the preparation of silver nanocages coated with an anionic and anionic amphiphilic monolayer displaying high tendency to interact with small lipid vesicles.

**METHOD:** By varying the feedstock ligand ratio of a binary combination of hydrophilic, and hydrophobic thiol ligands, namely sodium-11mercaptoundecane-sulfonate (MUS), and 1octanethiol ligands (OT), we achieved different mixed monolayers as well as the corresponding homoligand monolayers.

**RESULTS:** A successful replacement of the Poly(vinylpyrrolidone), (PVP) (capping that induces the formation of AgNCs enclosed by  $\{1,0,0\}$  facets) by MUS/OT on the AgNCs surface was confirmed by monitoring the ligand exchange reaction with surface-enhanced-Raman-scattering (SERS). Moreover, SERS signals give insight of their disorder/order evolution and about the kinetic of the PVP exchange reaction. To gain more details about the surface properties of the monolayers, the surface charge and the packing density were explored by  $\zeta$ -potential and UV-vis,



along the ligand exchange reaction.

Figure 1. (a) Raman C-C stretching region for different reaction times in the mix-ligand MUS:OT replacement 5:1 ratio as well as several Raman and SERS used as reference.(b) UV-vis spectra in PBS (1X), (c) cryo-TEM images showing the vesicle trapping by the AgNCs (5:1 monolayer).

The combination of MUS/OT increases the colloidal stability of the AgNCs more than using

only MUS, the later needed more time to achieve a similar packing than in the mixed ligand approach. The anionic amphiphilic monolayer with a feedstock ratio of 5:1 gave rise the best colloidal stability in high ionic strength media.



Figure2. Example of cryo-TEM image showing the vesicle trapping by the AgNCs (1:1 monolayer).

Both the anionic and the anionic amphiphilic AgNCs induces high capacity to interact with SUVs (cut-off of 40 nm). By increasing the hydrophobicity of the monolayer in the feedstock ratio, the interaction with larger vesicles, between 40-100 nm, is observed to the expense of the decrease in the interaction with SUVs smaller than 20 nm.

**CONCLUSIONS:** This is the first study that applies the mixed ligand approach based on a hydrophilic linker with sulfonate ending groups (MUS) and hydrophobic ligand such as OT, in larger NPs with high capacity to interface with SUVs beyond the scope offered by NPs based on a small and spherical gold cores.<sup>1</sup>

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# FORCE SPECTROSCOPY OF UNFOLDING METAL-LIGAND SINGLE CHAIN POLYMER NANOPARTICLES

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**INTRODUCTION:** Directional supramolecular interactions can form non-covalent bonds, which are important in many biomimetic materials.<sup>1</sup> Accordingly, an improved understanding of these interactions is desirable, and single molecule force spectroscopy (SMFS) is a unique tool to study their mechanically induced scission and reversible formation on the molecular level. Metal-ligand (ML) complexes are of particular interest, because their interaction strength and dynamic nature can be tuned by simple variation of the metal ions, ligands, or counter-ions.<sup>2</sup>

In this project single chain polymeric nanoparticles (SCPNs) are prepared by formation of intramolecular ML complexes.<sup>3</sup> Their forced unfolding by means of SMFS is used to investigate the complex scission under mechanical stress at the molecular level. This framework permits an analysis of the binding parameters of different bior tri-fold coordinated ML complexes.

**METHODS:** A side-chain functionalized polymer was prepared by RAFT-mediated copolymerization of butyl acrylate and an acrylic monomer carrying the methylbenzimidazolyl pyridine ligand. The copolymer with 5 mol% pendant ligands was collapsed into SCPNs by intramolecular complex formation that occurred upon slow addition to dilute solutions of metal ions (Fe<sup>2+</sup>, Zn<sup>2+</sup>, Eu<sup>3+</sup>). The particles were thoroughly characterized and SMFS by means of atomic force microscopy (AFM) was used to measure the forces associated with the dissociation of the ML complexes. The experiments were performed in tetrahydrofuran solutions and repeated extension-retraction cycles furnished the force versus extension profiles of these SCPNs.



*Fig.* 1: *Schematic depiction of the SMFS experiments with SCPN.* 

**RESULTS:** Successful formation of SCPNs with various metals (Fe<sup>2+</sup>, Zn<sup>2+</sup>, and Eu<sup>3+</sup>) was demonstrated by means of dynamic light scattering, AFM imaging, and Taylor dispersion measurements. The nanometer-sized Fe<sup>2+</sup>–SCPNs thus obtained were then employed in SMFS experiments. The dissociation of intramolecular ML complexes was reflected by discrete transitions in the recorded extension profiles. The profiles were fitted to the worm like chain (WLC) model of elasticity yielding the persistence length and force constants for these ML complexes.<sup>4</sup>



Fig. 2: Force versus extension profile for (a) the polymer and (b) the same polymer collapsed into a  $Fe^{2+}$ -SCPN with multiple transitions. The transition is associated with dissociation of intrachain metal-ligand complexes.

**DISCUSSION & CONCLUSIONS:** Single-chain polymeric nanoparticles were successfully prepared by intramolecular complex formation of a side-chain functionalized polymer with iron ions. The characterization of  $Fe^{2+}$ –SCPNs by SMFS yields parameters that fit well with the scission of the complexes and their expected binding parameters. In ongoing work, we are analysing SCPNs prepared by coordination of zinc and europium ions in order to investigate how coordination geometry and binding characteristics influence the behaviour.

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## Decode polydiacetylene-peptide interaction mechanism at raft boundaries

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**INTRODUCTION:** Information transfer between cells always starts with forces applied to the membrane. Opening Ion channels, cellular virus infection and killing bacteria by antimicrobial peptides, all apply forces to the bilayer of the cell. However, until now there is no possibility to measure the local molecular forces in lipid bilayers. Therefore, the goal of this project is to develop a calibrated fluorescence probe by the mechanosensitive polymer PDA.

Biosensors are used to convert a biological response into a signal. The sensor is triggered by its analyte e.g. viruses, proteins and peptides. Here, the conjugated polymer PDA is investigated because of its optical characteristic in visible range and its easy self assembling property like bilayer and vesicles. By perturbation of the backbone chain, PDA undergoes a mechanochromism from the blue to the red conformation. The disturbance is induced by a peptide which penetrates the bilaver. But as previous experiments have shown, the sensitivity of a 100% PDA film is very limited. Hence, the layer is enhanced by mixing it with a fluidic lipid. The peptide interacts at the raft boundaries between the lipids in solid and liquid phase. The right ratio is a key element to improve the system. The next step is to understand how the peptide exactly rotates the pedant side groups.

**METHODS:** The first step is to improve the sensitivity of the system. Therefore, a series of different ratios between lipids in solid and liquid phase in solution has been studied by UV-VIS Spectroscopy before and after adding peptides. We selected DOPC as an example for a lipid in liquid phase and Melittin as a representative peptide. Furthermore, bilayers were investigated by inverted fluorescence microscopy.

**RESULTS:** A quantitative value for the blue-to-red transition of PDA is given by the colorimetric response:

$$%CR = (\Pi B_0 - \Pi B_1) / \Pi B_0$$

(1)

 $PB=A_{blue}/(A_{blue}-A_{red})$ , A is the absorbance at either the blue (550nm) or red (650nm) maximum of the UV-VIS Spectrum.  $PB_0$  is the ratio of the control sample without the peptide.



Fig. 1: Absorbance spectrum of different DOPC/PDA ratios with (dotted line) and without Melittin (continuos line.)



*Fig. 2: Colorimetric response for different ratios of PDA/DOPC.* 

**DISCUSSION & CONCLUSIONS:** As we could show, a minimum amount of soft lipid is required for proper PDA polymerisation. The optimal ratio was 80/20. The colorimetric response depends on the ratio of lipids in solid to liquid phase. The next step is to investigate a bilayer instead of vesicles in order to monitor the peptide-lipid interaction at the boundaries by fluorescence microscopy.

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#### MECHANOSENSITIVITY OF POLYDIACETYLENE WITH A PHOSPHOCHOLINE HEADGROUP

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**Abstract:** Membrane forces play pivotal roles in numerous physiological processes such as endocytosis, cell mutations and calcium signaling. Currently used characterization methods such as atomic force microscope (AFM) or optical tweezers allow for the controlled force application but not for the detection of the forces applied to the bilayers. Micro-aspiration of giant unilamellar vesicles (GUV) enables the quantification of surface tension, however, its conversion into local forces is difficult.



# Figure 1: The chemical structure of DiynePC and polydiacetylene. The scheme shows the concept of the membrane force sensor we are developing.

We are developing a mechanosensitive membrane probe that enables direct measurement of molecular forces applied within lipid bilayers. We employ a mechanochromic polymer polydiacetylene (PDA, Figure 1) that changes its color and fluorescence intensity upon application of forces (Figure 2B). As a first step, we demonstrated a PDA vesicle assay that detects melittin, a transmembrane peptide from bee venom. First we fabricated PDA vesicles by selfassembling the lipid monomer and subsequently crosslinking by UV. Figure 2B shows the absorption spectra before (blue) and right after (red) addition of melittin to the PDA vesicle solution. These spectra overlap, suggesting no colorimetric response due to the addition of melittin. However, we found that the spectra shifted over the next several hours (Figure 2B). After 4 hours, the shape of the spectra changed completely, as the color change was clearly visible also by naked eyes (Figure 2A). The slow response from our PDA sensor against melittin is different from what has been reported with other types of PDA sensors<sup>[1][2]</sup>.



Figure 2: A. PDA vesicle samples before and four hour afteraddition of melittin. B. UV-Vis spectra before and after the addition of melittin. A spectra shift was observed depending on the incubation time.

In this work, we further analyze the unexpectedly slow interaction kinetics, fluorescence spectra of PDAs, and discuss possible origin of the slow kinetics<sup>[3]</sup>.

The developed assay proved that DiynePC PDA is sensitive to mechanical stimuli. The advantage of our PDA sensor is that it has a phosphocholine head group that mimics cell membranes. Its combination of sensitivity and the biocompatibility will allow us to incorporate this probe in live cells in future, providing us a further possibility to investigate force distribution during mitosis, cell migration, and interactions with medical implants etc.

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# Hybrid materials based on layered double hydroxides

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**INTRODUCTION:** Layered double hydroxides (LDHs) have been extensively investigated in the recent years due to their promising prospective applications in drug delivery, catalysis, wastewater treatment and polymer nanocomposites formation. In particular, development of novel polymer-inorganic nanomaterials is a thriving research area due to enhanced mechanical, thermal and flammability properties.

**METHODS:** LDH particles were synthesized by co-precipitation method followed the bv hydrothermal treatment in order to improve the polydispersity of the particles. Confirmation of the successful synthesis was achieved by X-ray experiments diffraction (XRD) while the transmission electron microscopy (TEM) and dynamic light scattering (DLS) were employed to further characterise the particles. Electrokinetic properties of the bare LDHs and the ones coated with different amount of various polymers, namely, negatively charged statistical copolymers of acrylic acid (AA) and butyl acrylate (BA) (P(AA)-(BA)) and naturally occurring anticoagulant heparin were investigated by electrophoresis. In addition, DLS was also utilized in order to probe the colloidal stability of the LDH nanoplatelets at different dose of polymer and at different ionic strength.

**RESULTS:** All polyelectrolytes adsorbed strongly on the surface of oppositely charged LDH platelets leading initially to charge neutralisation until the isoelectric point (IEP). As it is predicted by the DLVO theory, particles are unstable in the dispersion at IEP due to the loss of double layer repulsions. However. further addition of polyelectrolytes resulted in overcharging and significantly more stable nanocomposites in comparison to the bare nanoparticles (Fig. 1 a). Stable dispersion is a consequence of repulsive electrical double layer forces and steric repulsions among polymer chains adsorbed on the surface of the particles. Eventually, we were able to make highly stable LDH-MacroRAFT nanocomposites even at high ionic strength<sup>1</sup>. On the other hand, the enormously stable, biocompatible LDH-heparin composites can be used in biomedical processes (e.g. drug delivery and enzyme formulations)<sup>2</sup>. In general, significant overcharging, due to the adsorption, occurs in the case of all polymers, which is one of the major reasons for improved colloidal stability due to the strong electrostatic repulsion.



Fig. 1: Colloidal stability of material as a function of polyelectrolyte dose (a). TEM images of LDH dispersions before IEP (b), at IEP (c) and after IEP (d). Stability ratio values close to unity correspond to the fast aggregation, while higher values indicate slow aggregation and stable systems.

**DISCUSSION & CONCLUSIONS:** Several LDH-polyelectrolyte materials of different compositions with advanced properties and resistance to aggregation induced by elevated ionic strength were designed. Face to face orientation of the aggregates was confirmed by the TEM images (Fig. 1 b-d).

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# **Interaction of Organic Ions with Proteins**

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**INTRODUCTION:** Proteins are complex structures formed by aminoacids which determine the interaction of proteins with themselves and their environment. In this regard, the hydrophobic interaction plays a major role in protein folding. adsorption and aggregation.<sup>1</sup> External factors, as the presence of ions in solution, can alter the protein structure. Specific ion-protein interactions can influence the internal structure of proteins and protein–protein interactions.<sup>2</sup> Thus, understanding the protein-ion interaction is important from a fundamental point of view as well as for the numerous applications where proteins are involved. In this study, we used proteins of biotechnological interest, the most allergens of the cow's milk: βcasein and  $\beta$ -lactoglobulin, with big hydrophobic ions. Two ions with similar size and chemical structure ( $Ph_4B^-$  and  $Ph_4As^+$ ). The tetraphenyl ions have shown a deep impact when interacting with soft and hydrophobic interfaces.<sup>3</sup> In this work we explored to what extent tetraphenyl ions, acting as counter-ions or co-ions, are sensitive to the hydrophobicity and the charge of protein-coated surfaces.

METHODS: This study includes simulations and experiments with three different proteins (β-casein, β-lactoglobulin and BSA). Molecular Dynamics simulations were performed in order to estimate the hydrophobic degree of the proteins with the online calculation tool OPM. In the experimental part, we protein-coated polystyrene prepared (PS) microspheres by physical adsorption. The affinity of the tetraphenyl ions to these protein–latex complexes has been investigated by electrophoresis and colloidal stability. On the other hand, the adsorption of the proteins on a flat hydrophobic surface and their interaction with the tetraphenyl ions has been studied by using a quartz crystal microbalance with dissipation monitoring (QCM-D).

**RESULTS:** We have investigated how different proteins interact with big organic ions (Ph<sub>4</sub>B<sup>-</sup> and Ph<sub>4</sub>As<sup>+</sup>). First, a quantitative study to determine the hydrophobic degree of the proteins was performed. We found that the hydrophobicity of the proteins follows this order:  $\beta$ -casein > BSA >  $\beta$ -lactoglobulin. Then, electrokinetic and stability measurements on protein-coated PS microspheres as a function of the tetraphenyl ion concentration showed that the affinity of the organic ions depends

on the hydrophobicity of the interface. In addition, we studied conformational changes of the adsorbed proteins with QCM-D. Proteins were adsorbed onto hydrophobic flat substrates and then exposed to the tetraphenyl ions. The protein films collapsed at increasing concentration of counter-ions that screenning the electrostatic repulsion among proteins and swelled when charge inversion occurred (higher ionic concentrations) (see Fig. 1).



*Fig. 1: Structural changes experimented by the protein films in presence of the tetraphenyl ions.* 

**DISCUSSION & CONCLUSIONS:** All the results evidence that the accumulation of the organic ions on an interface depends directly on its degree of hydrophobicity. Big charge inversions and re-stabilization patterns were observed at very low concentrations of tetraphenyl ions for the most hydrophobic protein studied (β-casein). In addition, QCM-D experiments revealed that the tetraphenyl ions induce structural changes in protein films according to the co-ion or counter-ion role and the ionic concentration. Finally, we found that the same effect produced by Ph<sub>4</sub>B<sup>-</sup> over the protein interfaces, it is achieved by Ph<sub>4</sub>As<sup>+</sup> one order of magnitude higher in ionic concentration. We attribute the different interactions of the anion and the cation with these interfaces to their dissimilar hydration, which makes the anion show a more hydrophobic behaviour than the cation.

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# Soil-on-a-Chip: Probing the interplay between fungi, nematodes, bacteria and plant roots using microfluidic platforms

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**INTRODUCTION:** The study whole of organisms using microfluidic technology has only emerged in recent years. However, it is clear that this technology offers clear advantages over other approaches.[1-2] In nature, fungi defend themselves against antagonistic bacteria and nematodes using various toxic defence molecules. These defence molecules can be induced upon confrontation with the antagonist, however, little is known about the regulation, spatial distribution and specificity of the fungal defence response. Plant roots are highly sensitive, responding to a variety of environmental stimuli. However, there exists a limited amount of information concerning underlying molecular mechanisms the that translate an environmental stimulus into a response. It remains challenging to stimulate a plant organ in a defined manner that simulates environmental complexity.

**METHODS:** Photolithography techniques [3] were used to produce microfluidic devices made from poly(dimethylsiloxane) (PDMS). Using these microfluidic platforms, fungal hyphae, bacteria, nematodes and plant roots can be introduced into medium-filled microchannels to probe their interactions with the surrounding envrionment.

**RESULTS:** We have developed two novel microfluidic platforms for (i) studying the interplay between filamentous fungi and nematodes (Fig. 1 A-B) and (ii) applying combinations of stimuli to plant roots (Fig 1. C-H). The former enables the defence response of Coprinopsis cinerea upon confrontation by the fungivorous nematode Aphelenchus avenae to be investigated at the single hypha level. Specifically, our results have revealed for the first time that even undifferentiated mycelium can communicate within certain microdomains and is capable of transporting nutrient and signal molecules via previously unknown specialised hyphae. Secondly, we have developed the "dual-flow-RootChip" (dfRootChip) to provide guidance of the root tip and therefore create spatially divided microenvironments for Arabidopsis roots. Using this microfluidic platform, roots have been exposed to asymmetric growth environments, selectively stimulated with calcium elicitors and locally inoculated with microbes. A key finding is that developmental adaptation of root systems can be regulated at both the cellular and organ level.



Fig. 1: (A) fungal-nematode device, (B) communication through single hyphae, (C-D) dual-flow-RootChip. (E-H) developmental adaptation of root systems under phosphate rich and deficient conditions.

#### **DISCUSSION & CONCLUSIONS:**

Our microfluidic approach offers a novel method to study cellular interactions that are imposed by nature. Specifically, we have been able to probe the interaction between *C. cinerea* and *A. avenae*, providing – for the first time – novel insights into this interaction at a cellular level and in real-time. Further, the dfRootChip presents the opportunity to unravel the mechanisms by which plants perceive and respond to various stimuli, enabling an enhanced understanding of how roots interact with their environment.

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# **Spray Drying Amorphous Salt Nanoparticles**

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**INTRODUCTION:** Amorphous materials show distinctly different properties compared to their crystalline counterparts such as enhanced solubility or catalytic activity. These materials are therefore excellent candidates for pharmaceutical applications or in the large field of catalysis. Sodium Chloride (NaCl) has a very high propensity to crystallize and is thus extremely difficult to synthesis in an amorphous state. To avoid crystallization in NaCl solutions, very high cooling rates are required.

We produce amorphous NaCl nanoparticles using a recently developed microfluidic spray dryer <sup>1</sup>.

**METHODS:** The microfluidic spray dryer is made of Poly(Dimethylsiloxane) (PDMS) and is fabricated using soft lithography. It consists of one channel through which a salt solution is injected. Additional six channels guide compressed air of a few bars into the device to form tiny aerosol droplets. These droplets are accelerated along a main channel. The high air speed present in the channel enables fast solvent evaporation. The droplets are sprayed on a Silicon substrate and analysed using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

**RESULTS:** Using the microfluidic spray dryer we are able to produce non-aggregated nanoparticles in the range of 30 to 200 nm with narrow size distribution, as shown in figure 1. The device produces aerosol droplets with diameters of around 1  $\mu$ m that transform into multiple nanoparticles upon drying on the wafer.



Fig. 2: (a) SEM image of a patch of spray dried NaCl nanoparticles. A close-up of the center of the patch (b) shows particles with different morphologies.

We confirm the metastable amorphous state using TEM as indicated in figure 2. The high-energy electron beam is sufficient to induce crystallization and allows observing the crystallization in-situ in the TEM. During this transition, the volume of the particles is strongly reduced, which indicates that the amorphous particles are highly hydrated.

Changing the initial solution concentration increases the amount of particles per patch. Furthermore, the solution concentration influences the time when crystallization can begin and hence, the time ions have to arrange into a crystal structure. Thereby, we can observe nanoparticles with different degrees of crystallinity.



Fig. 2: High Resolution TEM image (a) and the corresponding Fast Fourier Transform image (b) of an amorphous NaCl nanoparticle. (c) shows a Bright Field image of a crystalline particle with its characteristic cubic shape.

**DISCUSSION & CONCLUSIONS:** We study the crystallization of NaCl if NaCl-containing aqueous solutions are rapidly quenched using a microfluidic spray dryer. This device allows the synthesis of nanoparticles with different degrees of crystallinity by fast solvent evaporation.

**REFERENCES:** <sup>1</sup> E. Amstad et al., **2015**, *Science* 349:956–960

# Effect of Shear Strength on Shear Aggregation Rates in the presence of Repulsive Electrical Double Layer Forces

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**INTRODUCTION:** Aggregation in shear flows occurs in environmental and industrial processes. Thus, understanding the shear-induced aggregation is still important in many fields. However, although the aggregation kinetic theory in a shear flow fundamental aspects in provides practical situations, the theory has not been sufficiently verified due to the lack of the quantitative comparison with experimental data. Particularly, the experimental aggregation rates in the presence of electrostatic repulsion<sup>1</sup>, which diminishes the rates, have not been compared with the theory, since the previous calculation can not be applied to the experimental data because of the used equation for the electrostatic repulsion with the linearized Poisson-Boltzmann(PB) theory that is only valid in the low surface potential case. Therefore, we examined a comparison between theory and experiments by Sato *et al*<sup>1</sup>. for aggregation rates in a Couette flow as a function of KCl concentration at different shear rates. To achieve this aim, we employed the trajectory analysis<sup>2</sup> with the repulsion calculated by the non-linear PB solution<sup>3</sup>.

METHODS: We used the trajectory analysis, which describes the relative motion between two particles in a shear flow, to calculate theoretical aggregation rates. And as a boundary condition to the PB theory, we set the surface charge density  $\sigma$ =-60 mC/m<sup>2</sup> determined by electrophoretic measurements<sup>1</sup>. We assumed the Hamaker constant  $A_{\rm H} = 2.0 \times 10^{-21}$  J which characterizes the magnitude of the van der Waals attraction. The relative position between two colliding particles can be evolved by integrating the relative particle velocities for time. Releasing a particle from many upper stream points on a plane normal to the flow direction  $u_v = Gx$ , each trajectory from the release point is tested whether the aggregation occurs or not. And each calculation was ended when the particle attached or flowed out. Determining the boundary between aggregation or not on the released plane, the integration of  $u_v$  over the inner region of the boundary on the plane can allow us to estimate the flux of particles to be attached which means aggregation rates.

**RESULTS & DISCUSSION:** We plotted capture efficiencies, which are defined as a ratio of the rate with and without particle interactions, for the polystyrene latex particles with a diameter of  $d = 1.96 \ \mu m$  against KCl concentration at different

shear rates G in Fig. 1. Symbols are experimental values<sup>1</sup> at  $G = 23(\triangle)$ ;  $46(\circ)$ ;  $92(\bigtriangledown)$  s<sup>-1</sup>. Lines indicate theoretical values by the trajectory analysis<sup>3</sup>. We can see that the capture efficiencies decrease with decreasing KCl concentration and increasing electrostatic repulsion below certain points so called CCC, and the present calculation can reasonably describe the experimental data as shown in Fig. 1. Especially, our calculations capture that the CCCs shift to higher concentration with shear rates, meaning that faster particles due to high shear pass through each other before they approach enough to stick by van der Waals attraction. However, we observed quantitative discrepancies between the experimental and theoretical values. These discrepancies might be caused by Brownian motion and a discrete charge effect which are not included in the present analysis.



Fig. 1: Capture efficiency vs. KCl concentration for particles with the diameter of  $d=1.96 \ \mu m$ : Symbols are experimental values taken from Sato et al<sup>1</sup>. and lines are calculated values with trajectory analysis<sup>3</sup>.

**REFERENCES:** <sup>1</sup> D. Sato *et al.*; **2005**; *Colloids Surf. A*; 266:150-154. <sup>2</sup> T.G.M. Van de Ven & Mason; **1977**; *Colloid Polymer Sci.*; 255:468-479. <sup>3</sup> T. Sugimoto *et al.*; **2014**; *J. Japan Soc. Civil Engineers, Ser. A2(Applied Mechanics)*; 70(2):I\_475-I\_482.

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# **Optical and Electrical Characterization** of Voltage Sensitive Dyes in Lipid Bilayers

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**INTRODUCTION:** Voltage sensitive dves (VSDs) are powerful tools for cell membrane potential monitoring. The main characteristic of VSDs is the change in their inherent fluorescence membrane potential changes. upon The characterization of VSDs is commonly performed either directly with living cells or with vesicles where the membrane potential is established by incorporating ion selective channels. However, both characterization methods lack the possibility to precisely control the voltage sequences, thus are unable to study the kinetics of the dyes. In this work, a new approach for the mechanistic and kinetics studies of VSDs in lipid membranes is proposed.

**METHODS:** First, pores ( $\varphi = 1 \mu m$ ) were fabricated in silicon nitride thin (200 nm) membranes by focused ion beam (FIB). Second, the membrane with pores was mounted in a homemade electrochemical cell where both sides of the membrane are electrically accessible. Third, freestanding lipid bilayers were formed over the pores either by preparation of black lipid membranes (BLMs) or by giant unilamellar vesicle (GUV) rupture. After the incorporation of VSDs (*e.g.* di-4-ANEPPS), the fluorescence signal from the bilayer is monitored by fluorescence microscopy while applying different voltage sequences with a four electrode system.

#### **RESULTS & DISCUSSION:**

*Free-standing lipid bilayer:* We performed impedance spectroscopy electrochemical experiments to electrically characterize the pored substrate. Fig. 1 shows the impedance changes of the pored Si<sub>3</sub>N<sub>4</sub> membrane before and after the lipid bilayer formation via painting of lipids in decane (BLMs). Pore spanning lipid bilayers formed by GUV rupture are more fragile and rupture easily making electrophysiology experiments impossible. To face the bad stability effect further chemical functionalization of the pored Si<sub>3</sub>N<sub>4</sub> membrane is required, an experimental step which is still under current optimization.

*Voltage-dependent Fluorescence of di-4-ANEPPS:* The electrochromic dye di-4-ANEPPS appears a voltage-dependent shift in the excitation or emission spectrum where the dye is assumed to be bound to the extracellular surface of the membrane and undergo charge distribution in its excited state. The magnitude of the spectral shift is linearly related to the change in the potential.



Fig. 1: Schematic representation of the whole experimental set up for VSDs' response studies(A) Electrochemical impedance spectrum of fourpored  $Si_3N_4$  substrate with and without lipid bilayer (B). Fluorescent imaging of voltage sensitive response of di-4-ANEPPS in lipid bilayer (C).

**CONCLUSIONS:** The proposed platform offers the possibility 1) to apply any voltage sequences, 2) to modify bilayer composition freely, and 3) to acquire two-dimensional mapping of the VSD activities, allowing more detailed studies of VSDs.

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# Forces between Silica Particles in Presence of Monovalent and Multivalent Coions

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Interaction forces between charged silica particles in aqueous solutions of salts containing mono and multivalent anions were measured by colloidal probe technique. These ions are coions, and so are repelled from the surface since both they and the silica particles are negatively charged. Measurements are done at pH=10 for a range of concentrations of different salts: KCl, K<sub>2</sub>SO<sub>4</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, and K<sub>4</sub>Fe(CN)<sub>6</sub>. For the monovalent salt, forces are measured at two different pH values; 5.6 and 10. For low salt concentrations, coions hardly adsorb on the surface and the forces are dominated by double layer repulsion [1]. At concentrations larger than about 200 mM, attraction is observed due to van der Waals forces. Also, the valence of the coion has an influence on the shape of the force curve (Fig. 1). At constant ionic strength, one observes softer profiles in presence of multivalent coions. These profiles have sigmoidal appearance in the semi-logarithmic representation. This characteristic shape can be explained by Poisson-Boltzmann theory. At large separations the force-curves follow the far-field Debye-Hückel limit, and at smaller separations force starts to deviate from this limit due to the expulsion of the coions from the area between the charged walls (Fig. 1).



Fig. 1 Forces between silica particles in KCl and  $K_4$ Fe(CN)<sub>6</sub> at pH=10 and a fixed ionic strength of 10.1 mM with Poisson-Boltzmann (PB) and Debye-Hückel fits (DH).



Fig. 2 Experimentally measured force curves for 1mM concentrations of KCl,  $K_3Fe(CN)_6$ , and  $K_4Fe(CN)_6$  at pH=10 with Poisson-Boltzmann (PB) fits.

Forces measured for the same concentration of different salts are shown in Figure 2. With increase of coion valence, forces are more short-ranged since the counterion concentration increases as  $z \cdot c$ , where z is the valence and c is the concentration of the salt. Higher concentration of potassium ions induces stronger screening.

The diffused layer potential dependence on the coion valence and concentration is also studied, and it follows the prediction based on the basic Stern model.

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## Production of mechanically robust capsules with ultrathin shells

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**INTRODUCTION:** Ultra thin shell double emulsions are stable capsule because the offset between the inner and outer drop caused by the difference in density is reduced. The membrane mechanical properties and thickness can be tuned by the chemical structure of the block copolymer used to form the membrane.

**METHODS:** We use water / oil / water double emulsion droplets as a templates to assemble the polymersomes. Block copolymers assemble into two monolayers, one at each liquid-liquid interface. Then the oil phase is removed to form the bilayer membrane of the vesicle.

To remove the oil we push those double emulsion drops through a micro channel containing a constriction as shown in fig 2.

We studied the influence of the flow rates and the wettability of the channels on the efficiency of oil removal.



Fig. 1: Schematic of the production of monodisperse polymersomes. First a double emulsion is formed using microfluidics. The amphiphilic copolymers dissolved in the oil adsorb at the liquid-liquid interface to form one monolayer at the outer interface of the double emulsion. Finally the oil is removed from the shell to form a bilayer.



Fig. 2: (A) Double emulsions formed initially. (B) Double emulsions are injected in a narrow channel and stack. (C) oil from the double emulsion shell is removed through the microcapillaries. (D) Ultrathin shell double emulsion of less than 300nm shell thicknesss are collected at the output

**DISCUSSION & CONCLUSIONS:** Double emulsion drops were used as templates to make capsules with thin shells produced using microfluidics as this method allows high encapsulation efficiency, good control over the size and composition of the capsules and polymersomes. Those double emulsions were used as templates for the production of capsules with thin shells. We decreased the shell thickness of he double emulsion droplets by mechanically confining thems; this results in a partial removal of the oil from the shell.

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