Swiss Soft Days

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Fribourg 14.04.2023

Adolphe Merkle Institute, University of Fribourg
Chemin des Verdiers 4, 1700 Fribourg

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Local organizers: Véronique Trappe
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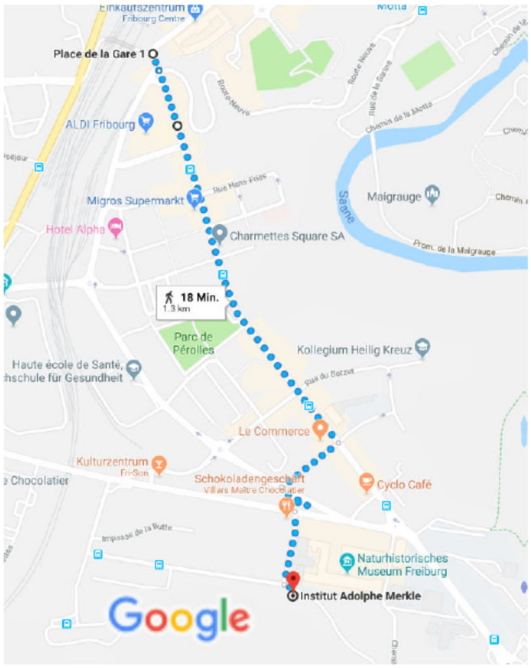
How to get there.

From Fribourg train station to the Adolphe Merkle Institute

On foot (~18Min)



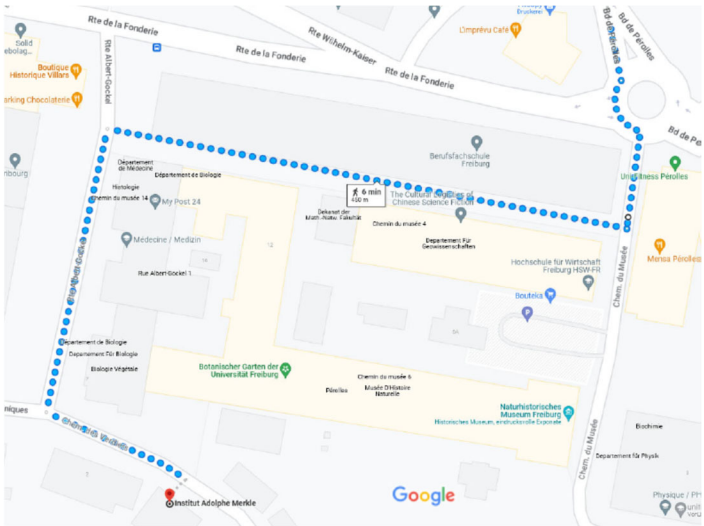
By bus (~9Min)

In front of the train-station (main road) take either 1 (Marly Gerine), 3 (Charmettes) or 8 (Marly Piscine).

Get off Charmettes.

You will need a bus ticket zone 10.

Then follow this root



PROGRAM

09.30-09.55	**Registration / Coffee**	
9.55-10.00	Welcome	
10.00-10.45 *invited*	M. Tibbitt (ETHZ)	Macromolecular engineering of dynamic biomaterials
10.45-11.00	A.J. Giacomin (UniQueen)	Recent advances in polymer viscoelasticity from general rigid bead-rod theory
11.00-11.15	I. Onori (AMI)	Double polymer networks featuring covalent and non-covalent cross-links
11.15-11.30	C.E. Giacomin (ETHZ)	Environmental effects for fish mucus rheology
11.30-11.45	G. De Angelis (EPFL)	The rheological properties of viscoelastic membranes vs bulk hydrogels
11.45 – 12.15	Sound bites	Introduction to selected posters
12.15-13.30	**Lunch / Poster Session**	
13.30-14.15 *invited*	G. Foffi (UniParisSaclay)	What did I learn using super simple models in Soft Matter?
14.15-14.30	T. De Geus (EPFL)	Criticality and nucleation of slip at the frictional interface
14.30-14.45	Z.C. Meijs (ETHZ)	Physical unclonable functions by capillary-assisted particle assembly
14.45-15.00	B. Zhou (PSI)	Concentration dependence of counter-ion cloud configuration with increasing particle stiffness studied with SANS
15.00-15.30	**Coffee / Poster Session**	
15.30-15.15	Y.Yuan (ETHZ)	Plasmonic amyloid tactoids
15.15-16.00	M. Debas (UniFribourg)	Supramolecular design of CO_2-responsive lipid nanomaterials
16.00-16.15	X. Huang (UniBasel)	Cell-derived vesicles with improved properties and functionality by equipping their membrane with a cross-linkable copolymer
16.15-16.30	B.F.B. Silva (EMPA)	General assembly behavior of core-shell lipid-polycation-nucleic acid nanoparticles as revealed with fluorescence cross-correlation spectroscopy

	Sound bites for the introduction of selected posters
M. Wolf (ETHZ)	Photoreversible resins for the detachment of human temporal bone samples
B. Tran (UniFribourg)	Self-assembly of polycationic polymers with viruses for advanced biomaterials
Q. Sun (ETHZ)	Thermo-responsive liquid crystalline phases of cellulose nanocrystals with polymer brushes
S.C. Erunsal (UniKonya)	Impact of varying kind of antioxidants on light-induced printing of hydrogels
P. Pradal (EPFL)	3D printing of rigid photonic microparticles
V. Maffeis (UniBasel)	Catalytic nano-compartments for complex cascade reactions in biomedicine
S. Tarvirdipour (UniBasel)	Nuclear-targeted delivery of oligonucleotides exploiting peptide nano-assemblies
J. Prabhu (UniFribourg)	An *in silico* osmotic pressure approach allows to characterize pressure-area isotherms of lipid monolayers at low molecular areas

Number		Posters
1	P. Pradal (EPFL)	3D-printing of rigid photonic microparticles
2	M. Hirsch (EPFL)	4D-printing of metal-reinforced double network granular hydrogels
3	E. Baur (EPFL)	Granular elastomers for 3D printing applications
4	S.C. Erunsal (UniKonya)	Impact of varying kind of antioxidants on light-induced printing of hydrogels
5	M. Wolf (ETHZ)	Photoreversible resins for the detachment of human temporal bone samples
6	B. Tran (UniFribourg)	Self-assembly of polycationic polymers with viruses for advanced biomaterials
7	Q. Sun (ETHZ)	Thermo-responsive liquid crystalline phases of cellulose nanocrystals with polymer brushes
8	V. Maffeis (UniBasel)	Catalytic nano-compartments for complex cascade reactions in biomedicine
9	K. Wei (EMPA)	Tailoring mechanical properties of gelatin hydrogels via diverse crosslinking strategies
10	S. Tarvirdipour (UniBasel)	Nuclear-targeted delivery of oligonucleotides exploiting peptide nano-assemblies
11	R. Freire (UniFribourg)	Unraveling nanostructure formation during simulated digestion of functional emulsions by *in situ* synchrotron SAXS
12	C.-R. Li (EPFL)	Charge-selectively permeable microcapsules
13	O. Eggenberger (UniBasel)	Bottom-up cell mimicry: ATP synthesis in giant polymersomes formed by microfluidics
14	V.Mihali (UniBasel)	Clusters of hard-soft assembly for bio-applications
15	K. Manne (UniFribourg)	Synthesis and characterization of structurally colored silica foams via colloidal templating
16	M. Skowicki (UniBasel)	The use of fibroblast activation protein inhibitor as a targeting ligand for enhanced cellular uptake

17	P. Ferdowsi (UniFribourg)	Investigating $MAPbBr_3$ Perovskite solar cells through interfacial passivation using ultrathin polymeric films
18	H. Wang (EPFL)	Investigation of single-walled carbon nanotubes enriched hydrogels for ascorbic acid sensing and release monitoring
19	J. Muñetón Díaz (UniFribourg)	From interaction potentials to rheological properties of microgel particles
20	H. Almohammadi (ETHZ)	Disentangling kinetics from thermodynamics in heterogeneous colloidal systems
21	J. Prabhu (UniFribourg)	An *in silico* osmotic pressure approach allows to characterize pressure-area isotherms of lipid monolayers at low molecular areas
22	M. Gora (EMPA)	Surfaces forces on nano-porous materials
23	L. Heuberger (UniBasel)	Microfluidic polymer GUVs – a versatile toolbox to study biological processes

INVITED CONTRIBUTIONS

Macromolecular engineering of dynamic biomaterials

Mark Tibbitt
Macromolecular Engineering Laboratory, ETH Zurich

Polymer materials provide solutions to many pressing biomedical, manufacturing, and environmental challenges. However, traditional polymer materials have a limited capacity for rearrangement, presenting difficulties in their processing, use, and recycling. Engineering reversible interactions within polymer networks enables the formation of dynamic and reconfigurable materials, opening new opportunities for use and re-use of polymer networks. In this talk, we will present fundamental insight and applications of dynamic polymer networks with an emphasis on their utility in biomedical applications. We provide a framework for engineering dynamic macromolecular systems by linking molecular behavior at the reversible junctions to macroscopic properties using modeling, spectroscopy, and mechanical characterization. We then present how we use this knowledge to design biomaterials with various topologies and reversible interactions for a range of biomedical challenges, including the thermal stabilization of complex biologics and additive manufacturing of drug delivery systems.

What did I learn using super simple models in Soft Matter?

Giuseppe Foffi
Université Paris-Saclay

In this talk, I will discuss how simple statistical mechanics models can be used in soft matter, in general, and in colloidal science, in particular. I will discuss different models and applications on which I worked ranging from colloids to proteins, from glasses to quasicrystal. As a working example, I will discuss some very recent work on granular systems that lead us to apply the same approach using different models of different level of complexity and to develop our own experimental model.

ORAL CONTRIBUTIONS

Recent advances in polymer viscoelasticity from general rigid bead-rod theory

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Keywords. Rotational diffusivity; general rigid bead-rod model; complex viscosity; viscoelasticity; orientation;

One good way to explain the elasticity of a polymeric liquid, is to just consider the orientation distribution of the macromolecules. When exploring how macromolecular architecture affects the elasticity of a polymeric liquid, we find general rigid bead-rod theory to be both versatile and accurate. This theory sculpts macromolecules using beads and rods. Whereas beads represent points of Stokes flow resistances, the rods represent rigid separations. In this way, how the shape of the macromolecule affects its rheological behavior in suspension is determined. Our work shows the recent advances in polymer viscoelasticity using general rigid bead-rod theory, including advances applied on the coronavirus. The coronavirus is always idealized as a spherical capsid with radially protruding spikes. However, histologically, in the tissues of infected patients, capsids in cross section are elliptical, and only sometimes spherical. This capsid ellipticity implies that coronaviruses are oblate or prolate or both. We call this diversity of shapes, pleomorphism. Recently, the rotational diffusivity of the spherical coronavirus in suspension was calculated, from first principles, using general rigid bead-rod theory. We did so by beading the spherical capsid, and then also by replacing each of its bulbous spikes with a single bead. In this paper, we use energy minimization for the spreading of the spikes, charged identically, over the oblate or prolate capsids. We use general rigid bead-rod theory to explore the role of such coronavirus cross-sectional ellipticity on its rotational diffusivity, the transport property around which its cell attachment revolves. We learn that coronavirus ellipticity drastically decreases its rotational diffusivity, be it oblate or prolate.

[1] Kanso, M.A., M. Naime, V. Chaurasia, K. Tontiwattanakul, E. Fried and A.J. Giacomin, "Coronavirus Pleomorphism," Physics of Fluids, 34(6), 063101 (2022).
[2] Kanso, M.A., J.H. Piette, J.A. Hanna and A.J. Giacomin, "Coronavirus rotational diffusivity," Physics of Fluids, 32(11), 113101 (2020).

Double polymer networks featuring covalent and non-covalent cross-links

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Double polymer networks (**DNs**) consist of two polymer networks (**PNs**) that have typically different physical properties. These materials usually combine a first, more brittle network (highly cross-linked) with a second, soft and ductile network (more loosely cross-linked). The first network acts as a *sacrificial network*, which fractures to dissipate energy under an applied stress, and allows the realization of tough **DNs**. The resulting mechanical properties, such as enhanced extensibility and tensile strength, make **DNs** interesting systems for a wide range of applications.[1],[2] Previous studies on **DNs** have been mostly limited to hydrogels comprising covalent interactions, while solvent-free materials have been little investigated, despite their advantages in terms of mechanical properties. To access such materials, we prepared **DNs** comprising supramolecular interactions. The introduction of non-covalent bonds leads to materials that are easier to reprocess, recover and tailor than their covalent counterparts.[3] One of the motivations to engineer **DNs** with supramolecular interactions consists in the fact that the latter can be employed as *reversible* sacrificial bonds,[4] since they can dissociate under mechanical stress to dissipate the energy and then reform after fracturing.

Here, we report the realization of a **DN** elastomer comprising a covalent and a supramolecular polymer network with different density of cross-links. The **DN** is based on a poly(butyl acrylate) (**PBA**) backbone. The first network (**PBA-UPy**) is prepared by reversible addition−fragmentation chain-transfer (RAFT) polymerization of butyl acrylate (**BA**) and comprises 5 mol% of the self-complementary hydrogen bonding motif 2-ureido-4[1H]pyrimidinone (**UPy**), which dimerizes into supramolecular cross-links.[5] The covalent polymer network (**PBA-BDA**) contains 2 mol% of 1,4-butanediol acrylate (**BDA**) as covalent cross-link, and it is synthesized by UV-initiated free-radical polymerization (UV curing).[6] (**Figure 1**).

The thermomechanical properties of the single networks and the **DN** were investigated by dynamic mechanical analyses (DMA). The DMA traces of the **DN** show features of both single networks. While the mechanical properties are similar to those of **PBA-UPy**, the presence of the persisting covalent network significantly improves the thermal stability. Finally, we show that **PBA-UPy** can be selectively extracted from the **DN**, and also thermally healed.

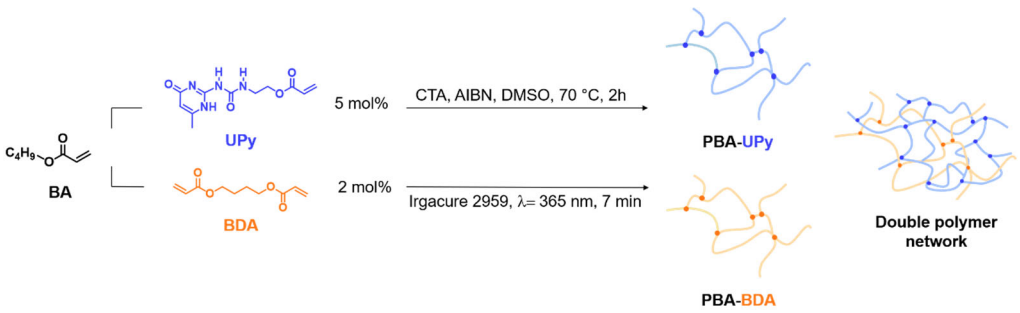

Figure 1. Synthesis of **PBA-UPy** by RAFT polymerization of **BA** and **UPy** (5 mol%) and of **PBA-BDA** by UV-initiated free-radical polymerization of **BA** and **BDA** (2 mol%). Combination of the two networks affords **DN**.

[1] Yang, J. et al., Adv. Funct. Mater. **2022**, 32, 2110244. [2] Creton, C. et al., Science, **2014**, 344. [3] Meijer, B. W. et al., Isr. J. Chem., **2020**, 60, 33–47. [4] Mareliati, M. et al., Macromolecules **2022**, 55, 5164-5175. [5] Weder, C. et al., Macromolecules, **2018**, 51, 5867- 5874. [6] Weder, C. et al., J. Am. Chem. Soc. **2021**, 143, 45, 18859–18863.

Environmental effects for fish mucus rheology

Caroline E. Giacomin and Peter Fischer

Food Process Engineering Laboratory, D-HEST, ETH Zurich

Mucin vesicles, sourced from the defense mucus of Atlantic Hagfish (*Myxine glutinosa*), are an uncontaminated and non-damaged source of isolated mucins [1]. Mucus is comprised of a mesh-like structure of mucins and limits conveyance of particles by pore size and viscoelasticity of the network [2], [3].

Mucus can be found acting as a barrier for many marine animals depending on the role of mucus or on surroundings, mucus can preferentially absorb particles of different sizes or surface charges [4]. The ability of microbes, drugs, nutrients, pollutants, or other particles to reach the epithelium is dependent on their ability to be conveyed by this mucus barrier. In aquacultural, fish transitioning between sea and fresh water have increased susceptibility to infections from bacteria, viruses, and parasites [5], [6]. To evaluate mucus structural changes during this transition extensional rheology is performed. Changes to extensional breakup behavior are observed in the presence of varied microparticles, and varied order of introduction to the mucus network.

[1] L. Böni, *et al.*, *Sci. Rep.*, 6, (2016).
[2] K. Rementzi, *et al.*, *Soft Matter*, 15, 42, (2019).
[3] L. J. Böni *et al.*, *Sci. Rep.*, 8, (2018).
[4] S. K. Lai *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, 104, (2007).
[5] S. Dash *et al.*, *Iran. J. Vet. Res.*, 19, 2, (2018).
[6] O. Torrissen *et al.*, *J. Fish Dis.*, 36, 3, (2013).

The rheological properties of viscoelastic membranes vs. bulk hydrogels

Gaia De Angelis[1], Viviane Lutz-Bueno[2] and Esther Amstad[1]*

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[2] Paul Scherrer Institute, Laboratory for Neutron Scattering and Imaging, 5232 Villigen PSI (Switzerland)

Researchers have recently become interested in hydrogels presenting metal coordination motifs because if ionically crosslinked, they are self-healing and adhesive. Inspired by nature, catechol-functionalized bulk hydrogels have drawn a lot of interest. By contrast, very little is known about thin viscoelastic membranes produced using equivalent ion-chelator pair motifs. This limitation is unexpected given that the characteristics of ionically crosslinked hydrogels, particularly their self-healing and adhesion properties, would be ideal assets for capsule shells, adhesives, or drug delivery. We recently showed that it is possible to synthesize catechol-functionalized surfactants that are ionically crosslinked at the liquid/liquid interface to form 10 nm thin viscoelastic membranes[1]. However, it is unclear if the vast knowhow existing on the influence of the chelator-ion pair on the mechanical properties of ionically crosslinked 3D hydrogels can be translated to 2D systems. To answer this question, we compare the dynamic mechanical properties of pyrogallol functionalised hydrogels with those of viscoelastic membranes crosslinked with the equivalent ion-chelator motif. We show that the viscoelastic membranes' storage and loss moduli exhibit a pattern resembling that of hydrogels, with the membrane becoming stronger as the ion-chelator affinity increases[2]. Yet, membranes relax far more quickly than their bulk equivalents. These observations make it possible to specifically design viscoelastic, adhesive, self-healing membranes with tuneable mechanical properties. By substituting the fluorinated block with a hydrocarbon-based one, such capsules may be utilized, for instance, in cosmetics, as granular inks, for medicine delivery, or even for food applications.

[1] G. De Angelis, N. Grey, V. Lutz-Bueno, and E. Amstad, Adv. Mater. Interfaces, 2202450 (2023)
[2] G. De Angelis, V. Lutz-Bueno, E. Amstad, Appl. Mat. and Interfaces, in review (2023)
* Correspondence: esther.amstad@epfl.ch

Criticality and nucleation of slip at the frictional interface

Tom de Geus

École Polytechnique Fédérale de Lausanne, Lausanne

Slip at a frictional interface occurs via intermittent events. Understanding how these events are nucleated, can propagate, or stop spontaneously remains a challenge, central to earthquake science and tribology. In the absence of disorder, rate-and-state approaches predict a diverging nucleation length at some stress, beyond which 'fracture' can propagate. We argue for a flat interface that disorder is a relevant perturbation to this description [1]. We justify why the distribution of slip contains two parts: a powerlaw corresponding to 'avalanches', and a 'narrow' distribution of system-spanning 'fracture' events. We derive novel scaling relations for avalanches, including a relation between the stress drop and the spatial extension of a slip event. We compute the cut-off length beyond which avalanches cannot be stopped by disorder, leading to a system-spanning fracture. We argue, however, that to understand nucleation the similarity to fracture is an unfortunate coincidence. Furthermore, we propose how the stress drop decreases with the system size, and how that depends on the surface properties through an armouring mechanism caused by inertia [2].

[1] T.W.J. de Geus and M. Wyart (2022), Phys. Rev. E, 106(6):065001.
[2] E. El Sergany, M. Wyart, and T.W.J. de Geus Armouring of a Frictional Interface by Mechanical Noise, arXiv:2301.13802

Physical Unclonable Functions by Capillarity-Assisted Particle Assembly

Meijs, Zazo Cazimir[1]; Yun, Hee Seong[2]; Fandre, Pascal[1]; Park, Geonhyeong[2]; Yoon, Dong Ki[2] and Isa, Lucio[1]

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Physical Unclonable Functions, or PUFs, are an exciting and relatively new field with immense chances for ingenuity and improvement from the wider soft matter community [1]. Worldwide there is enormous economic damage resulting from fake products. Moreover, in cases concerning health care it can even be dangerous [2]. Recent years have shown a push for robust strategies to prove the authenticity of products without any chance of failure or misuse. An ideal authentication technology has to produce truly unique identification tokens, which cannot be replicated, even if illegitimate manufacturers have access to the same techniques. One excellent way to guarantee these requirements is to use physically unclonable functions, or PUFs. A PUF is a physical object that for a given input under certain conditions (also known as the challenge) gives a unique, physically-defined output (the response). The effectiveness of PUFs depends on the uniqueness and reliability of the physical signature that defines them. In most current implementations a PUF is defined from a larger random pattern in which a sub-image or quantified parameters into a unique token. Upon reading these PUFs, the read image needs to be matched to the original one, either by alignment marks or by a certain degree of tolerance and mismatching between the two patterns.
In this work, instead of using a subset of a large area, we create pre-binarized systems of clearly distinguishable micro-tokens by using Capillarity-Assisted Particle Assembly (CAPA). The token consists of a square array of randomly deposited fluorescent colloids. As the colloids are stable and fully distinguishable we have a zero percent false positive rate with an encoding capacity that scales exponentially with the size of the full token. As the colloids are uniformly mixed, which particle ends up in which trap is a fully random process. For an equal mixture of M types of particles, the number of possible unique tokens scales exponentially with the number N of traps in the pattern as M^N. As example, if it takes 10 seconds to make and measure a 40×40 token with 3 different colloids it would on average take $0.5 * 3^{\wedge 1600} * 10s \approx 10^{360}s$ or about 10350 years of constantly making tokens to remake the same token. Furthermore, our workflow allows us to transfer the token to different materials. To showcase this capability, we have encapsulated the tokens in PDMS, i.e. a flexible elastomer, or transferred the into PMMA. In summary, our method allows for fail-proof, unclonable tokens that can easily be encased in different materials for different end applications.

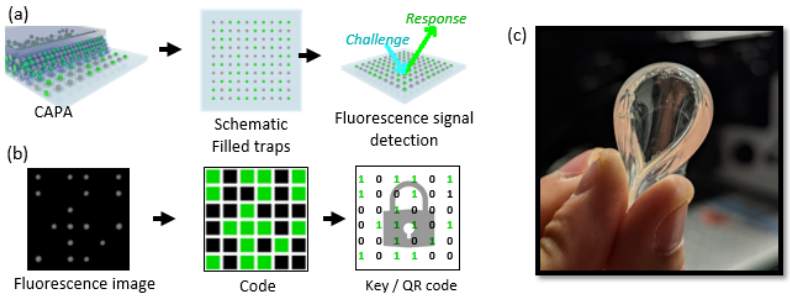

Fig 1. (a) shows schematically how we make our PUF-token, (b) presents the computational evaluation of the token and (c) is an example of the great flexibility of our token encapsulated in PDMS.

[1] Gao, Y., Al-Sarawi, S.F. & Abbott, D. Physical unclonable functions. **Nature Electronics** (2020)
[2] Jung Woo Leem *et al*. Edible unclonable functions**. Nature Communications** (2020)
[3] Qian Li *et al*. Physical Unclonable Ant counterfeiting Electrodes Enabled by Spontaneously Formed Plasmonic Core–Shell Nanoparticles for Traceable Electronics**. Advanced Functional Materials** (2021).

Concentration dependence of the microgel Counter-ion Cloud configuration with increasing particle stiffness studied with Small-Angle Neutron Scattering (SANS)

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[2] ICREA Research Professor at Universitat de Barcelona (UB)

Microgels are formed by cross-linked polymer networks that exist in and reversibly change between a swollen and collapsed state in response to changes in external conditions. In particular, due to their compressibility, soft particles exhibit a phase behavior that is more complex than their hard-particulate counterparts. As a result, there is no generally accepted model for their interactions and overall phase behavior at both dilute and concentrated conditions. Although pNIPAM is an uncharged polymer, pNIPAM microgels are peripherally charged due to charges remaining from particle synthesis. The corresponding counterion cloud has been found to play a crucial role for the observed spontaneous deswelling behavior at high concentrations; particles deswell before reaching random close packing density Φrcp [1]. This deswelling was found to be triggered, above a critical concentration ζ_c, by a sharp increase of the suspension osmotic pressure set by counterions originating from charged groups in the periphery of the microgel [2]. $\zeta = (N_{tot}V_{sw})/V_{tot}$ is the generalized volume fraction calculated with the particle's swollen radius. Our recent SANS measurements have confirmed that the counterion cloud bound to the initiators' SO_3^- groups indeed locates at the particle surface. For entropic reasons, a fraction of the counterions overcome the electrostatic attraction and set to the suspension osmotic pressure. At high concentrations, the counter-ion clouds percolate and, as a consequence, the number of effectively free counterions and the osmotic pressure show a marked increase. When this pressure becomes larger than the particle bulk modulus, the microgels are isotropically compressed [2,3]. Here, we focus on the variation of microgel softness set by the crosslinker concentration and the effect on the distribution of fixed charges in the microgel. We have studied microgels with various softness, set by the crosslink (BIS) density of 0% (microgels with ultra low crosslinking, ULC), 2.5% and 5%, and suspensions with concentrations from ζ=0.02 to ζ=1 were measured. We replace the counterions with either Na+ or NH4+ via dialysis, which results in a small but measurable change of the microgel form factor and allows obtaining detailed information on the configuration of the counter-ions and charged groups. All measurements were done at 18℃ where particles stay at their fully swollen size as long as the osmotic pressure is lower than the bulk modulus. We find the deswelling at high concentrations to depend on microgel softness: For microgels with 2.5% BIS, the counterion cloud persists at the particle surface at all conditions. For ULC, we notice our model that pictures the cloud as a spherical shell becomes insufficient to describe the data. For 5.0%BIS, the expected cloud signal is observed at low and moderate concentrations but disappears at high concentration where particle deformation might occur. Our results allow exploring the concentration-, and particle-stiffness dependence of the deswelling behavior. We find that the osmotic pressure due to the counterions must be included for a comprehensive understanding of microgels at high concentrations. The cloud configuration appears to depend on the microgel softness. Further work is needed to clarify the behavior of very soft microgels and of quite stiff microgels at high concentrations. Our findings stress the importance of microgel softness, and the osmotic pressure set by counterions for developing a more systematic understanding of pNIPAM microgels at high concentrations.

[1] A. St. John Iyer and L.A. Lyon, Chem. Int. Ed. 48, 4562-4566 (2009
[2] A. Scotti, U. Gasser, E.S. Herman, M. Pelaez-Fernandez, J. Han, A. Menzel, L.A. Lyon and A.Fernandez-Nieves, Proceedings of the National Academy of Sciences 113, 5576 (2016).
[3] U.Gasser, A. Scotti, and A. Fernandex-Nieves, Physical Review E99, 042602 (2019).

Plasmonic Amyloid Tactoids

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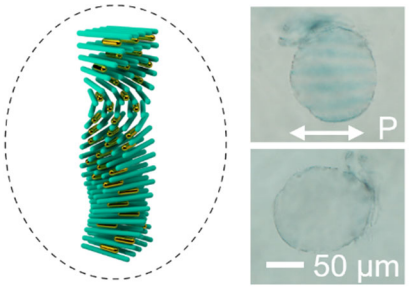
Despite their link to neurodegenerative diseases, amyloids of natural and synthetic sources can also serve as building blocks for functional materials, while possessing intrinsic photonic properties. Here we demonstrate that orientationally ordered amyloid fibrils exhibit polarization-dependent fluorescence, and can mechanically align rod-shaped plasmonic nanoparticles co-dispersed with them. The coupling between the photonic fibrils in liquid crystal phases and the plasmonic effect of the nanoparticles leads to selective activation of plasmonic extinctions as well as enhanced fluorescence from the hybrid material. These findings are consistent with numerical simulations of the near-field plasmonic enhancement around the nanoparticles. Our study provides an approach to synthesize the intrinsic photonic and mechanical properties of amyloid into functional hybrid materials, and may help improve the detection of amyloid deposits based on their enhanced intrinsic luminescence.

Y. Yuan *et al*. Plasmonic Amyloid Tactoids. *Adv. Mater.* **33**, 2106155 (2021)

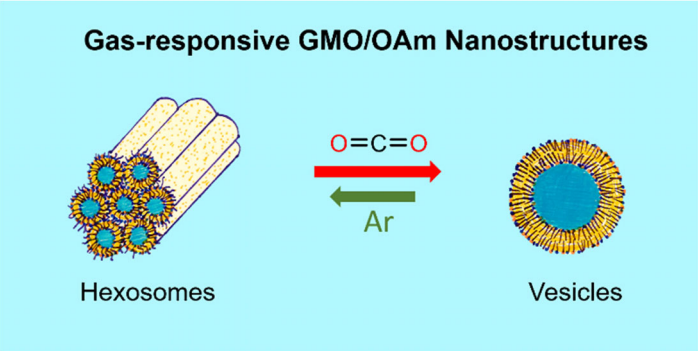


Plasmonic amyloid tactoid in cholesteric phase. The schematic on the left illustrates how gold nanorods (rods in metalic golden color) are aligned by amyloid fibrils (green rods) in a cholesteric tactoid. Micrographs on the right show plasmonic blue stripes corresponding to the cholesteric layers within such a hybrid tacoid and their disappearance when rotated.

Supramolecular Design of CO_2-responsive Lipid Nanomaterials

Meron Debas, Rafael V. M. Freire, Stefan Salentinig

Department of Chemistry, University of Fribourg



Stimuli-responsive materials can innovate in various fields, including food and pharmaceutical sciences. Their response to a specific stimulus can be utilized to release loaded bioactive molecules or sense their presence. The biocompatibility and abundance of CO_2 in the environment make it an exciting stimulus for such applications. We hypothesize the formation of CO_2-responsive liquid crystalline nanoparticles by integrating an amidine surfactant into glycerol-monoleine-based (GMO) cubosomes. The CO_2-triggered transformation of a non-charged acetamidine surfactant to its cationic amidinium form ($OAmH^+$) will trigger curvature changes that ultimately induce phase transitions. The CO_2-switchable lipid (E)-N,N-dimethyl-N-((Z)-octadec-9-en1-yl)acetimidamide (OAm) is synthesized and formulated into emulsions and dispersed liquid crystals with GMO. The supramolecular structure and its response to CO_2 are characterized using small angle X-ray scattering (SAXS), dynamic light scattering (DLS), and cryo-TEM. Depending on the composition, OAm is discovered to self-assemble into a variety of CO_2-responsive lyotropic liquid crystalline structures that can be dispersed in excess water. CO_2-triggered colloidal transformations from unstructured OAm-in-water emulsions to direct micelles; dispersed inverse hexagonal phase to direct rod-like micelles, and sponge phase to vesicles are discovered. These structural changes are driven by the reaction of OAm's amidine headgroup with CO_2, which strongly impacts its polarity and self-assembly behavior. The results provide a fundamental understanding of CO_2-triggered functional nanomaterials and may guide their future design into delivery platforms and biosensors.

Cell-derived Vesicles with Improved properties and Functionality by Equipping their Membrane with a Cross-linkable Copolymer

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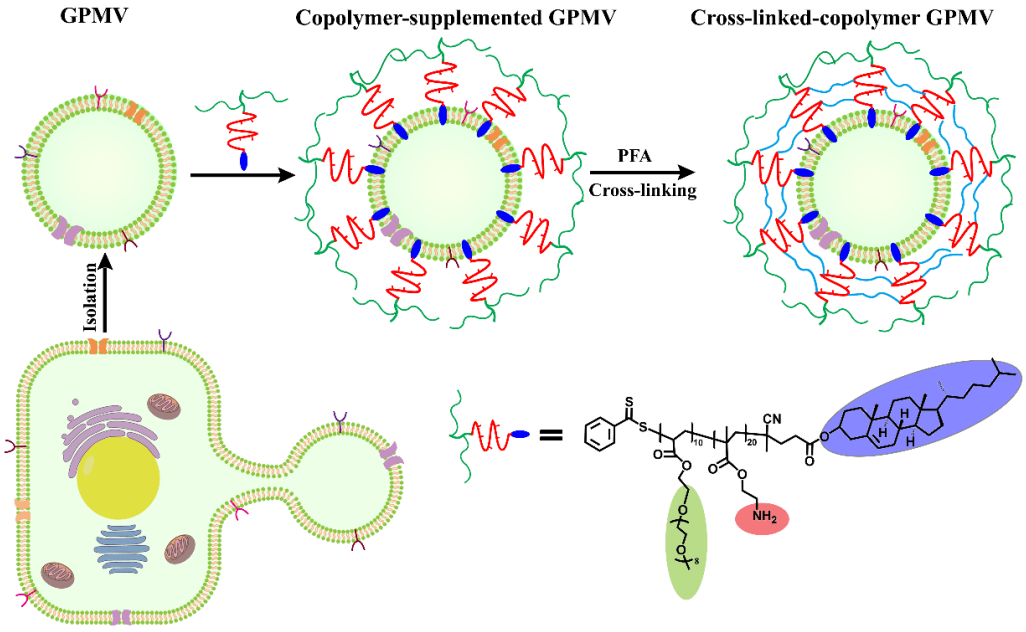
Cell-derived vesicles are on focus in the analysis of membrane biophysics, the production of top-notch drug delivery systems or complex molecular factories because they retain the cytoplasm and much of the native cell membrane composition. However, there is an imperative demand to develop novel strategies for addressing their membrane fragility and high aggregation risk during storage, which still limit the biological applications. Herein, we introduce an approach to improve the properties of cell membranes by decorating the surface of giant plasma membrane vesicles (GPMVs) with a cholesterol-terminated diblock copolymer. Benefiting from the cross-linking of inserted copolymer chains, the GPMV membrane exhibit improved resistance against surfactants and enhanced stability over time. Furthermore, the pH-responsiveness of the copolymer layer allows for a controlled cargo loading/release, which will support various bio-applications. Importantly, the cross-linked-copolymer GPMVs are not cytotoxic and preserve *in vitro* the membrane integrity and functionality. Taken together, our results demonstrate the possibility to successfully engineer the cell membranes by equipment with stimuli-responsive cross-linkable copolymers to achieve enhanced properties and functionality.



General assembly behavior of core-shell lipid-polycation-nucleic acid nanoparticles as revealed with Fluorescence Cross-Correlation Spectroscopy

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Abstract: Hybrid core-shell lipid-polymer-nucleic acid nanoparticles (LPNPs) have emerged as a promising platform for nonviral gene therapeutics, including mRNA vaccines. However, due to the intricate interactions among their three main components, namely, the polycations and nucleic acids in the core and the lipid bilayer as the shell, their preparation and characterization are challenging. In this study, we aim to shed light on the physics of LPNP formation by investigating the interactions among the three components using fluorescence cross-correlation spectroscopy (FCCS) (1). Our results demonstrate that the interaction between the polycation (polylysine) and DNA is robust and not disrupted by the addition of cationic liposomes. Therefore, for LPNP particles to form, the net charge of the polycation-DNA core must be opposite to the lipid shell. Importantly, we also identify the liposome:core number ratio (ρ_N), which naturally emerges from FCCS, as the crucial parameter governing stable LPNP formation. We establish that $\rho_N \geq 1$ is necessary to ensure that every polycation-DNA core (anionic) is enveloped by a cationic liposome, thereby inverting the charge of every core, and preventing the coexistence of oppositely charged species that would otherwise cause aggregation. Our findings have important implications for the design and optimization of soft matter-based composite nanomaterials and LPNPs, which are poised to impact nonviral gene therapeutics.

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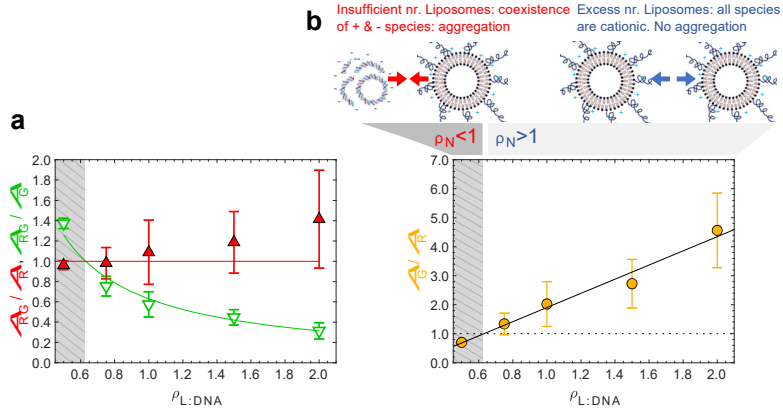

Fig 1. Quantification of association between cationic liposomes and polycation-DNA cores with FCCS. By labelling the polycation and cationic liposomes with a green and red fluorescent label, respectively, the ratios of the amplitudes of cross-correlation (A_{RG}) to autocorrelation of both species (A_R and A_G) provide the fraction of cores converted to LPNPs and the fraction of liposomes used in LPNPs, respectively. Symbols are data points; lines are the expected result for a 1:1 liposome-core binding stoichiometry. **(b)** the A_G/A_R ratio, which is equivalent to the liposome:core ratio (ρ_N) shows that colloidal stability for LPNPs is reached when $\rho_N>1$.

POSTER CONTRIBUTIONS

1) 3D printing of rigid photonic microparticles

Pauline, Pradal

Soft Materials Laboratory (SMaL) – EPFL

In the past 30 years, many biological materials having structural colors, and more specifically photonic crystals, have been studied. [1–3] These periodic structures of colloidal particles are attractive because they possess bright and vivid colors due to the constructive interferences of the monochromatic reflected light. Such colors can be obtained in synthetic materials if, for example, silica nanoparticles with diameters close to the wavelength of visible light are arranged into regular assays. [4, 5] However, the assembly of nanoparticles into well-ordered crystalline structures at the centimeter scale is challenging because the high defect density at the macroscopic scale lowers the brightness of the structural colors and the material composed of nanoparticle assemblies can only attain basic structures because of the limitations in terms of processing of these nanoparticle assemblies on the sub-mm length scales. To address these challenges, I will introduce spherical microparticles composed of assembled nanoparticles that can be 3D printed into macroscopic photonic materials. I will demonstrate how the composition of the microparticles and the printing parameters influence the optical appearance of the material and its mechanical properties.

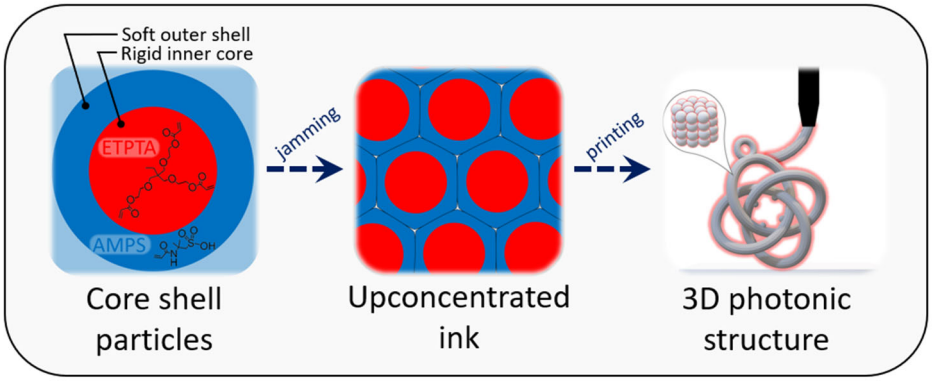

Figure 1. 3D printing process of rigid photonic microparticles from the building blocks to the ink extrusion.

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2) 4D Printing of Metal-Reinforced Double Network Granular Hydrogels

Matteo Hirsch, Livia D'Onofrio, Qinghua Guan, Josie Hughes, and Esther Amstad

Soft Materials Laboratory (SMaL) – EPFL

Recent developments in soft actuation demand for new resilient materials that can bear significant loads yet, whose mechanical properties can be changed with a high spatial resolution. A technique that offers tight control over the composition of a wide variety of materials on length scales down to 100 µm is extrusion-based 3D printing. However, the number of inks that enable 3D printing of hydrogel-based materials is limited and those that can be 3D printed yield in weak hydrogels that prevent bearing significant loads. This shortcoming can be addressed by formulating hydrogels into microparticles, so-called microgels, that can be up-concentrated until they are jammed. These jammed microgels display a rheological behavior that is ideal for 3D printing. However, the weak inter-particle interactions typically again yield soft 3D printed granular hydrogels that cannot bear significant loads. Granular hydrogels can be mechanically reinforced through a percolating hydrogel network that is formed after they have been processed into the appropriate shape, resulting in double network granular hydrogels (DNGHs). Yet, these hydrogels are rather brittle. To address this limitation, we introduce 3D printable metal-reinforced double network granular hydrogels that can bear loads up to 3 MPa while displaying a fracture energy up to 12 $MJ \cdot m^{-3}$, a value that exceeds those of previously 3D printed hydrogels 20-fold. By selectively reinforcing only certain regions of DNGHs, we locally vary their degree of swelling, thereby introducing shape morphing properties to them without compromising their mechanical performance. We anticipate the freedom in varying the mechanical properties of 3D printable DNGHs locally without the need to change the material system and hence, to introduce joints that hamper miniaturization and compromise the durability of this system to present a paradigm shift in the design of soft actuators.

3) Granular Elastomers for 3D Printing Applications

Eva Baur, Esther Amstad

Soft Materials Laboratory (SMaL) – EPFL

The rising interest in the field of soft robotics demands for elastic soft materials whose mechanical properties can be locally varied to design materials that can deform in a pre-defined fashion while bearing significant loads. Such materials have the potential to enable the design of a soft robot that possesses a high dexterity, can interact safely with humans and adapt itself to different environments. The stiffness-toughness compromise inherent to elastomers can be overcome if they are formulated as multi-network materials.[2,3] However, the elastomeric liquid precursors are difficult to process, limiting the complexity of shapes that can be formed with them. The involved processing of a second network further reduces the shape control and hence applications of these elastomers.

In my poster, I will present a strategy to 3D print double network elastomers with a high spatial resolution. This is achieved by loading elastomer-based microparticles with a second precursor solution. These microparticles are jammed to enable their printing into complex structures before the second elastomer network is formed. I will also demonstrate how the composition of the microparticles influence the macroscopic mechanical properties of the resulting double network granular elastomer.

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4) Impact of varying kind of antioxidants on light-induced printing of hydrogels

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[1] Department of Food Engineering, Konya Food and Agriculture University, Konya, 42080, Turkey

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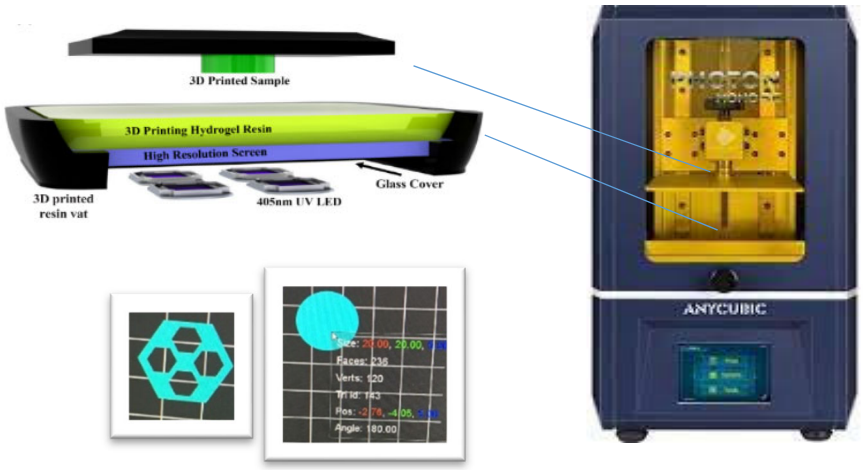
Personalized nutrition/medicine is one of today's hot topics for personalized treatment such as manipulating target agent dosage with the change of geometries in printed gels. Stereolithography (SLA) printing is a powerful technique relying on photopolymerization reaction for fabrication of complex or personalized geometries. Hydrogels as attractive candidates for drug delivery, encapsulation of phenolic compounds, wound dressing and soft implant could be manufactured by solidification of polymer resin upon exposure to UV light in SLA printer [1]. However, there are still concerns about the toxicity of photo-initiators (PIs) used in resin formulations. Regarding this obstacle, we confirmed the use of riboflavin as a natural and non-toxic alternative in a poly(ethylene glycol) dimethacrylate (PEGDMA) based light-induced gel formulations. Additionally, various kinds of antioxidants having different molecular weights and solubilities were encapsulated into the gels to examine their printability and release behavior from the printed gels at different surface area/volume ratios. This study paves the way for future contributions in different areas from pharmaceutical applications to tissue engineering.



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5) Photoreversible resins for the detachment of human temporal bone samples

Morris Wolf[1], David Bächinger[2], Andreas Eckhard[3], Mark W. Tibbitt[1]

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[3]Otopathology Laboratory, Department of Otolaryngology, Harvard Medical School, Massachusetts Eye and Ear Infirmary, MA, USA

The embedding of human temporal bone for histology samples relies on the celloidin method since decades.[1] The long sample preparation time and high cost motivated the development of a new methyl methacrylate-base embedding method, reducing time and cost significantly by an order of magnitude.[2] In addition, the new embedding method preserves DNA and allows for genetic analysis including next-generation DNA sequencing methods. To conduct such analyses, however, the tissue sample sections need to be removed from the glass slide to which they are attached during processing. Current adhesives suitable for the process only offer the option of removal through heat, which can result in thermal degradation of the DNA – decreasing DNA quality[3] – and negatively impact morphologic preservation of the tissue section. The development of a novel resin based on a reversible photopolymer that can be cured (hardened) with one wavelength of light and de-crosslinked (softened) later via irradiation with a second wavelength of light could serve as a suitable alternative. Our approach is based on a thiol–ene resin with a photodegradable cross-linker. While a suitable photoinitiator initiates the cross-linking through thiol-ene click chemistry at 405 nm UV light, the photodegradable cross-linker degrades the network by cleaving under irradiation with DNA preserving UV light at 365 nm. An *ortho*-nitrobenzyl (*o*NB)–diene was synthesized as the cross-linker, as the *o*NB chemistry has shown appropriate cleavage characteristics in the literature.[4] The current challenge lies in advancing the cross-linker molecule to combine efficient cleavage capability with the desired properties of the final resin including adhesive properties and solvent resistance.

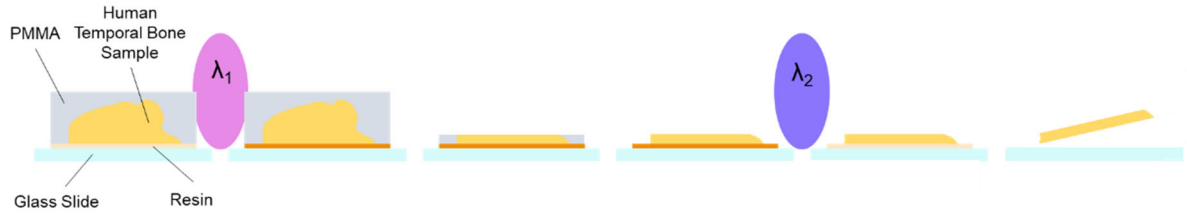

Figure 1: The embedded human temporal bone sample is glued on a glass slide with the photo-reversible resin, which is cured with 405 nm (λ_1) light. Then the sample is sliced and the poly(methyl methacrylate) (PMMA) dissolved. As a final step, the resin is dissolved with 365 nm (λ_2) light, leading to the detachment of the sample.

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6) Self-assembly of polycationic polymers with viruses for advanced biomaterials

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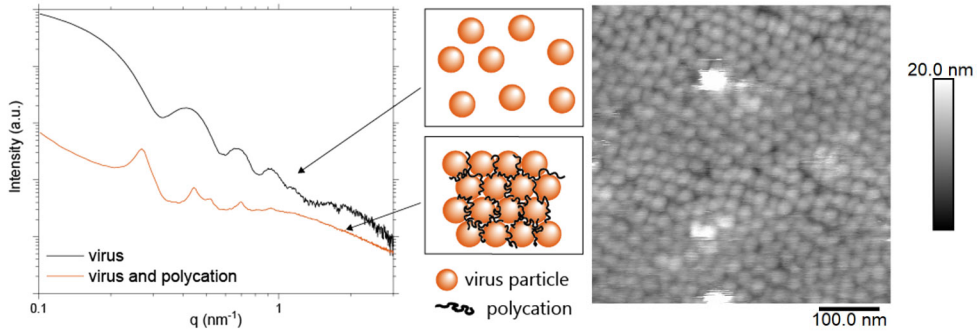
[1]Université de Fribourg, Switzerland. [2] Universität Bayreuth, Germany. [3]Umeå Universitet, Sweden.

Nature replicates viruses in a fast and precise manner. They can be used as nanoscale building blocks for applications in phage therapy, biotechnology and as energy material. [1] Polycationic polymer materials are known to interact with negatively charged viruses by adsorption. [2] However, the underlying colloidal interactions that can guide the design of advanced structural materials have not yet been studied in detail. [3] This works demonstrates the design of colloidal crystals triggered by chain-length-dependent polycation interaction with a virus. The results provide essential knowledge for the design of advanced materials for various applications.



Small-angle x-ray scattering (SAXS) with numerical data analysis shows the presence of core-shell protein nanoparticles with a dimension of around 30 nm (left figure), in agreement with results from dynamic light scattering (DLS). Upon addition of the polymer, a composition- and polymer length-dependent aggregation was discovered. SAXS demonstrated the arrangement of the viruses into geometrically organized colloidal crystals with lattice dimensions around 30 nm under certain conditions. These colloidal crystals could be imaged with atomic force microscopy (AFM) under aqueous environment (right figure). Further in-situ multi-angle DLS studies of the aggregation process show a fast gain in size from 30 nm to 1 µm.

The polymer-triggered assembly of the virus into micron-sized aggregates is driven by electrostatic interactions. The highly monodisperse virus dimensions further allowed the formation of colloidal crystals. The findings on composition-dependent structure and interaction from this study can guide the design of antiviral materials for applications including wastewater treatment. Moreover, the development of these systems into advanced nanopatterned bio-interfaces is also discussed. These interfaces may be additionally functionalised using surface or core-modified virus particles to trigger interactions with specific cells or for controlled drug release.

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7) Thermo-responsive liquid crystalline phases of cellulose nanocrystals with polymer brushes

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Smart hybrid materials with stimuli-responsiveness have been intensively researched for decades, which are normally composed of several elements, each contributing uniquely.Responsive polymers have been widely used because of their versatility and potential in biomedical and sensing applications. Cellulose nanocrystals (CNCs) have found to be an excellent candidate as a platform for smart hybrid systems, as they contribute to both optical and mechanical properties. They are also the most abundant polymer in nature and is considered as promising eco-friendly alternative for petroleum-based materials. CNCs are highly crystalline negatively charged nanorods and show the ability to form cholesteric liquid crystalline phases in aqueous dispersion. This highly ordered self-assembly ability has been particularly interesting for optical active systems, e.g., templating other materials such as plasmonic nanoparticles into complex structures[1].

In this study, thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) brush of varying length is attached onto CNC surface via atom transfer radical polymerization (ATRP)[2]. The attachment of PNIPAM brush is confirmed by Fourier-transform infrared spectroscopy (FTIR) and the grafted ratio is determined by X-ray photoelectron spectroscopy (XPS). Liquid crystalline phase nucleation, transition and re-equilibrium is systematically characterized by polarized light microscopy (PLM). Isotropic – cholesteric (tactoid) – nematic phase transition is observed from low to high concentration. The effect of polymer brush length on liquid crystalline phases are therefore studied, where cholesteric tactoid is observed with shorter polymer chain, whereas longer polymer chain tends to promote tactoid coalescence and even inhibits the tactoid formation. The thermo-responsiveness of the liquid crystalline phases are also explored when heated above the lower critical solution temperature (LCST) of PNIPAM. Immediate reversible disappearance and reappearance upon heating up and cooling down is observed, which is potentially useful for optical active biosensor and smart packaging applications.

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8) Catalytic Nanocompartments for complex cascade reactions in biomedicine

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Compartmentalization is fundamental in nature, where the spatial segregation of biochemical reactions within and between cells ensures optimal conditions for the regulation of cascade reactions. One of the most promising strategies to mimic nature compartmentalization is to combine synthetic nano-compartments with biomolecules in order to develop artificial organelles and to organize them into more complex architectures with cell mimetic functionality.
We present the exquisite spatiotemporal control of catalysis in polymeric nanosized compartments by means of a periodate sensitive linker that controls the opening of OmpF channels inserted in the compartment membrane.[1] Being able to precisely time confined reactions pave the way to controlling multifunctional cluster activity when specific substrates or products need to be made available at a specific site and with precise timing. In addition, the combinatorial and functional diversity of catalytic nanocompartments (CNCs) assembled into various supramolecular architectures can be exploited either in bulk[2]or on a surface,[3] whereby surface immobilization offers the advantage of highly controlled spatial organization. As an example, we developed CNC-functionalized DNA microarrays where individual reaction compartments are kept in close proximity by a distinct geometrical arrangement to promote effective communication (2). We demonstrate that polymer-based nano-compartment assemblies offer an ideal scaffold for the development of the next generation responsive and communicative soft-matter analytical devices for applications in catalysis and medicine.

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9) Tailoring mechanical properties of gelatin hydrogels via diverse crosslinking strategies

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Gelatin represents one of the most commonly used natural polymers for cell culture and tissue engineering, due to its intrinsic cell-adhesive and degradable nature.[1] However, pristine gelatin hydrogels formed below self-gelling temperature are usually not stable enough under physiological conditions. Additional cross-linking is therefore desirable, which can be achieved by introducing inter-polymer physical or/and chemical interactions. For this purpose, reactive functional groups can be conjugated to gelatin polymer backbones, thus giving rise to mechanically stable hydrogels for various biomedical applications. For instance, as the dominating gelatin hydrogel formulation in research, UV-curable gelatin methacryloyl (GelMA) hydrogels have been widely used for in vitro cell culture, 3D bioprinting, as well as in vivo drug/cell delivery.[2]

The ability to tailor the gelatin hydrogel mechanics with a diverse range of chemistries will broaden their applications. In this contribution, a few different ways for gelatin crosslinking will be discussed, as well as the corresponding mechanical properties of resultant gelatin hydrogels. Such crosslinking strategies include (1) bio-inspired enzymatic self-crosslinking, which offers tissue-adhesive properties and energy-dissipating network structures to the resultant hydrogels;[3,4] (2) host-guest supramolecular interactions, which enable chemical-functionalization-free stabilization of gelatin hydrogels, and provide injectable and self-healing hydrogel formulations for cell/drug delivery and in vivo tissue regeneration;[5] (3) solvent-exchange-induced hydrophobic interactions, which give rise to thermoplastic and stretchable gelatin hydrogels;[6] (4) thiol-ene "click" reaction, which results in fatigue-resistant matrix.

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10) Nuclear-targeted delivery of oligonucleotides exploiting peptide nano-assemblies

Shabnam Tarvirdipour[1,2], Michal Skowicki[1], Cora-Ann Schoenenberger[1], Larisa E Kapinos[3], Roderick YH Lim[3], Yaakov Benenson[2], Cornelia G. Palivan[1]

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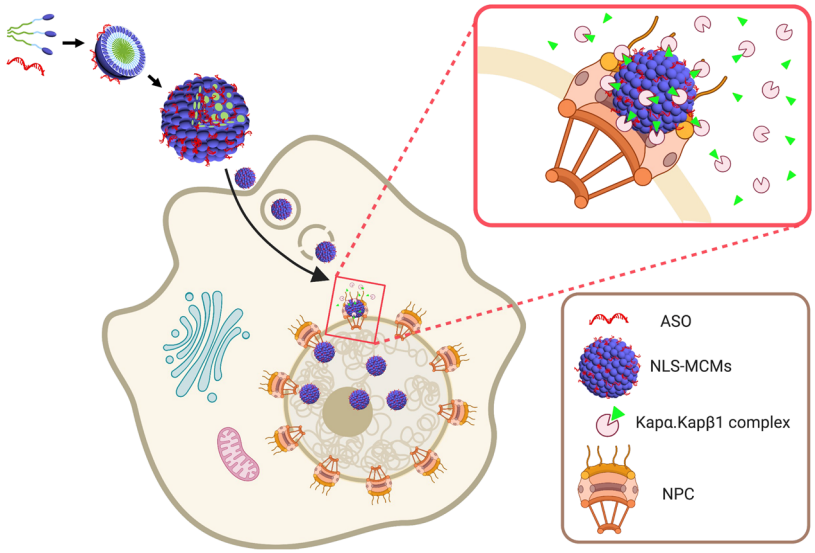
The delivery of nucleic acids as therapeutic agents has considerable potential in the treatment of many diseases. While viral delivery systems dominate in clinical applications, safety concerns led to the emergence of non-viral vectors. However, non-viral methods generally suffer from a low delivery efficiency. To sidestep this limitation, we developed a purely peptidic delivery system that is able to efficiently entrap and deliver antisense oligo nucleotide (ASO) into cells, in particular to the nucleus. For this purpose, we designed an amphiphilic peptide comprising an N-terminal KRKR sequence that functions as a nuclear localization signal (NLS) and a hydrophobic domain that promotes the self-assembly into micellar nanostructures [1].



Self-assembled multi-compartment micelles (MCMs) loaded with ASO, provided enhanced cellular uptake and nuclear translocation with no adverse effects on HeLa cell viability. Importantly, 86% BCL2 knockdown, an inhibitor of apoptosis that is overexpressed in more than half of cancers, was observed in MCF-7 cells treated with NLS-MCMs loaded with anti-BCL2 antisense oligonucleotides. Our data unravel the potential of this purely peptidic platform for the safe and efficient delivery of diverse genetic payloads to the nucleus.

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11) Unraveling nanostructure formation during simulated digestion of functional emulsions by *in situ* synchrotron SAXS

Rafael V. M. Freire[1], Linda Hong[1], Miroslav Peterek[2], Stéphane Canarelli[3], Serge Rezzi[3], and Stefan Salentinig[1]

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Functional food emulsions can help maintain and improve human health and lifestyle. The formation of lyotropic liquid crystalline (LLC) structures during lipid digestion can be explored to add functionality to food, boosting bioaccessibility of nutrients or influencing digestion kinects.[1] In particular, lipolysis products from monounsaturated triglycerides present interesting colloidal properties such as the self-assembly of pH-responsive structures, including LLC phases.[2] The oil from the Amazonian buriti fruit (*Mauritia flexuosa*) is rich in carotenoids, vitamin E and has a large amount of unsaturated fatty acids, known for their benefits on cardiometabolic health.

In this work, we design buriti oil-based emulsions and report its dynamic colloidal transformations during in vitro digestion using an innovative combination of multistep digestion model (oral, gastric, and intestinal steps) with *in situ* synchrotron Small angle X-ray scattering (SAXS). Additionally, cryogenic electron microscopy and dynamic light scattering are used to complement the investigation. The whey protein-stabilized buriti oil-in-water emulsion remains structured as emulsion droplets during oral and gastric digestion, and eventually transforms into LLC structures under compromised bile salt concentrations in the simulated intestinal digestion phase. The structure formation is found to be strongly pH- and bile salt-dependent and can be tailored with vitamin E supplementation in the oil. The colloidal digestion structures could maintain and even improve bioaccessibility of the hydrophobic nutrients.

These results can further guide the design of innovative food materials with a controlled rate of lipid digestion and absorption, with applications in newly designed delivery systems for bioactives and nutrients with improved bioaccessibility.

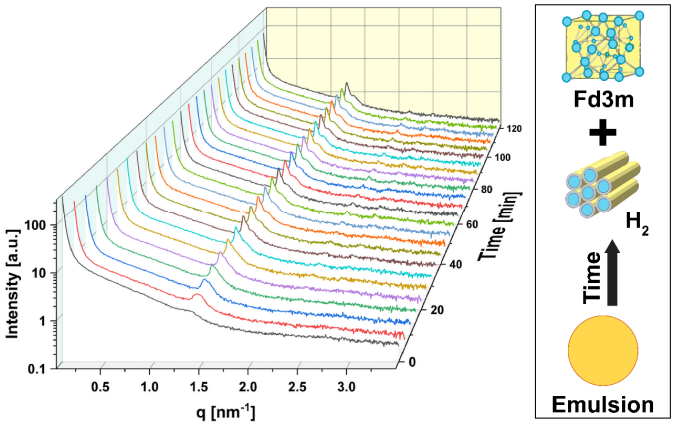

Fig. 1: Time-resolved *in situ* SAXS curves of simulated intestinal digestion of buriti oil emulsion and artistic representations of the observed structures.

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12) Charge-selectively permeable microcapsules

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Swiss Federal Institute of Technology in Lausanne

Microcapsules whose shells display a selective permeability are well-suited vessels for conducting cell studies or prolonged chemical reactions that require the selective exchange of certain reagents over a prolonged time. The selective exchange of reagents within microcapsules has thus far been limited to their size. Here, we introduce a new type of capsule possessing viscoelastic shells that display a charge-selective permeability. The capsules are composed of chelator-functionalized surfactants that have been crosslinked with appropriate ion clusters. We demonstrate that the charge-selective permeability of the capsule shell can be tuned with the choice of crosslinking ions. These capsules have the potential to be used, for example, for wastewater treatment, or as picoliter-sized reaction vessels to selectively conduct chemical reactions only within capsule cores.

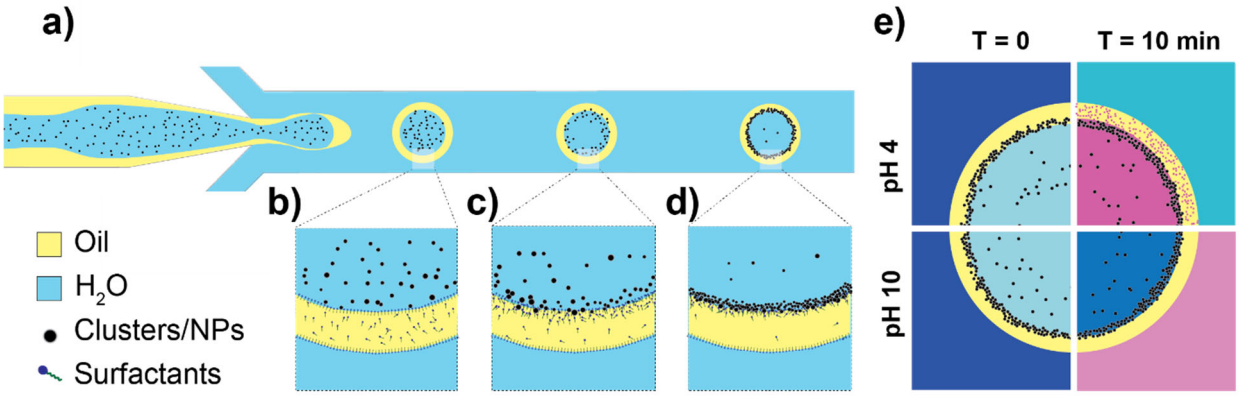

Figure 1. a) Schematic illustration of the assembly of viscoelastic capsules composed of the HOPO functionalized surfactant that is crosslinked by ion-Tris clusters. **b-d)** Water-oil-water double emulsions are stabilized with (b) HOPO functionalized surfactants that initially populate the interface. (c) The high affinity of HOPO towards metal ion-Tris clusters attracts clusters towards the interface to form (d) viscoelastic capsules that are functionalized with metal ion-Tris clusters. e) Schematic illustration of the charge-selective permeability of the resulting capsules. Under acidic conditions, capsules are permeable to negatively charged substances, such as Rhodamine B (RhB), whereas at basic pHs, capsules are permeable to positively charged substances, such as Methylene Blue (MB).

13) Bottom-up cell mimicry: ATP synthesis in giant polymersomes formed by microfluidics

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University of Basel

To investigate cellular mechanisms that require the cooperation of different membrane proteins, giant unilamellar vesicles (GUVs) made of amphiphilic block copolymers make an excellent cell mimic due to their similar size and increased stability over that of lipid vesicles. Microfluidic systems allow for the formation of a monodisperse population of GUVs at a rate of around 1 kHz with close to 100% encapsulation efficiency. For this study, we embed two different membrane proteins into the membrane of each GUV: NapA, a sodium-proton antiporter that functions to build and maintain a membrane potential, and ATP synthase, which generates ATP from ADP and free inorganic phosphate and is powered by the membrane potential. The formation of a contained cellular process system has far-reaching implications for the increased understanding of cell membranes and the cell as a whole.

14) Clusters of Hard-Soft Assembly for Bio-Applications

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Nano-objects can self-organize into complex architectures to create novel systems with emerging properties and functionalities in fields such as electronics, technology, and chemistry [1–3]. To achieve this, DNA hybridization between synthetic assemblies like polymersomes, nanoparticles, and micelles is crucial for developing interconnecting artificial organelles, favor cascade reactions between different catalytic compounds encapsulated/entrapped inside, and are capable to mimic cell signaling or interactions[4,5]. In this study, a new approach is proposed for developing a multifunctional hybrid system for specific bio-applications by investigating the self-organization of clusters between "hard" Janus nanoparticles (JNPs) and "soft" polymersomes. These polymer-based JNPs provide an asymmetric platform suited for directional interaction [6,7] with soft polymersomes. The hybridization of complementary ssDNA strands attached to each components links them into clusters. The soft polymersomes deform upon adhesion to the hard Janus nanoparticle surface but maintain their integrity, thanks to the inherent mechanical robustness of the block copolymer membrane. Furthermore, the integrity of the vesicular architecture of the polymersomes after assembly into JNP-polymersome clusters allows for encapsulating various kinds of functional cargo. Lastly, the biocompatibility of the clusters and their interactions with cell surfaces mediated by scavenger receptors were also investigated.

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15) Structurally Colored Silica Foams via Colloidal Templating

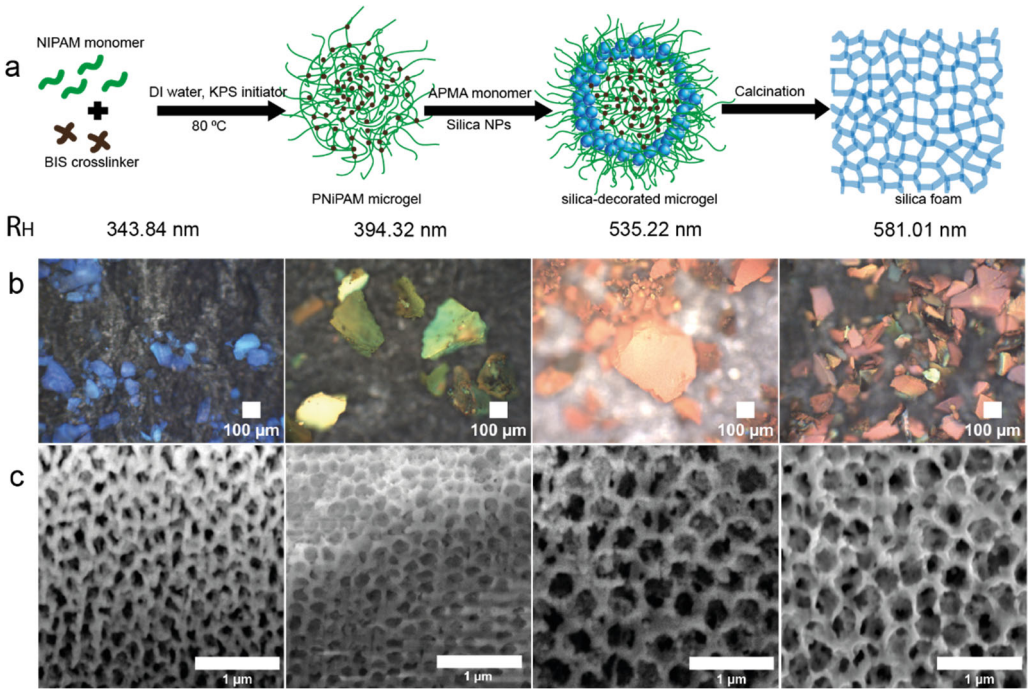
Kalpana Manne, Sofia Magkiriadou, Pavel Yazhgur, Ahmet F. Demirörs and Frank Scheffold

University of Fribourg, Department of Physics

Foams are widely used in various fields such as food, acoustics, and cosmetics, making them an important class of materials in chemistry. While some foams are colored using chemical pigments, nature offers another method of coloration through structural correlations of dielectric materials at the nanoscale. These so-called 'structural colors' are non-fading and more environmentally friendly than pigment-based colors. To mimic nature's structural coloration and take advantage of its benefits, researchers are exploring top-down and bottom-up approaches to create these structures.

In this study, we present a method of fabricating solid silica dry foams with structural colors using colloidal templating. Our approach involves densely packed microgel particles that are decorated with silica nanoparticles. By compressing and shrinking the microgel particles, we can tune their morphology, resulting in faceted particles with tetrahedral geometries that are favorable for their optical response potentially leading to bright colors. This faceting behavior sets microgels apart from hard-sphere particles, which cannot be compressed.

We obtain inverse structures by burning the organic polymer, leaving behind silica networks, as we have previously demonstrated. Here, we focus on the synthesis of structurally colored foams and their optical and structural characterization. The resulting foams exhibit brilliant structural colors that are tunable by varying the size and shape of the microgel particles. Our study offers insights into the creation of novel materials with structural colors using colloidal templating.



a) Illustration of silica foams fabrication from silica decorated microgels, with synthesis of microgels. b) Micrographs of colored silica foams in bright field,10x/0.25 NA . c) Corresponding cross-sectional scanning electron micrographs of the colored foams shows porous silica networks (bright region is silica and dark region is air) Color red-shifts with increase in the pore-size.

16) The use of fibroblast activation protein inhibitor as a targeting ligand for enhanced cellular uptake

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Despite progress in the development of anticancer therapies cancer remains leading cause of mortality. Modern chemotherapies still display numerous side effects due to their lack of specificity and systemic toxicity. Solutions offered by nanomedicine can contribute to development of more precise and effective therapies. Recently, fibroblastic element of tumor microenvironment received much attention as a target for treatment and diagnosis of different types of cancer [1]. In this study we present polymersomes functionalized with the inhibitor of fibroblast activation protein (FAPi) - overexpressed by activated fibroblasts of the tumor stroma (Fig. 1). Obtained FAPi-functinalized polymersomes potential nanocarriers to target fibroblastic component of tumor environment and find their application in the anti-cancer treatment.

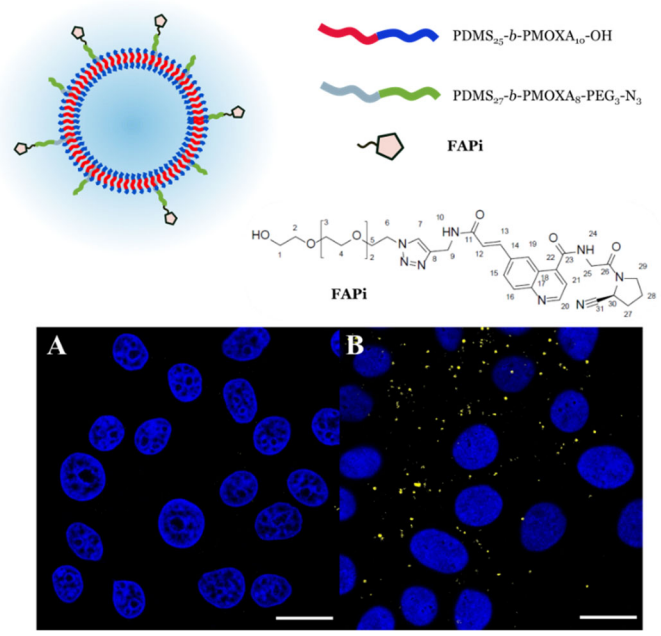

Fig. 1 Top: Schematic representation of bioconjugation of FAP inhibitor to diblock polymer (AB) based—, azide exposing, polymersomes and the chemical structure of FAPi [2]. **Bottom:** CLSM images of polymersome treated MCF-7 cells: A- unfonctionalized polymerosmes; B – polymerosmes functionalized with FAPi (5%). Images present merged fluorescence channels of polymersomes loaded with Atto 633 (yellow) and cell nuclei stained with Hoechst 33342 (blue). Scale bars = 20 μm.

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17) Investigating $MAPbBr_3$ Perovskite Solar Cells through Interfacial Passivation Using Ultrathin Polymeric Films

Parnian Ferdowsi, Ullrich Steiner, Michael Saliba

Soft Matter Physics, Adolphe Merkle Institute, University of Fribourg

Perovskite solar cells based on $MAPbBr_3$ received less attention due to their high bandgaps that are unsuited for high-performance solar cells. However, if realized, high open-circuit voltages (V_{OC}) offer considerable opportunities for different applications such as water splitting and the pathway to an all-perovskite multijunction device that urgently requires wide band gap perovskite with high V_{oc}s.
Thus, investigating the reasons why high voltage with adequate output power have not been achieved is an underexplored part in perovskite research.
Interfacial carrier recombination leads to reduced carrier lifetimes and voltage loss. To address this issue and to further improve the high Voc of methylammonium lead tri-bromide ($MAPbBr_3$) perovskite solar cells, interface passivation techniques are an important strategy. Here we demonstrate two ultrathin polymeric passivation layers consisting of PCBM and PMMA: PCBM mixture as well as PMMA that can effectively passivate defects at the perovskite/ ETL and perovskite/ HTL interfaces, respectively, where they significantly suppress interfacial recombination.
Crystallization and film-formation are key for high quality perovskite materials. Thus, perovskite crystallization was investigated with the established anti-solvent and the novel flash infrared annealing (FIRA) with and without passivation layers. This is the first demonstration of FIRA for $MAPbBr_3$ revealing altered film morphology and therefore a novel strategy to control the crystallization process (1-4).

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18) Investigation of Single-walled carbon nanotubes enriched hydrogels for ascorbic acid sensing and release monitoring

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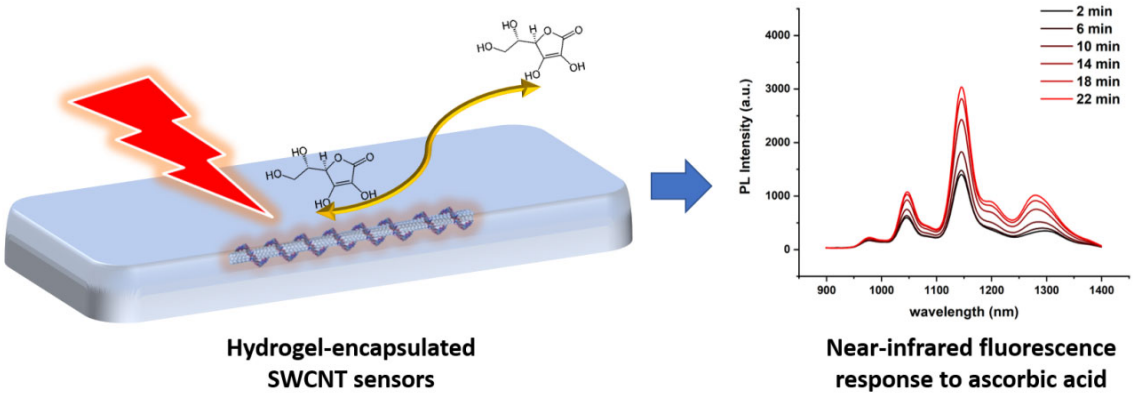
b. Konya Food and Agriculture University, Department of Food Engineering, 42080, Konya, Turkey
c. Henan Agricultural University, No.63, Nongye road, Zhengzhou, Henan, China

Single-walled carbon nanotubes (SWCNTs) have excellent optical properties for sensing applications. On excitation, semiconducting SWCNTs emit fluorescence that varies with the chirality and the environment of the nanotube. Because the near-infrared fluorescence emissions are minimally absorbed by biological tissue and biofluids, SWCNTs can be used for deep-tissue imaging and sensing. These applications, however, require SWCNT immobilization and encapsulation strategies that are stable and biocompatible.



Hydrogel-encapsulated SWCNT sensors | **Near-infrared fluorescence response to ascorbic acid**

Herein, we develop a hydrogel-encapsulated SWCNT sensor to study the release of ascorbic acid, a model agent for delivery applications. We examine the response of SWCNTs wrapped in $(GT)_{10}$, $(GT)_{20}$, $(GT)_{40}$, $(CCG)_4$, $(CCG)_8$ and $(AT)_{15}$ DNA sequences to ascorbic acid. The strongest response is observed for the $(GT)_{10}$ sequence. The $(GT)_{10}$-wrapped SWCNT sensors also show the greatest sensitivity to ascorbic acid concentrations over the range of 10 - 100 μM. We further compared the performance of the $(GT)_{10}$-wrapped SWCNT sensor in different hydrogels, including alginate, hyaluronic acid, and agarose matrices loaded with ascorbic acid. The agarose gels show the most promising performance, undergoing the largest intensity change on release of 100 μM ascorbic acid. Scanning electron microscopy (SEM) images of the agarose hydrogel loaded with and without the SWCNTs confirm no significant perturbation of this matrix on SWCNT encapsulation under the tested conditions. Finally, the encapsulated sensor was applied to monitor cyclic ascorbic acid loading and release. These results highlight the promising application of SWCNT hydrogels for the reversible optical monitoring of bioactive agents.

19) From interaction potentials to rheological properties of microgel particles

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University of Fribourg, Department of Physics, Chemin de Musée 3

Poly(N-isopropyl-acrylamide) (PNIPAM) microgel particles are thermoresponsive colloid-sized polymer systems whose properties have been widely investigated. Below their lower critical solution temperature (LCST), they are swollen, and as their temperature is increased, they expel water and shrink. To establish a relation between their internal structure, their interparticle potential and their rheological properties below the LCST, we developed a simple model that describes microgel particle interactions as coupled repulsive potentials coming from its different regions (core and shell). We extract information from static light scattering and dynamic light scattering measurements to account for the model's free parameters. Finally, using an optical tweezers setup, we measure the interparticle potential and attempt to connect it to the bulk rheological properties of microgel suspensions.

20) Disentangling kinetics from thermodynamics in heterogeneous colloidal systems

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Nucleation and growth (N&G) - the emergence of a new phase within an initially homogeneous one - is one of the most important physical phenomena by which gas-liquid, liquid-liquid and solid-liquid phase separation takes place. Accordingly, thermodynamics sets the asymptotic boundaries towards which the system must evolve, while kinetics tries to cope with it by imposing the transport rates at which phase separation is realized. In all heterogeneous colloidal systems observed in nature, the composition, shape, structure and ultimately physical properties result from the trade-off between thermodynamics and kinetics [1,2]. In this work we demonstrate, by carefully selecting colloidal systems and controlling phase separation in microfluidic devices, that it becomes possible to go beyond N&G, disentangling kinetics effects from thermodynamics in composition, structure and physical properties of the final system [3]. Using amyloid fibril and cellulose nanocrystal filamentous colloids for which the binodal curve defining the two-phase region in the phase diagram is given by two separate vertical lines, we extrude a solution set at one thermodynamic branch inside the other branch, realizing nematic or cholesteric droplets where the composition is set by thermodynamics, while the structure and morphology are defined by dynamic flow parameters (Fig. 1). We demonstrate that departing from the N&G paradigm unveils new physical phenomena, such as orders of magnitude shorter timescales, a wider phase diagram and internal cholesteric structures that are not observable via conventional LLPS. We also show that by co-dispersing plasmonic gold nanoparticles within colloidal liquid crystalline droplets, our approach enables on-demand fabrication of multicomponent heterogeneous liquid crystals, enhancing their potential, and introducing original fundamental and technological directions in multicomponent structured fluids.

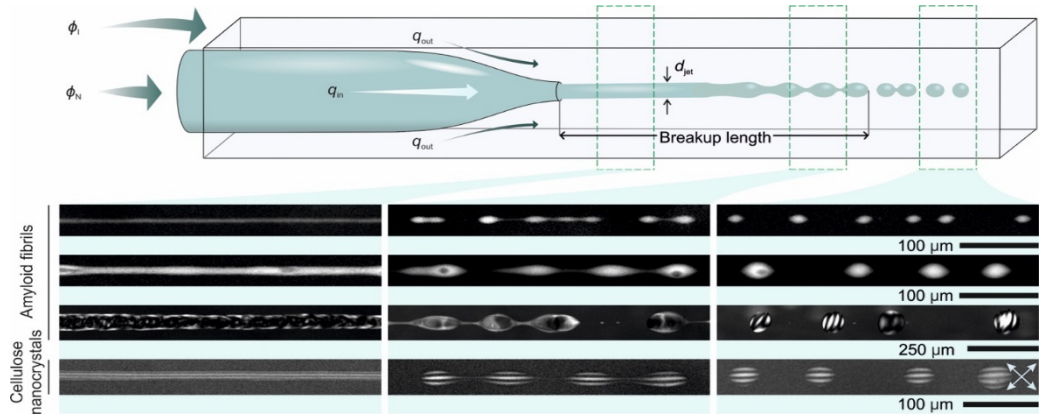

Fig. 1 Disentangling kinetics from thermodynamics effects by careful selection of a colloidal systems and controlling phase separation in microfluidic devices

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21) An *in silico* osmotic pressure approach allows to characterize pressure-area isotherms of lipid monolayers at low molecular areas

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[#]J.P. and A.P.S. contributed equally to this work and share first authorship.

Surface pressure-area isotherms of lipid monolayers at the air-water interface provide essential information about the structure and mechanical behaviour of lipid membranes. These curves can be readily obtained through Langmuir trough measurements [1] and, as such, have been collected for decades in the field of membrane biochemistry. However, it is still challenging to directly observe and understand nanoscopic features of monolayers through such experiments, and molecular dynamics (MD) simulations are generally used to provide a molecular view of such interfaces. In MD simulations, the surface pressure-area (Π-A) isotherms are generally computed using the Kirkwood-Irving formula, that relies on the evaluation of the pressure tensor. This approach, however, has intrinsic limitations when the molecular area in the monolayer is low (typically < 60 $Å^2$ per lipid). Recently, an alternative method to compute (Π-A) isotherms of surfactants, based on the calculation of the three-dimensional osmotic pressure via the implementation of semipermeable barriers was proposed [2].

In this work, we investigated the feasibility of this approach for long-chain surfactants such as phospholipids. We identified some discrepancies between the computed values and experimental results, and we proposed a semi-empirical correction based on the molecular structure of the surfactants at the monolayer interface [3]. To validate the potential of this new approach, we simulated several phosphatidylcholine and phosphatidylethanolamine lipids at various temperatures using all-atom and coarse-grained force fields, and we computed the corresponding surface (Π-A) isotherms. Our results show that the surface Π-A isotherms obtained using the new method are in very good agreement with experiments and far superior to the canonical pressure tensor-based method at low molecular areas. This corrected osmotic pressure method allows for the accurate characterization of molecular packing in monolayers in various physical phases. We also conclude that such a method could be helpful for future developments of computational molecular force fields.

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22) Surfaces forces on nano-porous materials

Michał Góra [1,2], Paula Navascués[1], Urs Schütz[1], Dirk Hegemann[1], Manfred Heuberger [1,2]

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Nano-porous materials are receiving increasing interest in materials science and related applications [1-3] as a result of their unique properties. The interfacial interaction of the porous materials with the environment is determined by the heterogeneous surface forces occurring on that materials surface, namely its effect on local fluid structure, solvation and confinement induced in presence of a second surface. Porosity creates inhomogeneity and increases the amount of internal surface, accessible through small openings, which are expected to gives rise to characteristic surface force kinetics. A systematic research of surface forces on nano-porous surfaces is original and provides a chance of revealing and understanding novel equilibrium and non-equilibrium processes that are unique.
In this work, we use the atomic force microscope and the extended Surface Force Apparatus (eSFA) in order to detect at different time- and lengths scales. The nano-porous model with nano-pores was fabricated using plasma-enhanced chemical vapor deposition, resulting in highly cross-linked plasma polymer films (PPFs) with pore dimensions below 10 nm in diameter [4]. First eSFA experiments with such films in air suggests a heterogeneous charge distribution on the PPF surface. The eSFA surface force measurements in water shows time-dependent evolution of the free Gibbs energy of the fluid, which is hypothesized to relate to a dipolar orientation of water molecules on such porous films at the nanometer scale. Furthermore, model surfaces with larger pores were fabricated using focused ion beam technique on muscovite mica, resulting in adjustable pore dimensions in range of few hundred nanometers in diameter. Measurement of surface forces on such various sized nano-porous models can be used to study novel effects occurring in confined fluids.

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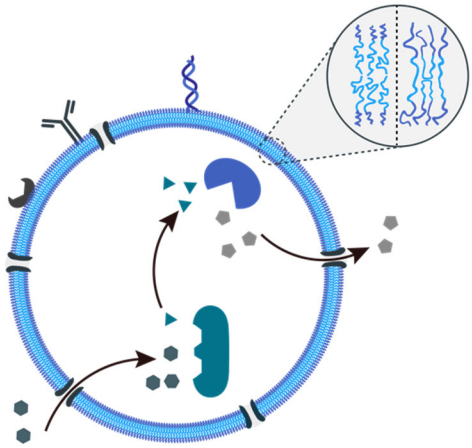
23) Microfluidic Polymer GUVs – a Versatile Toolbox to Study Biological Processes

Lukas Heuberger, Daela Milinkovic, and Cornelia G. Palivan

Department of Chemistry, University of Basel

Giant unilamellar vesicles (GUVs) are micrometer-sized vesicles that can be applied as synthetic reaction vessels and artificial cell models.[1] GUVs are usually made from amphiphilic molecules composed of hydrophilic and hydrophobic moieties, e.g., lipids, peptides, or polymers. Amphiphilic block copolymers can be synthesized in a variety of compositions, block ratios, and functionalizations and have higher stability than their lipidic counterparts. By using double emulsion microfluidics, monodisperse GUVs can be prepared.[2] The modularity and design of this system facilitate the formation of monodisperse GUVs with controllable internal composition, polymer membrane, and membrane functionalization.[3] Through the use of high-throughput methods, GUVs can be used for screening assays. By adjusting the internal composition, enzyme cascades, smaller vesicles, organelles, and whole living organisms can be encapsulated in GUVs.

In the presented work, GUVs are prepared using the diblock copolymer PDMS-b-PMOXA. Thanks to their cell-like size, GUVs can be studied using flow cytometry. Using these techniques, tens of thousands of GUVs can be analyzed, making them a practical alternative to W/O/W double emulsions. This allows their application as microreactors or cellular models. When their otherwise impermeable membranes are permeabilized, GUVs can be used as incubation chambers for bacterial growth or as enzymatic reaction compartments. This approach highlights the versatility of double-emulsion templated polymer GUVs for the study of compartmentalized biological systems and deepens insight into fundamental biological processes.



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