# 17th Zsigmondy Colloquium 2022

of the German Colloid Society

From interactions to structures in colloids

*Aachen, April 6, 11:30 am – April 8, 01:30 pm, 2022*

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|---|---|
| *Topics:*<br>• chemistry and physics of functional colloids<br>• phase behavior and dense systems<br>• formulations<br>• theory and simulations | Abstract Deadline:<br>*February 27th*<br>Registration Deadline:<br>*March 3rd*<br>More Information on our website:<br>**zsigmondy22.pc.rwth-aachen.de** |
| *Registration fee:*<br>PostDoc/Professor: 160.00 €<br>Students/PhD Students: 100.00 € | The registration fee includes one lunch, coffee breaks, the conference dinner and one guided tour through Aachen. |

## Confirmed Speakers

- Prof. Mathias Karg - *Chair of Colloids and Nanooptics at the Heinrich-Heine-University, Düsseldorf*
- Prof. Janne-Mieke Meijer - *Assistant Professor in the Theory of Polymers and Soft Matter group in the Applied Physics department of Eindhoven University of Technology (TU/e)*
- Dr. Yuri Gerelli - *Tenure track researcher at the Department of Life and Environmental Sciences of the Polytechnic University of Marche (Ancona, Italy)*
- Dr. Thomas Mosciatti - *Polyurethanes Product R&D PU Global Development Center, Correggio DOW Italia*

**Location:** RWTH Aachen University, Templergraben 57, 52062 Aachen, Germany

# Phase transition behaviour in single solid-supported lipid bilayer

Yuri Gerelli

*Marche Polytechnic University, Molecular Biophysics group, Ancona, Italy*

Concepts derived from the physics and chemistry of colloids can be applied to complex systems as biological membranes to understand lipid supramolecular structure, self-assembly, interactions and phase behaviour.

Solid-supported lipid bilayers (SLBs) are widely used tools in biological- and technological-oriented studies, for the investigation of interactions and molecular processes involved in cell functioning, diseases and for sensing applications. Coexistence of ordered and disordered domains, structural and dynamical coupling between leaflets and the structural responses to changes in the environmental parameters such as temperature, are of fundamental interests in all these scientific fields. Moreover, SLBs are one of the prototypes of natural self- assembling systems.

We applied time- and temperature-resolved neutron reflectometry for the real-time characterization of the structural changes taking place across phase transitions in SLBs. This new method allowed to determine the presence of an isothermal phase transition, characterized by a symmetrical rearrangement of lipids molecules in both bilayer leaflets, followed by a thermotropic phase transition characterized by an independent melting of the two leaflets. Contrary to recent results on similar samples by atomic-force microscopy we demonstrate that the presence of a substrate equally increases the enthalpy of melting for both SLB leaflets with respect to that reported for free standing bilayers. These results are of extreme importance for the further understanding of cooperative structural dynamics in SLBs and for their use in biophysical and biological studies, as for example, for the investigation of thermally activated processes as the lipid flip-flop.

Further readings

Y. Gerelli, ***PRL*** 122, 248101, **2019**

# Shape Matters: Visualizing the Self-Assembly of Anisotropic Colloids

Janne-Mieke Meijer[1]

[1] Eindhoven University of Technology, Department of Applied Physics, Einhoven Netherlands

The recent availability of rationally designed colloidal building blocks opens up new ways to study complex materials. At the same time, these colloids are of interest as the building blocks for the preparation of the next generation of functional materials with specific mechanical, optical or magnetic properties.

However, a main challenge in colloid physics remains understanding the relationship between the colloidal building block properties and the order/disorder in self-assembled structures.

In this talk I will show how studying colloidal crystal materials with both x-ray scattering techniques and quantitative microscopy is uniquely powerful for visualizing structural defects on a single-particle level. I will show how small shape changes from a sphere to a cube or a bowl, leads to marked differences in phase behaviour, such as the appearance of plastic crystals, in which particles rotate on their lattice sites, and other unique dense packings. I will further address the influence of directed self-assembly methods such as solvent evaporation, critical Casimir forces and electric fields on the crystal and defect structures of these anisotropic colloids.

# Tailoring thermal conductivity in polyurethanes foams: challenges and perspectives

**Thomas Mosciatti[1]**, Ernesto di Maio[2], Cosimo Brondi[2], Maria Rosaria di Caprio[2]

[1] *Dow Polyurethanes R&D*, PU Global Development Center, Dow Italia srl, Correggio, RE, Italy,
[2] *Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale*, University of Naples Federico II, P.leTecchio 80, 80125 Naples, Italy

Polyurethane foams are the leading insulation material in many applications: from appliances to buildings, from refrigerated transport to pipelines, they play a pivotal role in reducing energy dissipation in different environments, saving millions of eq. MT of $CO_2$ each year. Albeit their wide diffusion, fundamentals of polyurethane foams, such as nucleation, growth, expansion, curing and their effect on the final foam morphology, are still not completely understood. Moreover, polyurethanes foams are produced by mixing two components, one of which is usually a formulation of different chemicals, with a blowing agent. The intricate interactions among components during the reaction, which occurs while the mixture is expanding and changing viscosity, are difficult to be disentangled and accounted singularly for their contribution.

Tailoring the final foam morphology is the main way to impart desired characteristics, such as the foam thermal conductivity, a parameter of great importance in insulation science, and strictly correlated to the foam cell size.[1]

On this regard, in collaboration with University of Naples, we have developed a new optical setup to observe the foam during the different stages. In particular we have focused on the effect of different chemical and physical blowing agents, and on the outcome of adding nucleation air, a common industrial technique.[2] For the first time we have shown how the bubbles collapse by different mechanisms depending on the introduced external air in the system. One of this mechanism is the Ostwald Ripening (OR) and is the main process that reduces bubble density during foam expansion. We have proposed different formulations, where, dedicated fluorinated additives, can be used to reduce the OR.[3] The final result of the use of such OR inhibitors are foams with reduced average cell size and improved insulation properties.[4]

The approach we have implemented, however, can only bring small improvements in the insulation properties. In order to achieve larger enhancements, new paradigms need to be pursued. Dow has proposed in collaboration with University of Naples and CANNON AFROS SPA a novel process to obtain microcellular foams at macroscopic scales.[5] This process is based on the innovative concept of “chasing the synthesis reaction with the pressure”.[6] Such extreme foam morphology can reduce the thermal conductivity of more than 30% with respect to the current state of the art materials. This proof of concept is the first step towards a new journey, yet to be explored.

*References*

1. Smits, G. F., Effect of Cellsize Reduction on Polyurethane Foam Physical Properties. *Journal of Thermal Insulation and Building Envelopes* **1994,** *17* (4), 309-329.
2. Brondi, C.; Di Maio, E.; Bertucelli, L.; Parenti, V.; Mosciatti, T., Competing bubble formation mechanisms in rigid polyurethane foaming. *Polymer* **2021,** *228*, 123877.
3. Brondi, C.; Maio, E. D.; Bertucelli, L.; Parenti, V.; Mosciatti, T., The effect of organofluorine additives on the morphology, thermal conductivity and mechanical properties of rigid polyurethane and polyisocyanurate foams. *Journal of Cellular Plastics* **2022,** *58* (1), 59-102.
4. Kramer, T. M. H. Rigid polyurethane foam made with a hydrocarbon blowing agent and 1,1,1,4,4,4-hexafluorobut-2-ene. WO2021045887A1, 2020.

5. Parenti, V., Cavalca, Sara , Mosciatti, Thomas , Di Maio, Ernesto, Di Caprio, Maria Rosaria , Brondi, Cosimo , Iannace, Salvatore Methods for Producing Polyurethane Foams. US20200109249A1, 2020.

6. Brondi, C.; Di Caprio, M. R.; Scherillo, G.; Di Maio, E.; Mosciatti, T.; Cavalca, S.; Parenti, V.; Corti, M.; Iannace, S., Thermosetting polyurethane foams by physical blowing agents: Chasing the synthesis reaction with the pressure. *The Journal of Supercritical Fluids* **2019,** *154*, 104630.

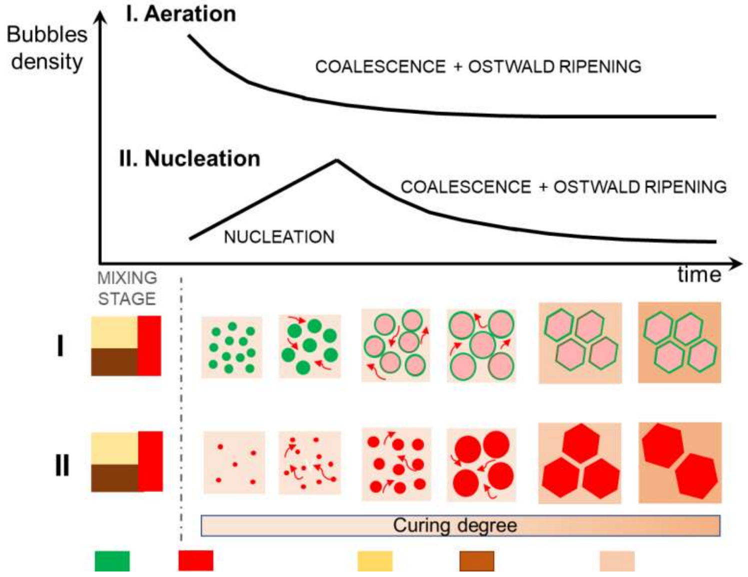

**Figure 1.** Bubble density in a polyurethane foam in formation: I. with external nucleation air, II. Without nucleation air. On the bottom a visual representation of the different stages is reported. Adapted from [2]

**Wednesday, 06.04.2022**

| Time | Name | Title |
|---|---|---|
| 11:00-12:00 | *Registration* | |
| 12:00-12:10 | *Welcome* | |
| **Chair** | **Max Hohenschutz** | |
| 12:10-13:10 | Mathias Karg | |
| 13:10-13:25 | Selim Basaran | Plasmonic Stimulation of Gold Nanorods for the Control of Living Materials |
| 13:25-13:40 | Flore A. F. Mees | Tuning the Magnetic Properties of Hematite Nanospindles |
| 13:40-14:10 | *Break* | |
| **Chair** | **Lukas Zeininger** | |
| 14:10-14:30 | Johanna R. Bruckner | Lyotropic Liquid Crystal Phase Behavior of High Molar Mass Reverse Poloxamers and their Use as Structure-Directing Agents |
| 14:30-14:45 | Johannes Menath | Defined core-shell particles as the key to complex interfacial self-assembly |
| 14:45-15:00 | Friederike Gräbitz-Bräuer | Structure and stability of DOPG model membranes in the presence of the saponin aescin |
| 15:00-15:15 | Suna Azhdari | Block Copolymers in 3D Confinement: Janus Nano Cups |
| 15:15-15:45 | *Break* | |
| **Chair** | **Mathias Karg** | |
| 15:45-16:00 | Max Hohenschutz | Chaotropic nano-ion binding as a gelation motif in cellulose ether solutions |
| 16:00-16:15 | Ahmet F. Demirörs | 3D Printing of Photonic Colloidal Glasses into Objects with Isotropic Structural Color |
| 16:15-16:30 | Martin Reifarth | A Spiropyrane-based dual pH- and Photoswitchable Surfactant for the Targeted Manipulation of Emulsions and Other Colloids |
| 16:30-16:45 | Simon Schog | From Single Microgels to Dense Microgel Layers – Investigation by Atomic Force Microscopy |
| 16:45-17:00 | *Break* | |
| 17:00-19:00 | *Poster Session* | |

**Thursday, 07.04.2022**

| Time | Name | Title |
|---|---|---|
| **Chair** | **Janne-Mieke Meijer** | |
| 08:30-09:30 | Yuri Gerelli | Phase transition behaviour in single solid-supported lipid bilayer |
| 09:30-09:45 | Santanu Maiti | Interface Driven Atomically Oriented 2D Assembly of Colloidal Gold Nanodisks Leads to Tunable Plasmonic Resonance |
| 9:45-10:05 | Andrea Scotti | Phase behavior of super soft spheres in two- and three dimensions |
| 10:05-10:35 | *Break* | |
| **Chair** | **Martin Reifarth** | |
| 10:35-10:50 | Quirin Prasser | Modification of Interfacial Block Copolymer Structures: Electrochemical Switching of Interfacial Tension and Interfacial Viscoelasticity |

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|---|---|---|
| 10:50-11:05 | Ekaterina Buvalaia | Structure and dynamics of polyelectrolytes in water solution |
| 11:05-11:20 | Amit Kumar | Optimization and fabrication of silica-coated nanoemulsion as reservoir for essential oils |
| 11:20-11:35 | Bahar Rouhvand | Surface topography quantification of DNA-functionalized colloids via super resolution microscopy |
| 11:35-13:00 | *Lunch* | |
| **Chair** | **Stefanie Schneider** | |
| 13:00-13:15 | Tom Höfken | A core-shell model describing the deformation behavior of microgels in crowded environment |
| 13:15-13:30 | Esther E. Jaekel | All-natural Pickering emulsion gels for high-fidelity direct ink-writing |
| 13:30-13:45 | Kevin Gräff | pH dependent Foam Film Properties of β-lactoglobulin Foams in comparison to Silica Sphere stabilized Foam Films |
| 13:45-14:00 | Tomáš Omasta | Self-Assembly of Sugar Surfactants in Deep Eutectic Solvents and Their Solubilization of Terpenoids |
| 14:00-14:30 | *Break* | |
| **Chair** | **Johanna Bruckner** | |
| 14:30-14:50 | Janne-Mieke Meijer | Shape Matters: Visualizing the Self-Assembly of Anisotropic Colloids |
| 14:50-15:05 | Judith Elizabeth Houston | Method to simultaneously probe the bulk modulus and structure of soft compressible objects using small-angle neutron scattering with contrast variation |
| 15:20-15:50 | Fabian Kollmann | Building mechanism and controlled synthesis of eumelanin particles |
| 15:50-16:20 | *Break* | |
| **Chair** | **Jerome Crassous** | |
| 16:20-16:35 | Binyu Zhao | Elasticity vs. capillarity: How soft is a substrate soft? |
| 16:35-16:50 | Meriem Saadli | Hybrid soft magnetic micro-actuators with thermo-programmable response to external magnetic field |
| 17:00-18:30 | *Social Event* | |
| 18:55-21:30 | *Conference Dinner* | |

**Friday, 08.04.2022**

| Time | Name | Title |
|---|---|---|
| **Chair** | **Dominik Wöll** | |
| 08:30-08:50 | Thomas Mosciatti | Tailoring thermal conductivity in polyurethanes foams: challenges and perspectives |
| 08:50-09:10 | Lukas Zeininger | Janus emulsions as adaptive material platform for the transduction of (bio-)chemical information |
| 09:10-09:25 | Peter Vogel | Charging of dielectric surfaces in contact with aqueous electrolyte – the influence of CO2 |
| 09:25-09:40 | Thomas Witzmann | Repulsive interactions of eco-corona covered microplastic particles quantitatively follow modelling of polymer brushes |
| 09:40-09:55 | Mark Vis | Effect of polymer chain stiffness on depletion layers in colloid–polymer mixtures |

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|---|---|---|
| 09:55-10:25 | *Break* |  |
| **Chair** | **Judith Houston** |  |
| 10:25-10:40 | Andreas M. Stadler | Effect of Red Blood Cell Shape Changes on Haemoglobin Interactions and Dynamics: A Neutron Scattering Study |
| 10:40-10:55 | Philipp Menold | Experimental Evidence of a Transition from a Sponge-Like to a Foam-Like Nanostructure in Water-Rich L3 Phases |
| 10:55-11:10 | Stephan Müssig | Supraparticles as identification taggants with spectral magnetic readout |
| 11:10-11:25 | Robert F. Schmidt | Phase Behaviour of a Biocompatible Microemulsion based on Tween 20,Ethylhexylglycerin and Isopropyl Palmitate |
| 11:25-12:05 | *Poster Prize* |  |
| 12:05-12:15 | *Closing Remarks* |  |

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## Talks Abstracts

# Plasmonic Stimulation of Gold Nanorods for the Control of Living Materials

Selim Basaran[1], Sourik Dey[1], Shardul Bhusari[1], Aránzazu del Campo[1], Shrikrishnan Sankaran[1], Tobias Kraus[1]

[1] INM – Leibniz Institute for New Materials, Saarbrücken, Germany

Composites of living cells in polymer gel matrices are called “Living Materials”. They are useful for the controlled release of drugs that are secreted by the cells while protecting them and their environment. Here, we establish optical control of drug production by introducing gold nanorod composites (GNC) as cores inside Living Materials shells that contain engineered thermoresponsive *Escherichia coli* bacteria. Incident near-infrared light is absorbed by the GNC core, which generates heat that diffuses to shell layer and activates the thermoresponsive bacteria, for example inducing the production of Green Fluorescence Proteins (GFP) (see illustration below). Requirements for this enhanced Living Materials include homogenous GNC distribution and the thermal stability of GNC.

In this contribution, we will introduce the colloidal and physico-chemical properties of the gold nanorods and their composites. The colloidal stability of the GNC was investigated by UV-VIS spectroscopy and cryo-TEM. The photothermal conversion efficiency (PCE) of the Living Material was then determined by Roper´s Method [1]. Heating from an initial 22°C to 45 °C was induced by illumination. Heating rates were analyzed as a function of optical power density and the concentration of the Gold Nanorods in the core layer. Thermography on the shell layer surface indicated the temperature distribution on the surface of the material sample. Finally, the GFP production with and without light stimulation was observed by fluorescence microscopy.

The goal of this project is to develop stimuli-responsive Living Therapeutic Materials, that can be used in biomedical applications and supplement existing schemes for drug delivery (oral, injection, nasal, ocular). The concept profits from the wide range of engineered bacteria that can provide different drugs. The optical stimulus discussed here can be combined with other stimuli.

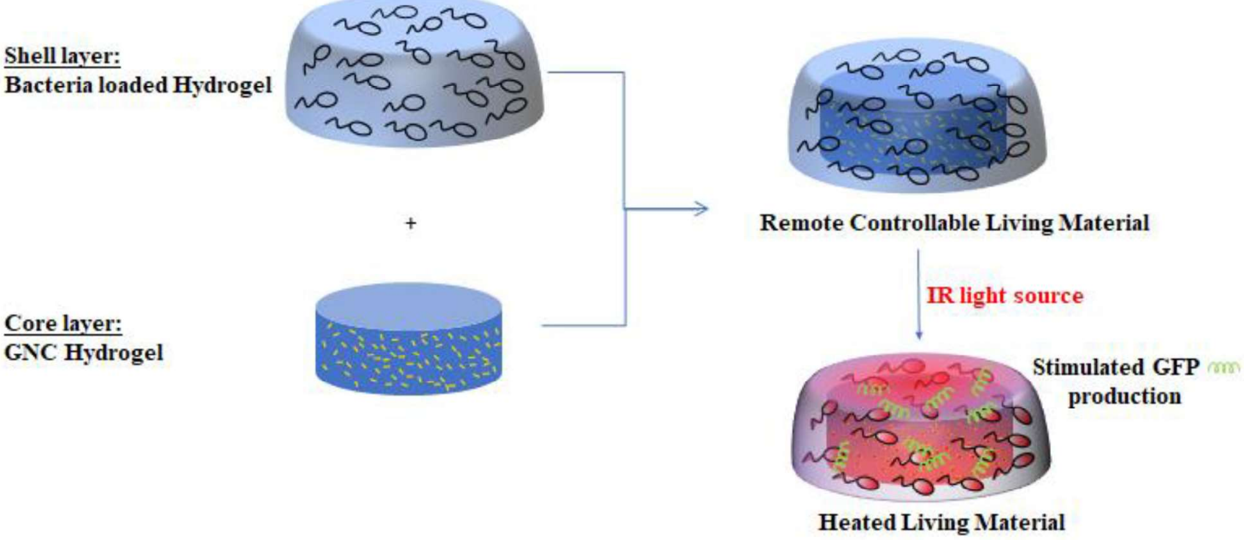

**Figure 1.** Schematic depiction of the GNC core-shell construct. The shell layer includes bacteria which is externally stimulated to produce GFP.

[1] D.K. Roper, W. Ahn, M. Hoepfner, Microscale Heat Transfer Transduced by Surface Plasmon Resonant Gold Nanoparticles, The Journal of Physical Chemistry C 111 (2007) 3636-3641.

# Tuning the Magnetic Properties of Hematite Nanospindles

Flore A. F. Mees[1], David Patrun[1], Dominika Zákutná[2] and Sabrina Disch[1]

[1] Universität zu Köln, Department of Physical Chemistry, Cologne, Germany
[2] Charles University, Department of Inorganic Chemistry, Prague, Czech Republic

Hematite nanospindles receive great attention due to their uncommon orientation behavior towards magnetic fields. In contrast to most elongated magnetic nanoparticles that are dominated by shape anisotropy, weakly ferromagnetic hematite nanospindles bear a strong magnetocrystalline anisotropy that drives the alignment of their long axis perpendicular to an applied magnetic field [1-3]. This leads to interesting behavior in static and dynamic magnetic fields [4-6] and makes them relevant for technological applications such as nanoprobes, sensors, active matter, or directional anisotropic materials [7,8]. To further tune their magnetic properties and the associated orientation behavior, we follow the approach to structurally convert hematite nanospindles into a magnetic core-shell morphology.

In this contribution we will present our latest results on the formation of a ferrimagnetic shell surrounding hematite nanospindles. The preparation is based on the seeded growth of synthesized nanospindles with systematically varying amounts of iron oxide. The formation of an iron oxide coating is confirmed by a combination of transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), Mössbauer spectroscopy and field- and temperature dependent magnetization measurements. Mössbauer spectroscopy further reveals a complex magnetic morphology of the coated spindles. The magnetically composite structure is in line with exchange interactions observed by magnetization measurements.

The coexistence of the two different magnetic materials and the corresponding interface promises tunable magnetic properties of the nanospindles, that will be further exploited towards directionally anisotropic materials [9].

[1] H. M. Lu, X. K. Meng et al., J. Phys. Chem. C, 114 (2010), p. 21291-21295.
[2] M. Reufer, P. Schurtenberger et al., J. Phys. Chem. B, 114 (2010), p. 4763-4769.
[3] C. Märkert, J. Wagner et al., J. Appl. Crystallogr., 44 (2011), p. 441-447.
[4] D. Zákutná, S. Disch et al., Nanoscale, 11 (2019), p. 7149.
[5] C. Glinka, S. Disch et al., J. Appl. Crystallogr., 53 (2020), p. 598-604.
[6] D. Honecker, S. Disch et al., ChemRxiv, preprint, http://dx.doi.org/10.26434/chemrxiv-2022-c0hh4, (2022).
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[9] The authors acknowledge funding from the DFG (DI 1788/2-1) and the UoC Key Profile Area Quantum Matter and Materials (QM$^2$).

# Lyotropic Liquid Crystal Phase Behavior of High Molar Mass Reverse Poloxamers and their Use as Structure-Directing Agents

Charlotte Vogler[1], Selina Itzigehl[2], Stefan Naumann[1], Johanna R. Bruckner[2]

[1] Institute of Polymer Chemistry, University of Stuttgart, Stuttgart, Germany
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Poloxamers, also known as “Pluronics”, are amphiphilic block copolymers composed of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) with the generic structure $PEO_{m/2}PPO_{n}PEO_{m/2}$ (Figure 1, top). Due to their non-toxicity and their surface-active properties, these polymers find broad use as industrial surfactants, as additives for cosmetics or pharmaceutics and as structure directing agents for the production of mesoporous materials. Unsurprisingly, they have been subject to many fundamental scientific studies, e.g. concerning their micellization or lyotropic liquid crystal (LLC) phase behavior.

In contrast, little is known about the LLC properties and potential applications of their counterpart, the Reverse Poloxamers $PPO_{n/2}PEO_{m}PPO_{n/2}$. To close this knowledge gap, we synthesized Reverse Poloxamers, with systematically varied block lengths of $n/2 = 32 – 278$ and $m = 90 – 454$, using a recently developed, metal-free polymerization approach [1]. By screening numerous Reverse Poloxamers, we determine the hydrophilic to lipophilic balance range in which LLC phases form and investigate them by polarizing optical microscopy, differential scanning calorimetry and small-angle X-ray scattering. Compared to the few commercially available Reverse Poloxamers [2, 3], we find that our custom-made versions with high-molar masses form a much broader variety of different LLC phases with extraordinary temperature stability (Figure 1, bottom), which makes them excellent candidates for various applications. We verify the latter by subjecting the Reverse Poloxamers to the true liquid crystal templating process, producing ordered mesoporous silica materials with regular structure and narrow pore size distributions. Most impressingly, the accessible pore diameters range from approximately 5 to 20 nm, which has been unprecedented so far with the applied process [4].

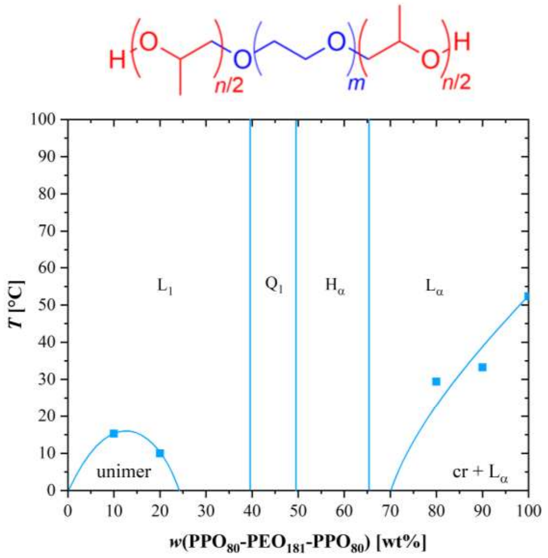

**Figure 1.** Generic structure of Reverse Poloxamers (top) and phase diagram of a Reverse Poloxamer with water (bottom).

[1] C. Vogler, S. Naumann, RSC Adv. 10 (2020), 43389.
[2] K. Mortensen, W. Brown, E. Jørgensen, Macromolecules 27 (1994), 5654.
[3] G. D’Errico, L. Paduano, A. Khan, J. Colloid Interface Sci. 2 (2004), 379.
[4] C. Vogler, S. Naumann, J. R. Bruckner, submitted (2022).
[5] Financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 358283783 – SFB 1333 is gratefully acknowledged. This project is supported by the Ministry Of Science, Research and the Arts Baden-Württemberg.

# Defined core-shell particles as the key to complex interfacial self-assembly

Johannes Menath[1], Jack Eatson[2], Robert Brilmayer[3], Annette Andrieu-Brunsen[3], Martin Buzza[2], and Nicolas Vogel[1]

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[2] University of Hull, Department of Physics and Mathematics, Hull, United Kingdom
[3] Technische Universität Darmstadt, Macromolecular Chemistry, Darmstadt, Germany

Self-assembly of colloidal particles can yield defined surface patterns over macroscopic areas. However, the prevalence of hexagonal symmetries limits the structural versatility of self-assembling monolayers. In 1998 E. A. Jagla computationally modelled core-shell particles with two interaction length-scales and predicted the formation of complex minimum energy configurations [1]. Despite the elegance of this approach, its experimental realization has remained largely elusive. Here, we use iniferter-type controlled radical polymerization to create core-shell particles consisting of a silica core surface-functionalized with a non-crosslinked polymer shell (figure 1a) [2]. Upon interfacial compression, the resulting core-shell particles arrange in well-defined dimer, trimer and tetramer lattices before transitioning into complex chain and cluster phases. The experimental phase behavior is accurately reproduced by Monte-Carlo simulations and minimum energy calculations, suggesting that the interfacial assembly interacts via a pair-wise additive Jagla-type potential (figure 1b). The possibility to control the interaction potential via the interfacial morphology provides a framework to realize structural features with unprecedented complexity from a simple, one-component system [3].

[1] E. A. Jagla, Phase behavior of a system of particles with core collapse, Phys. Rev. E. Stat. Phys. Plasmas Fluids Relat. Interdiscip, Topics 58, (1998), p. 1478–1486.
[2] J. Menath, J. Eatson, R. Brilmayer, A. Andrieu-Brunsen, D. M. A. Buzza, and N. Vogel, Defined core–shell particles as the key to complex interfacial self-assembly, PNAS, 118, (2021), p. 1-10
[3] The authors acknowledge funding from the DFG under Grant VO1824/6-2, the Horizon 2020 research and innovation program under Grant Agreement 861950, Project POSEIDON. Tobias Salbaum is acknowledged for help with iniferter silane synthesis, Marcel Rey for helpful discussions, Salvatore Chiera for help with infrared spectra measurements, and Katrin Städtke for help with thermogravimetric analysis.

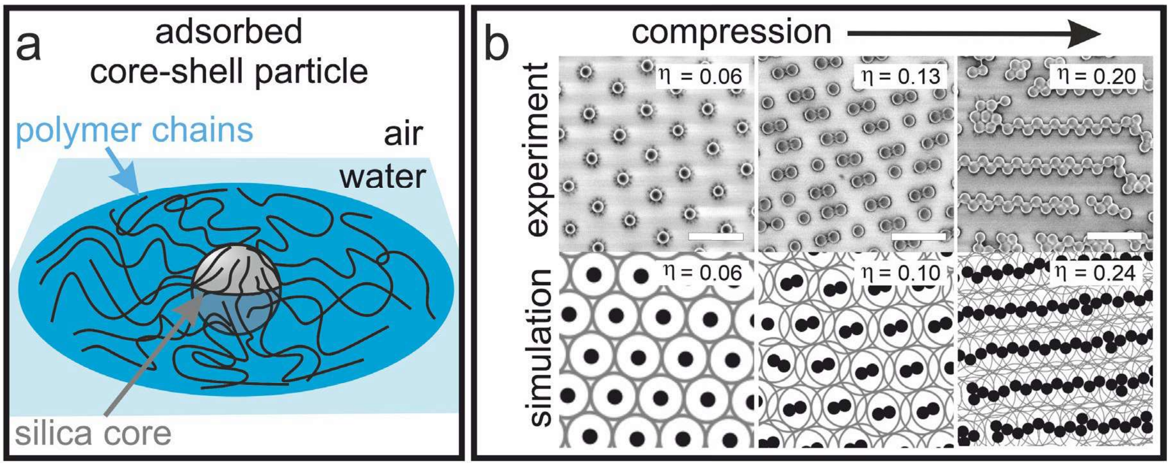

**Figure 1.** Particle morphology and phase behavior. a) Core-shell particle at the air/water interface. b) Scanning electron micrographs of the particle lattice upon interfacial compression and corresponding Monte-Carlo simulations. Scale bar: 1 µm.

# Structure and stability of DOPG model membranes in the presence of the saponin aescin

Friederike Gräbitz-Bräuer[1], Carina Dargel[1,2], Ramsia Geisler[1,3], Pascale Fandrich[1], Viktor Sabadasch[1], Yvonne Hannapple[1], Lionel Porcar[4], Ralf Schweins[4] and Thomas Hellweg[1]

[1] Physical and Biophysical Chemistry, University Bielefeld, Bielefeld, Germany
[2] Institute of Physical Chemistry, University of Münster, Münster, Germany
[3] Medical Department 2, Hematology/Oncology and Infectious Diseases, University Hospital of Frankfurt, Frankfurt am Main, Germany
[4] Institute Laue-Langevin, Grenoble, France

Plasma membranes of procaryotes are represented by a large share of lipids such as phosphatidylglycerols. In this study the role of charged lipids in the plasma membrane is investigated with respect to the interaction with the antiviral saponin aescin in the membrane.

Aescin is a natural surfactant which can be found in the horse chestnut and is known for its anti-inflammatory, anti-exudative, anti-oedematous and venotonic properties.[1-3] Small unilamellar vesicles (SUVs) made of 1,2-dioleoyl-*sn*-glycero-3-phosphoglycerol (DOPG) with different amounts of aescin are analysed by small angle neutron and X-ray scattering (SANS/SAXS) (Fig. 1 left). Furthermore, the chain-chain correlation distance of lipid/saponin mixtures in the SUV structures is studied by wide angle X-ray scattering (WAXS)(Fig. 1 right). Small angle scattering data are evaluated with the Kratky-Porod (KP) and Modified-Kratky-Porod (MKP) method as well as by the Guinier approximation. Afterwards the small angle scattering data is Fourier transformed with the software package *GIFT*.[4] Wide angle scattering data is analyzed by using Lorentzian fits to determine the chain-chain correlation distance. Complete miscibility of DOPG and aescin is found even at a lipid/saponin ration of 1:1.

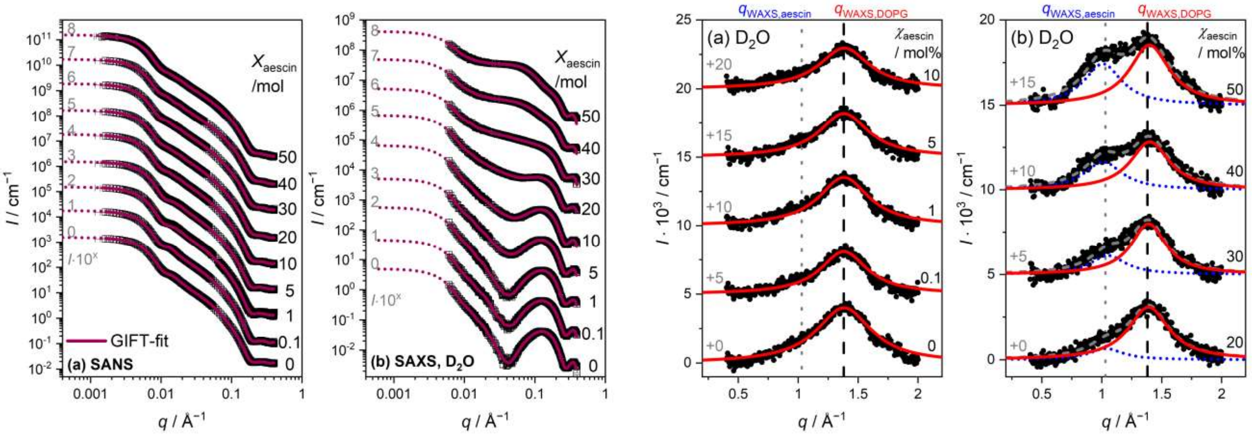

**Figure 1.** Left: SANS and SAXS scattering curves with fits from the software package *GIFT*. Right. WAXS scattering data with Lorentzian-fits to determine $q_{\mathrm{WAXS}}$.

[1] S. G. Sparg, M. E. Light, J. van Staden., Journal of Ethnopharmacology 94 (2-3) (2004), 219-243.
[2] C. R. Sirtori, Pharmacological research 44 (2001), 183-193.
[3] A. Vasiliauskas, L. Leonavičienė, D. Vaitkienė, R. Bradūnaitė, A. Lukšienė, Acta medica Lituanica 17 (2010), 123-132.
[4] Bergmann, A.; Fritz, G.; Glatter, O., Journal of Applied Crystallography 33 (2000), 1212-1216.

# Block Copolymers in 3D Confinement: Janus Nano Cups

Suna Azhdari,[1] Deniz Coban, [1] Manuel P. Trömer[1] Giada Quintieri,-[1] André H. Gröschel*[1,2]

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Block copolymer nanoparticles with unusual morphologies and complex surface are currently in high demand due to their unique physical properties as non-trivial soft matter.[1] Compared to topologies such as spheres, cylinders and vesicles,[2] the precise formation of patchy polymeric cups with defined surface structure are still rare. Geometrically controlled anisotropic Janus nanoparticles (JNP) have gained considerable interest in the polymer science community. However, currently only a few controlled bottom-up synthesis routes are known that enable JNPs synthesis with high selectivity towards the desired geometries.[3] In the present work, we aim to achieve cup-shaped JNPs and the control of their size and curvature. First, several ABC triblock terpolymers consisting of polystyrene-*b*-polybutadiene-*b*-poly (tert-butyl methacrylate) (SBT) are emulsified in conjunction with high-molecular poly (methyl methacrylate) (PMMA) in varying blending ratios through a SPG membrane, followed by evaporation-induced confinement assembly (EICA) process. This led to the formation of two hemispherical particles, with PMMA forming a hemisphere on its own and SBT instead, arranging in a concentric lamella-lamella morphology. In the second step, the PB microdomain is crosslinked with $OsO_4$, and the PMMA hemisphere is subsequently removed by washing with THF, whereby dispersed cup shaped JNPs are obtained. The curvature of the JNPs is controlled by the blending ratio of PMMA, as its content increases the more the curvature is decreasing, going from hemispheres to cups to disk like particles. The mechanical stability of the JNPs is controlled by the length of the PB phase through cross-linking, preventing the collapse of the cups. By removing the PMMA phase with THF and redispersing the SBT tulip bulb phase, it is possible to produce Janus nano cups in high yield. Further, the PT nanodomain is hydrolyzed, in order to produce negative charges, that can be paired with cationic species, *e.g.* Au NPs, in order to prove the Janus character. Due to the particular shape, the Janus nano-cups may find application in biotechnology and nanomedicine, as well as templating of inorganic materials and to perform as cargo in biotechnology and nanomedicine due to their cup-like shape.

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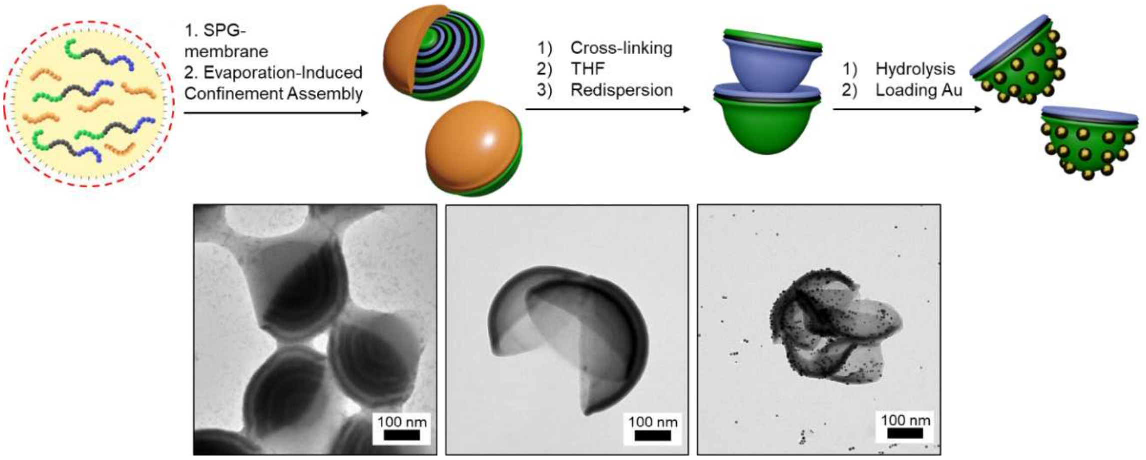

**Figure 1.** Self-assembly mechanism of Janus Nano Cups.

# Chaotropic nano-ion binding as a gelation motif in cellulose ether solutions

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Nanometer-sized ions (nano-ions), such as the polyoxometalate $SiW_{12}O_{40}^{4-}$ (SiW, structure in Fig.1a), interact strongly with non-ionic interfaces, such as polymers[1] and non-ionic surfactants[2], due to a water-mediated driving force, called the chaotropic effect.[3] Due to the drastic effects that these interactions have on the properties of the interface, nano-ions have emerged as promising soft matter additives. In this study, we investigated the effects of chaotropic nano-ions on cellulose ethers, such as hydroxypropylcellulose (HPC, Fig.1a). Cellulose ethers are non-ionic cellulose-based polymers that find ample application as rheology modifiers in cosmetics, foods and drilling fluids in particular due to their molecular stiffness and their intrinsic tendency to aggregate in solution. We find that SiW binds to HPC in the millimolar range and thus induces a drastic increase in viscosity by a factor of 100, see Fig.1b, leading to gelation at higher SiW-concentrations (≈ 50 mM). These rheological effects are unprecedented in comparison to classical additives such as salts, or ionic surfactants as exemplified for SDS, see Fig.1b and appear presumably due to physical nano-ion crosslinking between polymer chains. Small Angle Neutron Scattering further revealed the emergence of a correlation peak at low SiW-concentrations (Fig.1c) that disappears in the presence of an electrolyte like NaCl or at higher SiW-concentrations. This intermittent polyelectrolyte-like behavior relates to the observed rheology trends. Chaotropic nano-ions thus emerge as novel gelation agents and nano-ion/polymer complexes might serve as smart soft materials due to their UV and heat sensitivity.

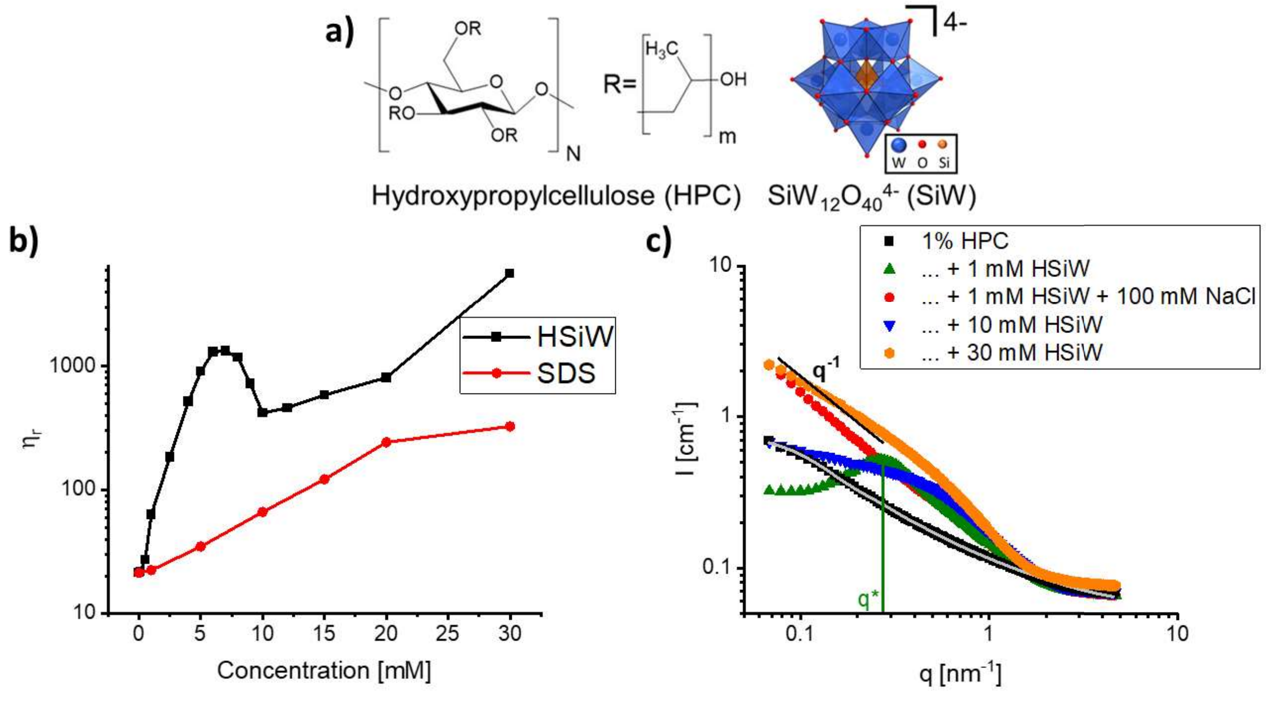

Figure 1. a) Chemical structures of HPC and SiW. b) Relative viscosities $\eta_r$ of 5% w/w HPC in water upon addition of SiW or the ionic surfactant SDS respectively. c) SANS-spectra of 1% HPC in $D_2O$ at different concentrations of HSiW and with NaCl. The spectra are in absolute scale.

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# 3D Printing of Photonic Colloidal Glasses into Objects with Isotropic Structural Color

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Structural color is frequently exploited by living organisms for biological functions and has also been translated into synthetic materials as a more durable and less hazardous alternative to conventional pigments. Additive manufacturing approaches were recently exploited for the fabrication of exquisite photonic objects, but the angle-dependence observed limits a broader application of structural color in synthetic systems. Here, we propose a manufacturing platform for the 3D printing of complex-shaped objects that display isotropic structural color generated from photonic colloidal glasses. Structurally colored objects are printed from aqueous colloidal inks containing monodisperse silica particles, carbon black and a gel-forming copolymer. Rheology and Small-Angle-X-Ray-Scattering measurements are performed to identify the processing conditions leading to printed objects with tunable structural colors. Multimaterial printing is eventually used to create complex-shaped objects with multiple structural colors using silica and carbon as abundant and sustainable building blocks.

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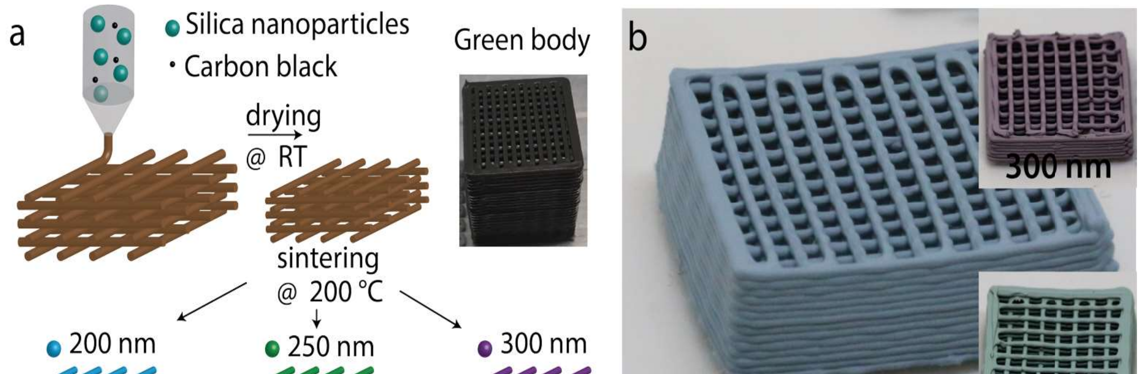

**Figure 1**. a) Sketch of the DIW 3D printing setup and the procedure of achieving structural color. b) Preliminary results we obtained by 3D printing low-index silica nanocolloids. The size of the nanocolloid dictates the color of the 3D printed object. Printlines of the grids are approximately 0.3 mm thick and the 3D printed grids are 1.2 cm x 1.2 cm.

# A Spiropyrane-based dual pH- and Photoswitchable Surfactant for the Targeted Manipulation of Emulsions and Other Colloids

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Stimuli-responsive surface-active molecules may alter their physicochemical characteristics upon the stimulation with an external trigger. Accordingly, their tendency to form micelles in solution, their adsorptive behavior on surfaces or the surface tension of aqueous solutions thereof can be manipulated by external stimulation with light, the pH value or other stimuli.[1, 2] These features render stimuli-responsive surfactants interesting materials for the manipulation of colloidal systems in an aqueous environment.[1] Recently, we demonstrated the synthesis and characterization of a surfactant, which possesses a spiropyrane moiety in its hydrophobic backbone (Figure 1).[3] This molecule, being able to switch from an apolar spiropyrane (SP) form to an ionic merocyanine (MC) counterpart, shows an interesting dual-responsivity to the pH value and light:[4] While under acidic conditions, a pronounced difference of the surface-activities between both forms is found, this behavior is suppressed at an elevated pH level. We exploited this behavior to manipulate the integrity of an oil-in-water emulsion. Furthermore, we are interested to extend the utilization of the surfactant also to other colloids for their targeted manipulation in an aqueous medium.

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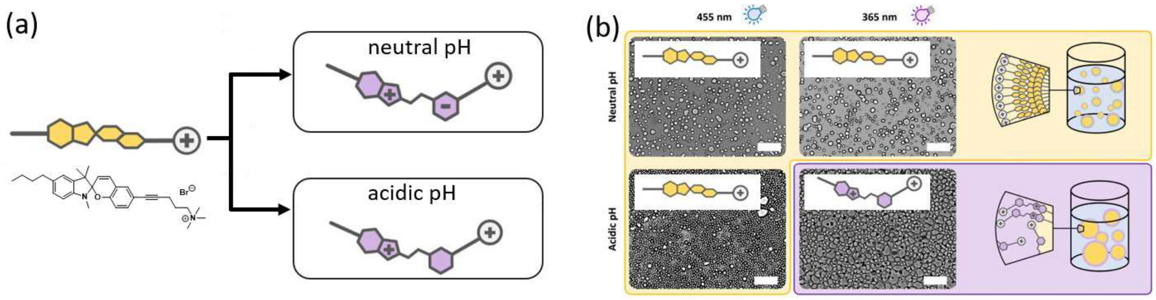

**Figure 1:** (a) Schematic representation of the prepared surfactant. The surfactant in its spiropyrane form (indicated as yellow) may isomerize to form a zwitterionic merocyanine (MC) under neutral, or a kationic $MCH^+$ form under acidic conditions. (b) The surfactant is used for the manipulation of an oil-in-water emulsion. An emulsion is stable under neutral conditions, while it can be demulsified via light irradiation under an acidic pH value.

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# From Single Microgels to Dense Microgel Layers – Investigation by Atomic Force Microscopy

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Microgels are three-dimensionally crosslinked polymer networks that swell in a good solvent. They can change their size and internal structure in response to external stimuli such as temperature, pH or ionic strength. In addition, they are highly interfacial active and possess a rich phase behavior due to their soft and inhomogeneous structure. Based on their interfacial properties, they can be used in various applications, e.g., as emulsion stabilizers or surface coatings. However, there is very little data on the internal structure of microgels in dense layers.

In this study, we used Langmuir-Blodgett type depositions to transfer microgel monolayers at different surface pressures onto solid substrates [1]. These monolayers were then investigated *ex-situ* by atomic force microscopy to investigate (a) their two-dimensional structure and (b) the topography and internal structure of the microgels within the monolayers via force volume measurements.

The results of our measurements show that the confinement of microgels within dense monolayers has a profound impact on their internal structure. Single microgels exhibit an inhomogeneous internal structure at the solid-liquid interface with a stiff core in the center and a decreasing stiffness towards the periphery of the microgels [2]. With increasing compression of the monolayer, the microgels become noticeably stiffer in their core (see fig. 1) [3].

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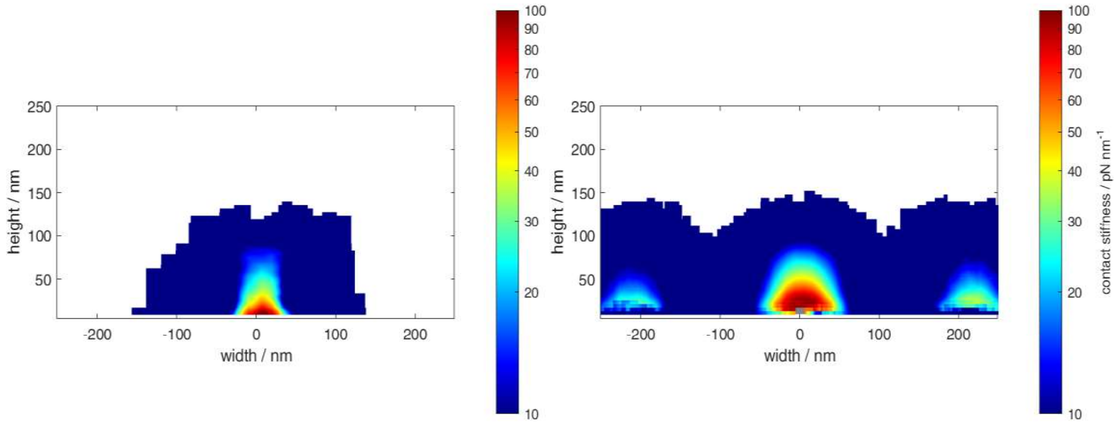

**Figure 1.** Averaged contact stiffness profile of single microgels (left) and microgels in a dense microgel layer (right) at 27°C at the solid-liquid interface.

# Interface Driven Atomically Oriented 2D Assembly of Colloidal Gold Nanodisks Leads to Tunable Plasmonic Resonance

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[2]Institute of Applied Physics, University of Tübingen, Tübingen, Germany
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Colloidal Nanoparticles (NPs) are broadly used to produce self-assembled superstructures, however, a little have been achieved on the 2D assembly of NPs with anisotropic shapes[1]. A key challenge with the anisotropic NPs is to assemble them into long-range positional and orientational order. We synthesize disk-shaped colloidal gold nanocrystals (AuNDs) and assemble them into two-dimensional iso-oriented ordered superlattices at the air-liquid interface using Langmuir method[2-3]. *In-situ* structural and optical properties of the ND assemblies have been monitored using grazing incidence small-angle X-ray scattering (GISAXS), X-ray reflectivity (XRR), grazing incidence X-ray diffraction (GIXD) and UV-vis spectroscopy. Au NDs assemble into a highly ordered 2D hexagonal superlattice and align preferentially with a specific atomic orientation at the air-liquid interface. A continuous blue shift of the plasmonic peak has been observed from the coherent ND assembles with increasing surface pressure[4]. Such preferentially oriented anisotropic NCs is expected to lead to novel optoelectronic properties, which have promising prospects for future applications.

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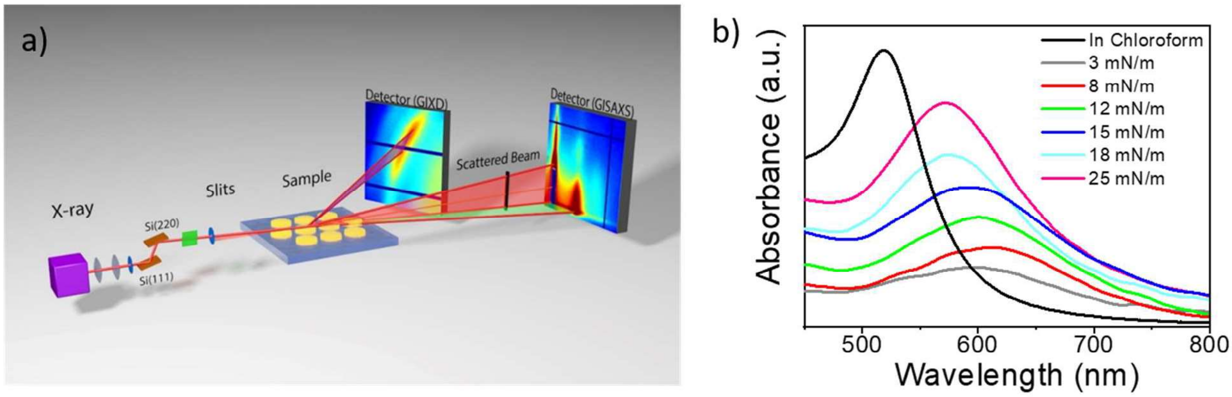

**Figure 1.** a) A schematic of simultaneous GISAXS, GIXD geometry to study *in-situ* self-assembly at the air-water interface. b) UV-vis absorption spectra of AuND superstructure films.

# Phase behavior of super soft spheres in two- and three dimensions

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In our recent publications [1-4], we explored the phase behavior of super-soft spheres using solutions of ultra-low crosslinked poly(N -isopropylacrylamide) based microgels as a model system.

We used SANS with contrast variation to directly access the microgel bulk modulus showing that is one order of magnitude smaller than for regular microgels. In bulk, the samples show a liquid-to-crystal transition at higher volume fraction with respect to both hard spheres and stiffer microgels. Furthermore, stable body centered cubic (bcc) crystals are observed in addition to the expected face centered cubic (fcc) crystals. Small-angle X-ray and neutron scattering with contrast variation allow the characterization of both the microgel-to-microgel distance, and the architecture of single microgels in crowded solutions. The measurements reveal that the stable bcc crystals depend on the interplay between the collapse and the interpenetration of the external shell of the ultra-low crosslinked microgels [1]. This peculiar phase behavior is due to strong defomations of the particles that we determine combining small-angle neutron scattering with contrast variation data and computer simulations [2,3].

Then we confine them at liquid-liquid interface [4]. Atomic force measurements are used to study their phase behavior. In addition, neutron reflectivity and interfacial rheology are used to both their vertical extension and the visco-elastic properties of the monolayer. Once confined at interfaces, these ultra-soft spheres show a behavior in between flexible macromolecules and hard particle.

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# Modification of Interfacial Block Copolymer Structures: Electrochemical Switching of Interfacial Tension and Interfacial Viscoelasticity

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Block copolymers can be crucial for several industrial or pharmaceutical products due to versatile and adaptable properties in solution. We investigated the properties of poly(ethylene oxide)$_{110}$-*b*-poly{[2-(methacryloyloxy)ethyl]diisopropylmethylammonium chloride}$_{170}$ in the bulk phase and at the interface. Potassium hexacyanoferrates (HCF), added as counterions, showed the ability to change the water-solubility of the polycationic block. The “charge compensation” in presence of ferrocyanide $[Fe(CN)_6]^{4-}$ is weaker compared to ferricyanide $[Fe(CN)_6]^{3-}$. Utilizing their electrochemical addressability, the ratio between ferro- and ferricyanide was changed, while interfacial tension was traced. A chemical oxidation/reduction was feasible, but also an electrochemical oxidation leads to a significant change in the interfacial tension. The corresponding reduction showed only a mild response under the same conditions. Micelles in the bulk phase were detected by dynamic light scattering in presence of ferricyanide ions. [1] Further, it was possible to detect a prolonged rearrangement of the block copolymer/ferricyanide mixture at the water/*n*-decane interface from adsorbed micelles to layers of connected unimers by interfacial shear rheology. This was discernible due to the formation of viscoelastic “gel-like” structures at the interface, since the interfacial viscosity increased drastically and the storage modulus $G'$ approached the loss modulus $G''$. Atomic force microscopy, dynamic light scattering, and small angle X-ray scattering accompanied the measurements. The gel formation at the interface was reversible by reducing ferricyanide ions or enhanced by generating Prussian Blue nanoparticles at the interface. [2, 3]

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# Structure and dynamics of polyelectrolytes in water solution

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Proteins are biological macromolecules built from a sequence of amino acids with varying characteristics as hydrophobicity, charge and side-group that determine their biological and physical properties. Unfolded proteins, like intrinsically disordered proteins (IDPs), share similarities with polymers in structure and dynamics. For thermal unfolded Ribonuclease A or the IDP myelin basic protein we showed already similarities to polymer dynamics reflected by Zimm-like dynamics with internal friction [1-3]. Also normal mode analysis based on explicit configurations resulted in improved description of the dynamics. Here we explore the dynamics of polystyrene sulfonic acid (PSS-H) and salt (PSS-Na) as a well-known polyelectrolyte well below the overlap concentration to examine the single chain conformation and dynamics. The aim is to observe the influence of the large charged sidechain onto the chain dynamics and to find similarities to the molecular dynamics of IDP that deviates from standard polymer dynamic models.

The structure of PSS-H can be described by a wormlike chain model with a finite thickness. A disclike cross-section indicating the extended side chains can be observed by SAXS due to the specific contrast conditions (Figure 1, left). Neutron Spin Echo (NSE) experiments, observing the molecular dynamics, clearly indicate a change of chain dynamics as a function of salt concentration and temperature. The dynamics shows a crossover between rigid body like behavior (stiff chains) to Zimm-like dynamics as expected for flexible polymer chains (Figure 1, right)..

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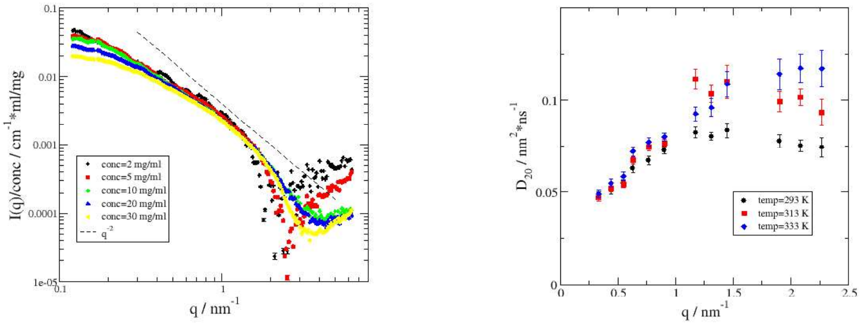

**Figure 1.** Left: SAXS data for PSS-H 39kDa 500mM NaCl for different polymer concentrations. Right: Effective diffusion coefficient from single exponential fits to NSE intermediate scattering function for 3 temperatures for PSS-H 39kDa at 500mM NaCl in $D_2O$. The diffusion coefficients are scaled by the $D_2O$ viscosity to represent the effective diffusion at 20°C.

# Optimization and fabrication of silica-coated nanoemulsion as reservoir for essential oils

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Essential oil-based nanoemulsions have garnered significant attention in the past few decades in the field of nanomedicine, food, and agriculture) [1]. However, they suffer from major shortcomings such as ageing (Ostwald ripening, coalescence), leakage of the encapsulated agent over time, burst release, or rapid degradation under harsh environmental conditions (pH and temperature change) [2]. Moreover, controlling the release of the encapsulated agent from the nanoemulsion matrix is a tedious task.

Coating the surface of the nanoemulsion droplet with some low-cost and biocompatible material like silica (US-FDA approved food additive) can enhance the nanoemulsion performance and can prevent premature degradation of the encapsulated agent. Moreover, silica-coated nanoemulsions can open up the window for functionalization of nanoemulsion to tune the release of encapsulated agents [3].

In this work, we fabricated eugenol nanoemulsions *via* the ultrasonication method using a mixed surfactant system of a non-ionic and cationic surfactant. Obtained nanoemulsions were stable with droplet size $< 100$ nm and zeta potential of $\sim$-40 mV. The effect of coating the nanoemulsion surface with silica using different silica precursors was then studied. The effect of ageing time on the thickness of silica shells under different pH conditions was investigated using FESEM and SAXS. A comparison between non-coated and silica-coated nanoemulsions in terms of encapsulation efficiency, sustained-release, stability against different pH, temperature, and storage conditions was drawn [4]. Results obtained from the investigation may have invaluable implications for fabrication of such silica coated formulations in the agri-food, pharmaceutical and cosmeceutical products

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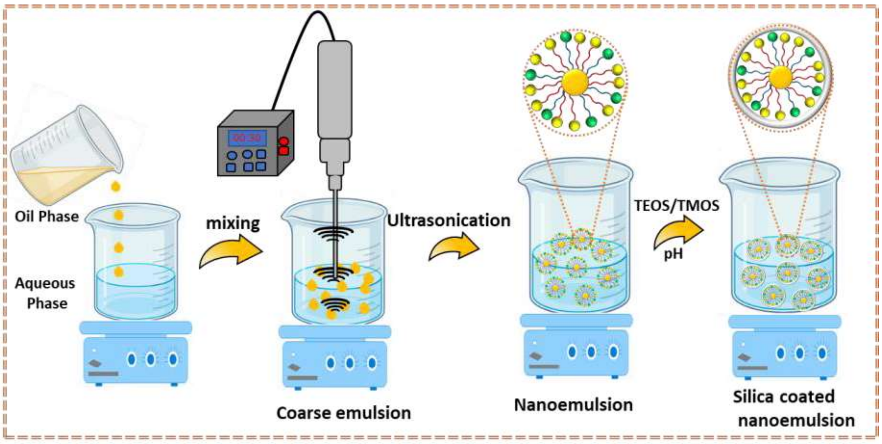

**Figure 1.** Schematic presentation for fabrication of silica-coated essential oil nanoemulsion

# Surface topography quantification of DNA-functionalized colloids via super resolution microscopy

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Microparticles have wide range of applications in materials and sensing. In a quest for programmable materials, DNA coated colloids are of great interest because they can self assemble and form crystal. However, if the DNA coatings are not synthesized correctly and/or homogeneously the self-organization can fail. Therefore, the quantification of the details of surface coating is necessary to understand the mechanisms of interactions between particles and how to control their synthesis in our favor. The aim of this work is to characterize the colloids' surface on a single particle level through single molecule microscopy and by developing quantitative analysis methods.

By employing STED and DNA-PAINT microscopy, we visualize the surface of DNA coated colloids on a nanoscale level [1]. Via DNA-PAINT and qPAINT we can quantify the amount of surface DNAs and correlate these numbers to bulk measurements with Flowcytometry, while STED microscopy enable us to identify the heterogeneity of the DNA groups, figure 1 [2,3]. These methods ultimately pave the path to modify synthesis protocols and produce programmable materials.

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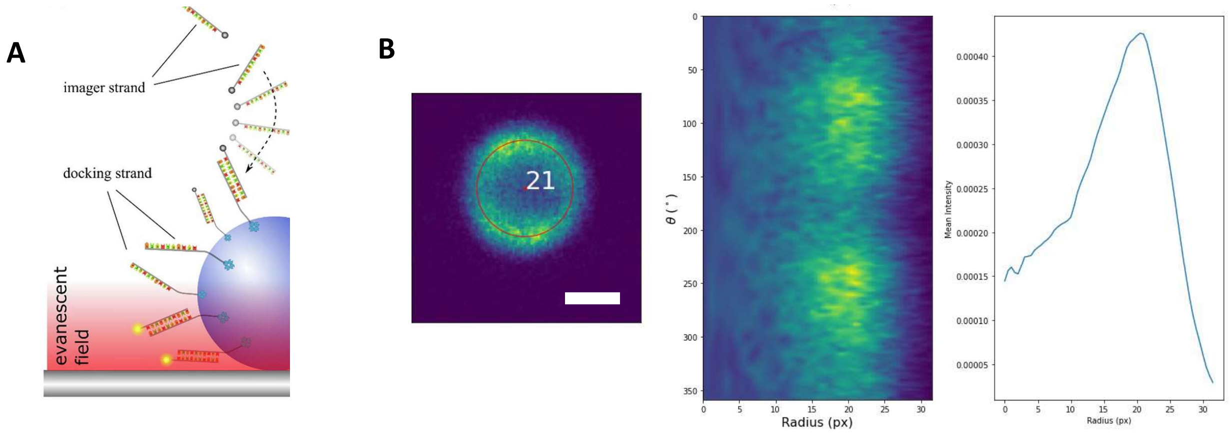

**Figure 1.** Image A, demonstration of DNA-PAINT method for streptavidin coated micron particles[1]. Image B, DNA distribution heterogeneity on the surface of 1µm polystyrene particle, imaged and analyzed with STED microscopy, scale bar: 500 nm.

# A core-shell model describing the deformation behavior of microgels in crowded environment

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Microgels, cross-linked polymer networks swollen by a solvent, are a well-studied model system for soft deformable spheres. In response to increasing the volume fraction of microgels in a suspension, they start to isotropically deswell or facet. Traditionally, small deformations of elastic spheres are modelled through the Hertz pair potential. However, recent simulation studies revealed that in highly concentrated suspensions, the approximation of small deformations is no longer valid. Additionally, microgels are intrinsically heterogeneous, with higher numbers of cross-links near their core. Thus, a more accurate description of microgel deformation was proposed in the form of the multi-Hertzian potential. Hertz-like terms with varying amplitudes are summed up for differently strong cross-linked microgel regions [1].

This study aims to additionally incorporate the free energy of swelling in that model, to enable the simultaneous description of deswelling and faceting of microgels in concentrated suspensions. A Flory-Hertz model for a homogeneous microgels is already known and will be extended to a heterogeneous distribution of cross-links [2]. The simple case of a concentrated system containing core-shell microgels – meaning two regions in a microgel – is simulated. We find that mainly parameters related to microgel softness influence the deformation behaviour in crowded environment. At medium volume fractions the interactions are mainly governed through the properties of the microgel shell. Less cross-linked shells are more inclined to be faceted, while vice versa highly cross-linked shells preferably deswell. The highest investigated volume fractions lead to deformations of the microgel core, depending on its size and softness. In those systems the shell is completely collapsed, which aligns with the experimental observations of core-shell microgels.

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# All-natural Pickering emulsion gels for high-fidelity direct ink-writing

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Direct ink writing (DIW) is especially interesting for biomedical applications due to gentle conditions and the possibility to create customized objects on-demand. Natural abundant polymers arise as sustainable and biocompatible alternatives to synthetic and bio-accumulating polymers. The printing of pure nanocellulose suspensions has proven difficult due to low loadings and high shrinkage, as well as unfit rheology. At the same time, emulsion gels have gained attention for their favorable viscoelastic properties [1].

Our novel sulfur-free cellulose nanocrystals (CNCs) with a low degree of substitution and a low positive surface charge [2] enable the straightforward employment of CNCs as Pickering emulsifiers. We present an emulsion gel ink co-stabilized by this new type of CNCs and α-cyclodextrin (α-CD) interfacial inclusion complexes, composed of entirely natural and biodegradable compounds. The produced inks are shear-thinning and exhibit a high storage modulus up to 70 kPa, allowing for the high fidelity and low shrinkage printing of even complex overhanging structures without requiring a support structure. A low yield stress of only 230 – 270 Pa should facilitate the inclusion of cells for biomedical applications into the formulation, as it was shown that a high shear stress in the nozzle has a negative impact on cell viability [3]. The gel can be tuned to desired rheological properties and equipped with both polar and apolar compounds due to the biphasic system, making it a promising platform for biocompatible additive manufacturing.

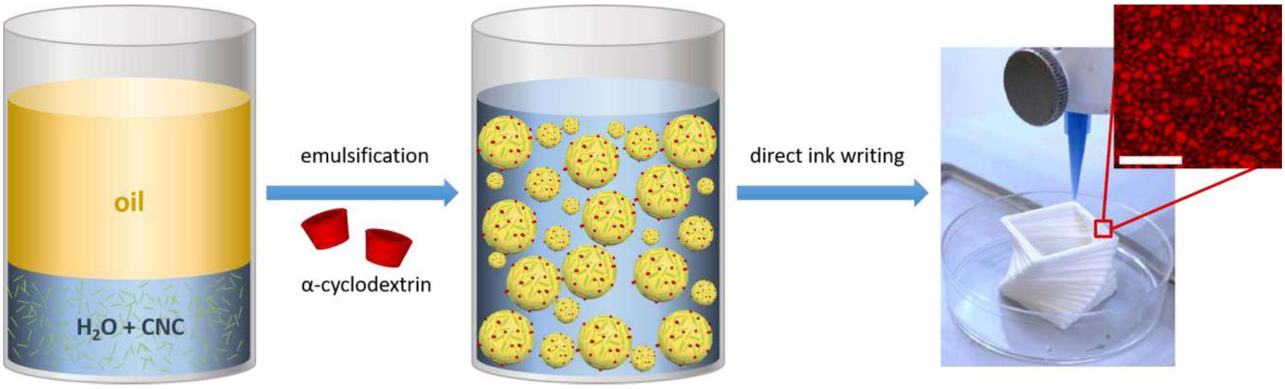

**Figure 1.** Schematic for the fabrication of an emulsion gel 3D printing ink from oil (sunflower), an aqueous CNC dispersion, and α-cyclodextrin with a picture of a support-free rotating square object printed with one of the inks. Scale bar: 50 µm.

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# pH dependent Foam Film Properties of β-lactoglobulin Foams in comparison to Silica Sphere stabilized Foam Films

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The properties of foams are of interest in many applications such as food technology, firefighting and in personal care products. For understanding macroscopic foam properties, it is important to investigate its single building blocks – the so-called foam films, which separate the air bubbles from each other. A widely known foam-stabilizing protein is β-lactoglobulin which appears naturally in milk and is responsible for milk froth. This protein shows an interesting pH dependent behavior.

Engelhardt et al. [1] found maxima of yield stress, storage modulus, dilatational storage modulus and foam film thickness of β-lactoglobulin foams at the isoelectric point around pH 5. These findings are explained by agglomerated β-lactoglobulin multilayers. At pH 3 and pH 7 significant discrepancies in terms of dilatational storage modulus appear despite the same distance to the isoelectric point. To ensure the reason for the discrepancies, more insights in the foam film properties are needed.

Therefore, we use a camera based thin film pressure balance to study protein and particle stabilized foam films in terms of disjoining pressure inside the foam films, drainage kinetics, and foam film stability. Film thickness profiles give insights into bridging, agglomerate and network distributions. Comparison with hydrophobized silica nano particle stabilized foam films helps to distinguish between steric stabilization effects affected by the spherical shape of the particles and protein specific stabilization effects [2].

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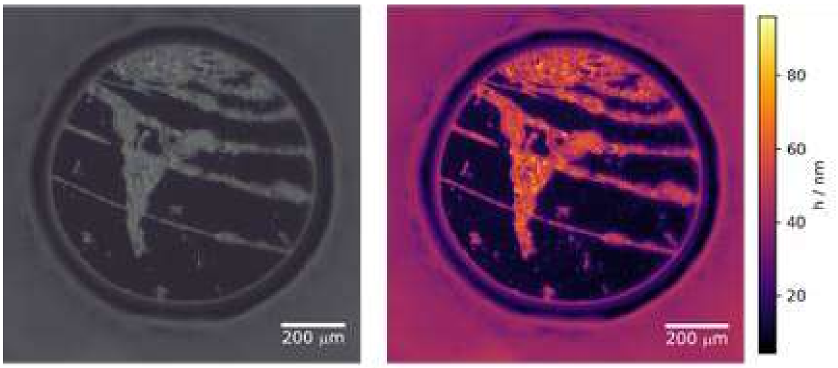

**Figure 1.** Thin foam film of β-lactoglobulin (c = $10^{-6}$ M, pH = 5.0) in natural color representation (left) and false color representation indicating the film thickness (right)

# Self-Assembly of Sugar Surfactants in Deep Eutectic Solvents and Their Solubilization of Terpenoids

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Amphiphilic self-assembly of surfactants in aqueous solutions is a well-studied phenomenon. Self-assembly of surfactants is also possible in deep eutectic solvents (DES), a novel class of polar solvents that has the potential to become a non-toxic and cheap alternative to conventional organic solvents, ionic liquids or even water[1]. Structure formation by surfactants in DES has been studied only to some extent, as their solubility in DES is often very limited[2]. The DES based on choline chloride and urea, known as "reline", has been reported to dissolve only a few anionic surfactants, e.g. SDS[2].

As a result of our experiments, we were able to widen the limited scope of reline-soluble surfactants with sugar surfactants. They can be easily produced from biomass and are readily biodegradable[3]. Interestingly, alkyl glucopyranoside solutions in "reline" could furthermore solubilize monoterpenoid compounds as limonene, menthol, pinene, eucalyptol and borneol, which are otherwise insoluble in neat "reline" or water.

All components were chosen thoroughly with the stress on biocompatibility, biodegradability and their potential use in medicine and cosmetics. Upon addition of menthol, the microemulsions exhibit remarkable viscoelastic properties, such as shear-thinning. The viscosity of such mixtures changes dramatically with the increase of menthol content. Such property could find application in creams and topical drug delivery.[4].

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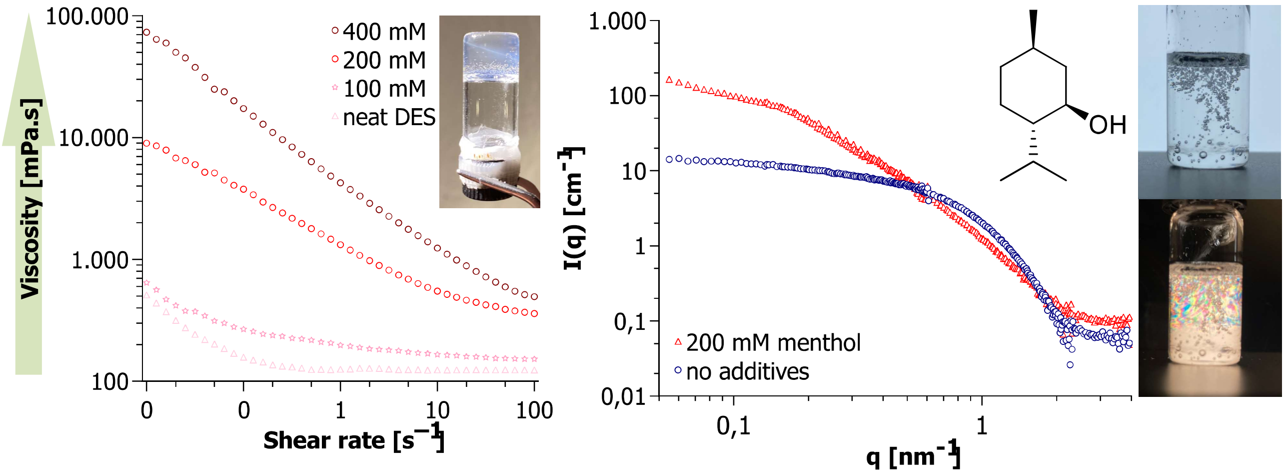

**Figure 1.** **(Left)** The viscosities of equimolar solutions of dodecyl-β-glucopyranoside and menthol in reline at 50°C as a function of the shear rate. Photo of the 400 mM sample upside down demonstrating its high viscosity. **(Right)** Small-angle neutron scattering (SANS) curves of the 200 mM samples with (red) and without menthol (blue) demonstrating major structural changes as supported by cross-polarized image of the sample.

# Method to simultaneously probe the bulk modulus and structure of soft compressible objects using small-angle neutron scattering with contrast variation

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An object's bulk modulus quantifies its resistance to an isotropic compression. For soft deformable colloids the bulk modulus must be known to predict their response to crowding. Here, we will present a new approach to obtain partially-deuterated, high molecular weight polyethylene glycol (dPEG), which is used to exert osmotic stress on soft objects. In this study, microgels were used as a model system for soft compressible spheres and their bulk modulus is determined by means of small-angle neutron scattering with contrast matching. By partial deuteration the scattering length density of the dPEG was matched in pure heavy water. Consequently, no contribution of the osmotic stress polymer is measured during the scattering experiments, and the form factor of the microgels was directly measured. Furthermore, in addition to the total radius, the variation of the different parts of the microgels can be also measured as a function of the external osmotic stress. Therefore, using this method the different elasticity along a single particle, such as proteins or viruses, can be determined directly.

# Building mechanism and controlled synthesis of eumelanin particles

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The biological pigment eumelanin protects various organisms from harmful UV radiation and shows interesting material properties like radical scavenging, paramagnetism and broadband absorption combined with low fluorescence. It can be synthesized biomimetically in aqueous solution starting with L-Dopa and catalyzed by tyrosinase, leading to oligomeric sheets. These undergo a subsequent particle formation, which is not yet fully understood [1]. A 3-step self-assembly process is suggested by previous findings. First, oligomeric sheets are formed which may stack to so-called protoparticles with a size of a few nm. In the second step, the protoparticles form type-A particles, which have a radius close to 20 nm. Finally, spherical particles with a diameter of 200 nm are formed, denoted as type-B particles [2]. The mechanism and the controllability of this supramolecular buildup has been investigated by us. Time-resolved combined static and dynamic light scattering (SLS/DLS) made possible to follow the formation of the final type-B particles from type-A particles under various conditions and indicated a monomer addition mechanism. The adjustment of the pH value enabled us to inhibit the formation of the final type-B particles at the level of type-A particles, characterized by SLS/DLS, scanning electron microscopy (SEM) [3] and Small Angle X-Ray Scattering (SAXS). Subsequent decreasing of the pH value of such type-A particle dispersions triggered the spontaneous formation of type-B particles even 24 h after completion of the formation of the type-A particles [3]. We could demonstrate that the formation of type-B particles is reversible during an initial period by re-inceasing the pH value. The loss of the reversibility with time indicates a consolidation of the type-B particles after their formation by aggregation of type-A particles. [5]

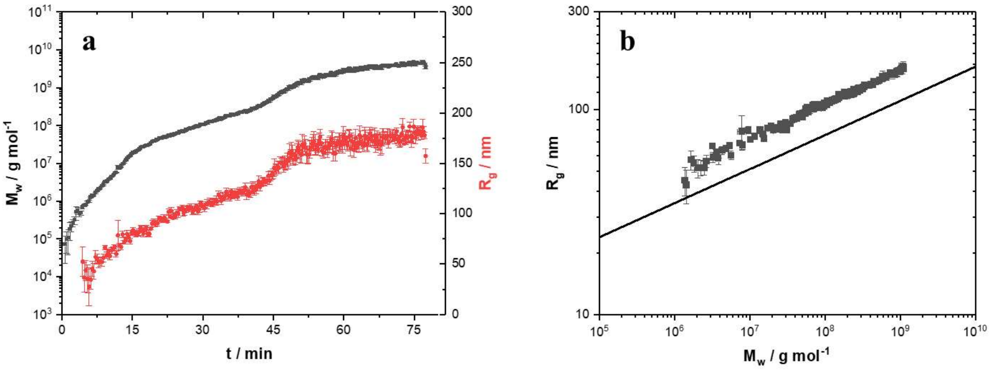

**Figure 1:** Weight averaged molar mass $M_w$ and radius of gyration $R_g$ of growing eumelanin particles followed by SLS (**a**) and respective correlation of $M_w$ and $R_g$ (**b**). The solid line indicates a slope of 1/6 which corresponds to a monomer addition mechanism [4].

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# Elasticity vs. capillarity: How soft is a substrate soft?

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Placing a small liquid droplet on a soft substrate deforms the substrate. The surface tension of the droplet rises a wetting ridge along the three-phase contact line and the Laplace pressure inside the droplet creates a depression (i.e., dimple) underneath the droplet [1,2] (Figure 1A). The deformation of the substrate is determined by the capillary and elastic energies, which is characterized by the softness ratio $\gamma_S/Gr$ (where $\gamma_S$ and $G$ are the surface tension and shear modulus of the substrate, respectively, and $r$ is the contact radius of the nanodroplet).

Using atomic force microscopy (AFM), we have probed the three-dimensional interfacial configuration of nanodroplets (with different $r$) and the deformed soft substrates (with different $G$). This allows measuring the ridge height and the dimple depth (Figure 1B) in a range of softness ratios. With increasing the softness ratio, the normalized ridge height increases and then decreases, while the normalized dimple depth increases and approaches to a limiting value. The substrate capillarity overcomes the substrate elasticity in dominating the substrate deformation when $\gamma_S/Gr \gtrsim 1$ (Figure 1C), illustrating that a substrate becomes soft when $\gamma_S/Gr \gtrsim 1$. Our results show a direct experimental observation of the elasticity-to-capillarity transition [3].

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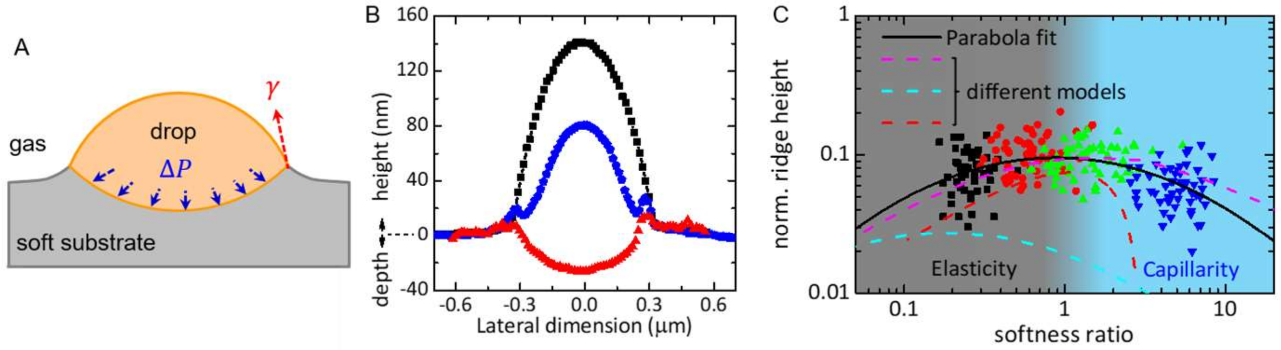

**Figure 1.** (A) Schematic illustration of the substrate deformation. (B) Profiles of nanodroplet, wetting ridge and dimple probed by AFM. (C) Normalized ridge height versus softness ratio showing the elasticity-to-capillarity transition.

# Hybrid soft magnetic micro-actuators with thermo-programmable response to external magnetic field

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Hybrid materials that can respond to multiple stimuli are promising materials with the potential to be employed as carrier materials in biological systems [1]. Poly(N-isopropylacrylamide) PNIPAm hydrogels are an excellent option to achieve such systems. Their thermo-responsive nature allows a reversible switch from a swollen to a shrunken state. By adding maghemite nanoparticles and pre-programing their alignment in the matrix of those hydrogels, thermo- and magneto-responsive systems can be designed.

Different microgel shapes with embedded maghemites were synthesized using Particle Replication in non-wetting template (PRINT). Their thermo-and magneto- responsivity were determined through swelling experiments and through the investigation of their response under rotating magnetic fields of different strengths. These systems were characterized by a maximum rotation speed $\omega_c$ marking their transition from a synchronous to an asynchronous rotation. $\omega_c$ showed to be strongly varying with the temperature (Figure 1a).

When the hydrogels were additionally coated with a metal layer, the restricted swelling of the soft layer enabled the creation of more complex shapes [2-3]. The conformations and polarizability to the applied magnetic field of such shapes can be controlled with the temperature (Figure 1 b). These properties were further utilized to create diverse actuations combining the response to temperature, magnetic field, and light. Additionally, active micro-swimmers made from such system can be designed and their swimming can be directed when an external magnetic field is applied [4].

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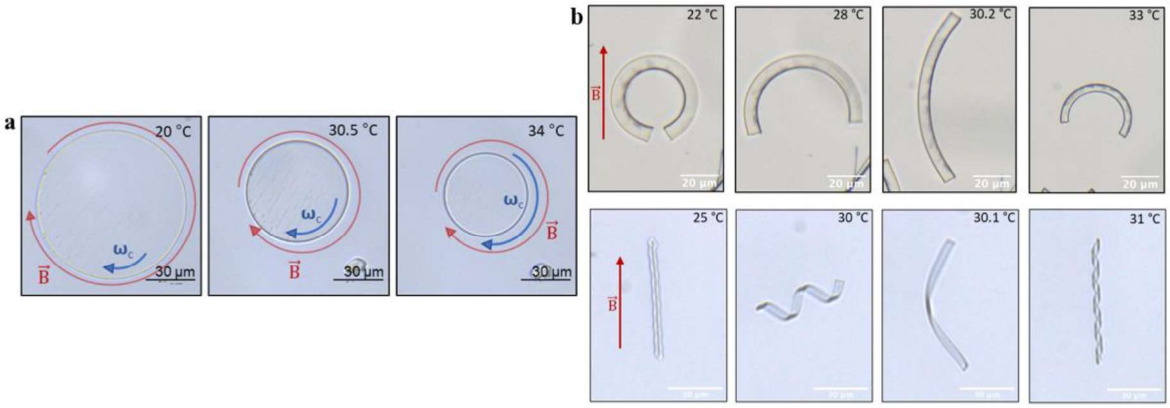

**Figure 1.** *Thermo-responsive and magnetic microgels a) Hybrid disks with tunable response under an applied rotating field b) Arc and helix bilayer structures that change their alignment to the field when the temperature is varied.*

# Janus emulsions as adaptive material platform for the transduction of (bio-)chemical information

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Autonomous regulation of chemical reactivity represents a fundamental ability of living organisms. Chemical information can be processed with high fidelity and highest substrate specificities are achieved as multiple individual or combinations of independent chemical equilibrium-driven non-covalent interactions and covalent chemical transformations are translated into a specific response. This cross-check capability and self-regulation behavior forms the basis for the high complexity and specificity achieved within biological systems and is further fundamental for the complex emergent behavior observed in multibody systems, for instance their self-regulated ability to communicate, move, evolve, and self-organize into patterns or networks.

An emulation of these individual capabilities within a synthetically minimal, biomimetic model system may help to better understand the underlying complex cascade mechanisms and pave the way towards artificial dynamic and self-regulatory adaptive materials that display unprecedented autonomous capabilities. In my group, we are interested in the bioinspired generation of artificial soft matter systems that exhibit chemo-intelligence in that they are capable to autonomously operate in response to (bio-) chemical cues. Guided by basic scientific questions we explore the creation of new, transformative application concepts with the goal to generate artificial chemo-intelligent microreactors that can ultimately rival the regulatory and motile behavior observed in Nature. Our complex colloidal microreactors (complex emulsions, hydrogel capsules, intricate polymer particles) usually comprise two or more phases, and multiple exquisitely sensitive interfaces. As a result, they can, for instance, selectively change morphology in response to a variety of external stimuli, including the presence of specific chemical and biological entities, small pH changes, light or high-energy irradiation, as well as an external electric or magnetic field. Such structures can also be designed to undergo programmed assembly or disassembly, and as a result of the density and refractive index contrast of the individual phases, manipulate the pathway of light. Demonstrations on how an associated understanding of the unique chemical-morphological-optical coupling inside these chemically active functionalized active soft colloids can be used in new and improved soft matter applications, including in biomimicry, droplet-based imaging platforms, as structural templates for the generation of functional precision objects, and as chemo-intelligent transducers in chemo- and biosensing applications will be presented.

# Charging of dielectric surfaces in contact with aqueous electrolyte – the influence of $CO_2$

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## ABSTRACT

The charge state of dielectric surfaces in aqueous environments is of fundamental and technological importance. We use super-heterodyne light scattering in a custom-made cell to study the influence of dissolved $CO_2$ on the charging of three, chemically different surfaces. We compare an ideal, $CO_2$-free reference state to ambient $CO_2$ conditions. Systems are conditioned under conductometric control at different low concentrations of NaCl. As expected for constant charge densities, $\zeta$-potentials drop upon increasing the salt concentration in the reference state. Presence of $CO_2$ leads to an overall lowering of $\zeta$-potentials. Moreover, for the inorganic dielectric, the salt dependent drop is significantly weakened, and it is inversed for the organic dielectrics. We suggest that at ambient conditions, the charge state of dielectric surfaces is related to dielectric charge regulation caused by the salt concentration dependent adsorption/desorption of $CO_2$.

# Repulsive interactions of eco-corona covered microplastic particles quantitatively follow modelling of polymer brushes

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Environmental fate and toxicity of microplastic particles is dominated by their surface properties. In the environment an adsorbed layer of biomolecules and natural organic matter forms the so-called eco-corona [1]. A quantitative description of how this eco-corona changes the particles' colloidal interactions is still missing. Here, we demonstrate with colloidal probe-atomic force microscopy that the formation of the eco-corona on microplastic particles introduces a soft film on the surface which changes the mechanical behaviour. We measure single particle-particle interactions and find a pronounced increase of long-range repulsive interactions upon eco-corona formation. These force distance characteristics follow well the polymer brush model by Alexander and de Gennes. The foundation of the eco-corona interacting like a polymer brush with its surrounding may help understand microplastic transport and aggregation in the environment [2, 3].

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[3] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG; German Research Foundation) project number 391977956–SFB 1357 Microplastics and 422852551 within the priority program 2171.

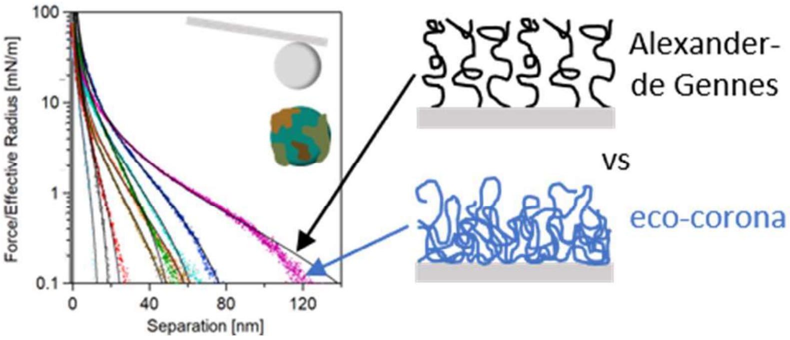

**Figure 1.** Interaction forces of the eco-corona quantitatively follow polymer brush theory of Alexander-de Gennes although its structure is different as outlined right.

# Effect of polymer chain stiffness on depletion layers in colloid–polymer mixtures

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Mixtures of colloidal particles with non-adsorbing polymers are ubiquitous both in science and in industry. The non-adsorbing polymers induce an effective attraction between the colloidal particles, known as the depletion interaction, and as a result colloid–polymer mixtures display rich physics. Theoretical descriptions of such systems historically assumed the polymer chains to be fully flexible coils, while in reality many polymers have a certain degree of chain stiffness. The effect of this stiffness on the depletion interaction and the resulting phase behavior of these mixtures is as of yet poorly understood, even though it is highly relevant for describing realistic systems.

We present a new analytical theory [1] that describes the concentration profile and depletion thickness of a solution of non-adsorbing semiflexible polymers next to a flat surface. Our theory covers both the dilute and semidilute regime. For fixed polymer radius of gyration, increasing the chain stiffness leads to a monotonic decrease in the depletion thickness in dilute conditions. However, in the semidilute regime, remarkably there is a maximum in the depletion thickness as a function of the chain stiffness. Furthermore, we present an extension of the theory towards semiflexible polymer solutions around spherical colloids, yielding insights into the phase stability of colloid–polymer mixtures. The analytical expressions are in quantitative agreement with numerical self-consistent field calculations [2].

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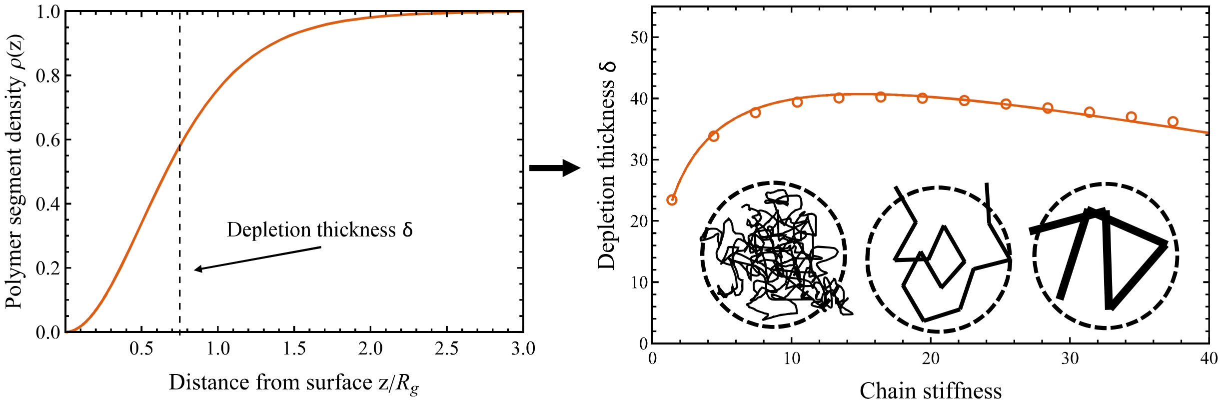

**Figure 1.** (left) Sketch of the normalized segment density of a non-adsorbing polymer near a hard wall. (right) The depletion thickness in the semidilute concentration regime at constant polymer radius of gyration has a maximum as a function of chain stiffness. Points: numerical self-consistent field lattice computations; curve: our new analytical theory.

# Effect of Red Blood Cell Shape Changes on Haemoglobin Interactions and Dynamics: A Neutron Scattering Study

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By using a combination of experimental neutron scattering techniques, it is possible to obtain a statistical perspective on red blood cell (RBC) shape in suspensions, and the inter-relationship with protein interactions and dynamics inside the confinement of the cell membrane. In this study [1], we examined the ultrastructure of RBC and protein-protein interactions of haemoglobin (Hb) in them using ultra-small-angle neutron scattering (USANS) and small-angle neutron scattering (SANS). In addition, we used the neutron backscattering method to access Hb motion on the ns time scale and Å length scale. Quasielastic neutron scattering (QENS) experiments were performed to measure diffusive motion of Hb in RBCs and in an RBC lysate. By using QENS, we probed both internal Hb dynamics as well as global protein diffusion, on the accessible time scale and length scale by QENS. Shape changes of RBCs and variation of intracellular Hb concentration were induced by addition of the $Na^+$-selective ionophore monensin and the $K^+$-selective one, valinomycin. The experimental SANS and QENS results are discussed within the framework of crowded protein solutions, where free motion of Hb is obstructed by mutual interactions [2].

[1] Shou et al. 2020 Effect of red blood cell shape changes on haemoglobin interactions and dynamics: a neutron scattering study. R. Soc. Open Sci. 7: 201507. http://dx.doi.org/10.1098/rsos.201507
[2] We thank ANSTO for provision of neutron beam time. The work was supported by a DFG grant STA 1325/2-1 to AMS. MS acknowledges the support of the International Helmholtz Research School of Biophysics and Soft Matter (BioSoft).

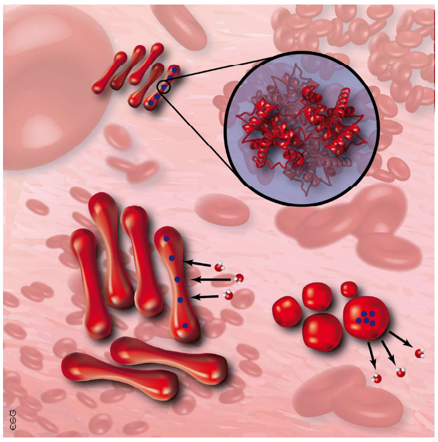

**Figure 1.** Neutron scattering experiments show the influence of the shape of red blood cells on the colloidal properties of the oxygen transport protein haemoglobin.

# Experimental Evidence of a Transition from a Sponge-Like to a Foam-Like Nanostructure in Water-Rich $L_3$ Phases

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Early studies [1-3] on water – *n*-alkane – ionic surfactant microemulsions provide first hints for the possible existence of a foam-like nanostructure, *i.e.* a dense packing of polyhedral nanometer-sized water droplets separated by a thin layer of a continuous oil phase. We chose the system water/NaCl – hexyl methacrylate ($C_6MA$) - dioctyl sulfosuccinate sodium salt (AOT) for two reasons. First, because AOT is a single, pure surfactant known to form inverse structures and, secondly, our ultimate goal is to polymerize the continuous oil ($C_6MA$) phase, *i.e.* to synthesize genuine nanoporous polymer foams. Inspired by the pioneering work of *Skouri* et al. [4] we were able to locate an isotropic one-phase channel, the $L_3$ phase, emanating from the pseudo-binary system water/NaCl - AOT at ambient temperature. In addition, there is an isotropic oil-in-water microemulsion found at high temperatures [5]. Already upon addition of small amounts of oil to the $L_3$ Phase the conductivities become very low and the viscosities very high [6]. Freeze fracture electron microscopy allows us to actually see the anticipated foam-like nanostructure (see Fig.1).

The structure is reminiscent of that of *Wolf* et al. [7] for a related system with a technical grade nonionic / anionic surfactant mixture. Currently, we are studying the kinetics of the oil ($C_6MA$) polymerisation. Subsequently, the structural transition in the $L_3$ channel will be investigated by small angle neutron scattering (SANS) and NMR self-diffusion (FTPGSE).

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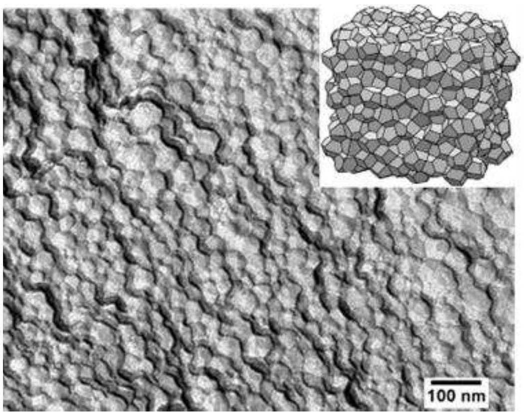

**Figure 1.** Freeze fracture electron microscopy (FFEM) image of an oil-continuous microemulsion $H_2O$/NaCl – $C_6MA$ – AOT with AOT mass fraction $\gamma = 0.15$ and $C_6MA$ mass fraction $\alpha = 0.037$. Scale bar = 100 nm [6]. The inset illustrates the polyhedral foam-like structure taken from [8].

# Supraparticles as identification taggants with spectral magnetic readout

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Complex global supply chains, counterfeit products or quality control demand the identification of arbitrary objects. Smart additives in form of (sub)micron sized particles that carry a unique code, provide a promising approach to overcome the drawbacks of RFID and barcode labels. [1] Going beyond optical signal carriers, magnetic signals can be transmitted through many materials that would not allow optical information to pass. The possibility to read out the magnetic signals out of a certain depth even when covert within dark solid objects, enables an easy incorporation of the marker during production of the materials and additionally protects the marker against environmental harm or easy reveal. Thereby, objects in different application fields could be equipped with such a smart additive (Fig. 1). [2]

**Figure 1.** A magnetic particle with a spectrally resolved magnetic code equips arbitrary objects with information. The readout independent of optical constraints, enables a vast variety of unexploited marking applications. Reprinted from [2].

In this work it is presented that nanostructured micron-sized particles (so called supraparticles [3]) have the potential to be *spectrally* encoded with more than 77 billion magnetic codes as resolved by magnetic particle spectroscopy (MPS). [2] Thereby, a magnetic identification taggant, that does not rely on the spatial arrangement of magnetic particles, is established. A chemical synthesis strategy was developed that enabled the control of nanoparticle-nanoparticle interactions within multi-hierarchical supraparticles in order to obtain a large number of different magnetic codes. This principle will be vividly demonstrated in analogy to a musical ensemble in order to explain the readout technique MPS. Additionally, it is shown that a luminescent code can be united within such supraparticles, yielding dual-*spectrally* encoded supraparticles. [4]

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[3] S. Wintzheimer, T. Granath, M. Oppmann, T. Kister, T. Thai, T. Kraus, N. Vogel, K. Mandel *ACS Nano* **2018**, *12*, 6, 5093–5120.
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# Phase Behaviour of a Biocompatible Microemulsion based on Tween 20, Ethylhexylglycerin and Isopropyl Palmitate

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A novel biocompatible microemulsion system based on Tween 20 (Tw20), ethylhexylglycerin (EHG) and isopropyl palmitate (IPP) as surfactant/co-surfactant, and oil is introduced. We show that a high solubilization capacity can be obtained by employing EHG as co-surfactant, a glycerol ether frequently employed in cosmetic applications [1]. The solubilization capacity is maximized for a Tw20 to EHG ratio of 1:5, i.e., for large excess of the co-surfactant. The phase behaviour is discussed as a function of co-surfactant and oil concentration. Monophasic samples are found for Tw20 to EHG molar ratios of up to 1:7. With increasing EHG concentration, the phase sequence: $L_1$, $L_a$, $L_3$ is reported. At even higher EHG concentrations, bi- and triphasic samples are formed.

The various phases were characterized by means of static and dynamic light scattering (SLS/DLS), small-angle neutron scattering (SANS), rheology, and conductivity measurements. The measurements confirm the formation of oil-in-water (O/W) droplets at lower Tw20 to EHG ratios. Without the addition of oil, the Tw20/EHG system first shows significant elongation with increasing EHG concentration before the aggregates become converted to bilayer structures. Here birefringent lamellar phases and finally a sponge phase are formed. When IPP is added this diverse phase behavior is lost in exchange for larger O/W droplets, which in size increase systematically with increasing EHG content. The structural evolution could in particular be followed in detail by the scattering experiments and this is a system that can structurally be controlled over a wide range and has potential for applications in the field of cosmetic or pharmaceutical formulations.

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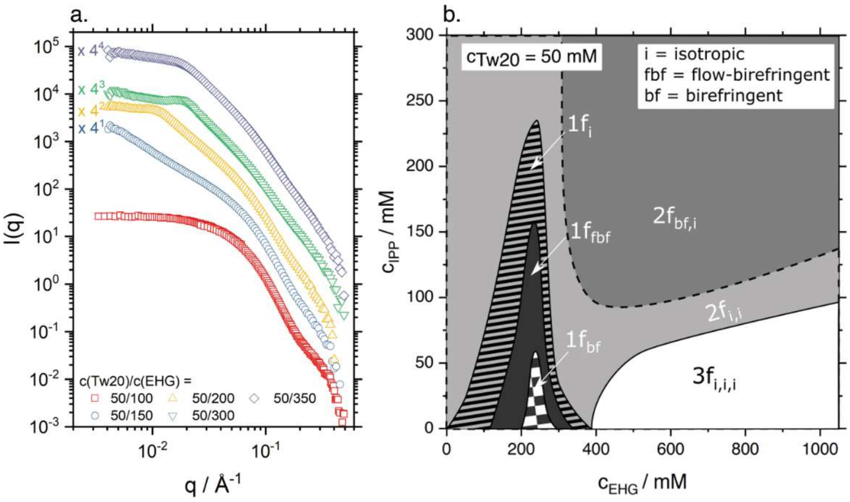

**Figure 1.** a. SANS intensities for samples are higher EHG concentrations. The spherical droplets first elongate before forming birefringent bilayer structures. b. Section of the phase diagram.

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From interactions to structures in colloids

## Poster Session Abstracts

# Dynamic Complex Emulsions for functional Janus particle design

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The synthesis of nano- to microscale Janus particles with unique functionality or morphology requires creative experimental conditions in opposition to Nature's most efficient surface-to-volume object, the sphere. While many impressive tools exist to generate Janus particles in a bottom-up or top-down approach, these methods are often flexible in their product or easily scalable, but seldom both. To this end, dynamic complex emulsions generated from two liquids miscible above a specific temperature offer one-step generation of a multi-responsive colloidal template. When we replace one or both droplet phases with a photo-polymerizable monomer, the exposed conditions of the monomer-phase on polymerization allow vast opportunity for particle design at each interface. In this context, interfacial assembly enables the self-organization of droplet phases and interfaces into a precision particle. With a dynamically tunable droplet morphology, droplet molds retain a uniform geometry independent of size at the micro- or nanoscale.[1] In one step utilizing amphiphile self-assembly, temperature, and light facilitates the chemical design and conversion of these droplets to particles; with defined form, functionality, and wettability.[2]

The result of this conceptual freedom is the ability to generate highly uniform Janus particles in one step. Morphological tuning of the liquid colloidal template enables the generation of structurally anisotropic Janus particles, which benefit from shape-controlled interfacial behavior and self-assembly due to intrinsic variation of the inter-particle packing density. Pre-assembled functional surfactants at the droplet interfaces can be locked in position upon polymerization, enabling side-selective post-functionalization schemes. In addition, the ability to tune the hydrophilic-lipophilic balance allows the generation of particles with fine-tuned wettability contrast, capable of stabilizing both water-in-air marbles and air-in-water bubbles. We utilized the unique self-assembly behavior of the amphiphilic Janus particles to enhance gaseous oxygen delivery in a liquid-phase catalytic oxidation reaction, improving the reaction rate twofold. Interfacial organization around dynamic complex emulsions facilitates the simple but powerful ability to design Janus particles with programmable size, shape, functionality, and hydrophilic-lipophilic balance, in one scalable step.[3]

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[3] Authors are thankful for funding by the Max Planck Society and acknowledge financial support through the Emmy-Noether program of the German Research Foundation (DFG) (grant no. ZE1121-3).

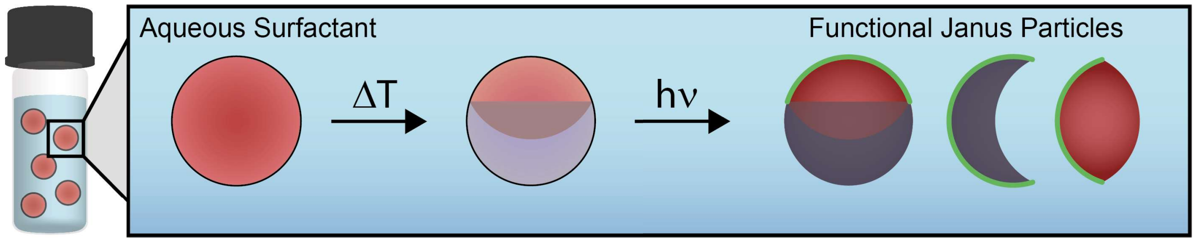

**Figure 1.** Functional & anisotropic Janus particles generated from complex emulsions, scalebar = 50µm.

# Controlled synthesis of poly(ionic liquid) nanovesicles

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Polymer nanovesicles find potential applications in drug delivery, catalyst carriers, and smart nanoreactors, but their controllable synthesis remains a challenge [1-2]. Herein, we report a straightforward, scalable approach towards the fabrication of poly(ionic liquid) (PIL), poly(3-*n*-Decyl-1-vinylimidazolium Bromide, homopolymer nanovesicles with a tunable size of 50-130 nm and shell thickness of 15-68 nm *via* free radical polymerization induced self-assembly. Intriguingly, the overall morphology of PIL nanovesicles has been tuned from hollow to solid vesicles, and finally to directional worms upon increasing the monomer concentration during polymerization as investigated by cryogenic transmission electron microscopy (**Figure 1 a-f**). The monomer concentration, counter anion, and the solvent have been shown to play crucial roles in the morphology transformation of PIL nanovesicles [3].

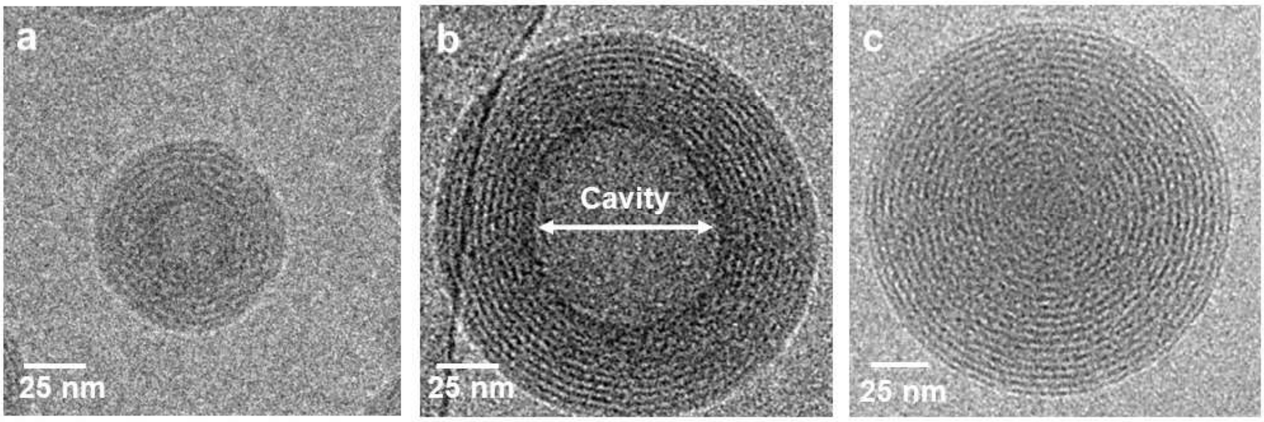

**Figure 1.** Cryo-TEM images of PIL assemblies prepared at various monomer concentrations: (a) 3 mg/mL, (b, f) 12 mg/mL, (c) 24 mg/mL.

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# Dynamic Janus emulsions as foodborne pathogen sensors using stimuli-responsive surfactants

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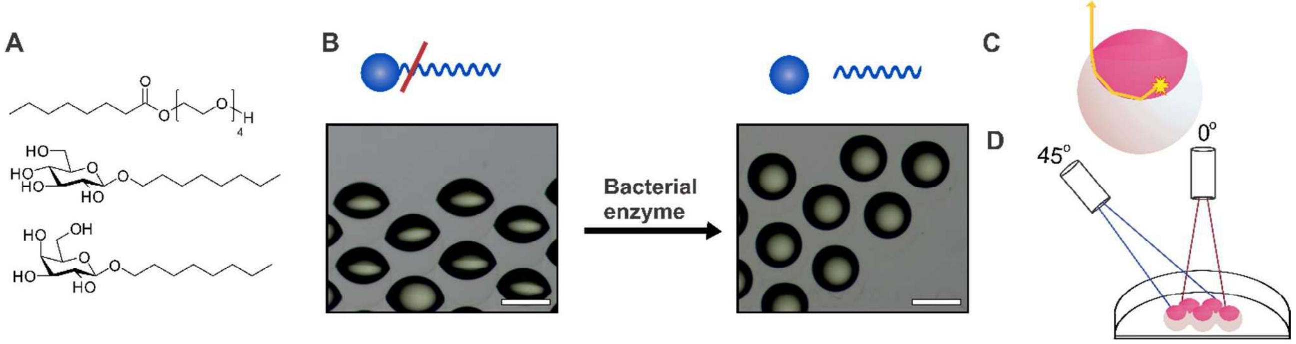
The development of fast and inexpensive point-of-care sensors is crucial to address the serious public health threat of foodborne pathogenic bacteria. Janus emulsion droplets, composed of hydrocarbon and fluorocarbon oils, are promising liquid sensing devices due to their dynamic nature [1]. The droplets were stabilized using a fluorocarbon surfactant and stimuli-responsive hydrocarbon surfactants, which serve as substrates targeting exoenzymes characteristic for major foodborne pathogenic bacteria, namely *Salmonella enterica, Listeria monocytogenes* and *Escherichia coli*. Upon enzymatic cleavage of the surfactants by extracellular enzymes, their hydrophilic head group is separated from the hydrophobic tail, resulting in a loss of amphiphilicity and therefore an increase of the HC/W interfacial tension at the droplet interface. As a result, rapid, optically detectable changes in the internal droplet morphology occur (Fig.1). We follow such morphological transitions using a customized optical readout platform that is based on a detection of an anisotropic emission signature of dyed complex droplets caused by total internal reflection. To this end, perylene emitters were selectively placed inside the higher refractive index droplet phase, resulting in optical confinement of the perylene emission which transduces changes in the internal droplet morphology. Our system proved to be highly specific, while affording a real-time response with a low detection limit of 10 CFU/mL within 2 h for *Salmonella enterica* and $<10^3$ for *Escherichia coli* and *Listeria monocytogenes*. The implementation of enzyme-cleavable surfactants and Janus emulsions in combination with a novel readout method based on anisotropic light emission both improves the sensitivity of existing liquid sensing platforms, and holds great promise for the sensitive and selective detection of foodborne pathogens.[2]

[1] Zeininger, L. *et al. ACS Cent. Sci.* 5, 789-795 (2019)

[2] Authors gratefully acknowledge funding from the Max Planck Society, and financial support via the Emmy-Noether program of the German Research Foundation (DFG) (grant no. ZE1121-3)

**Fig.1** A) Structures of cleavable surfactants. B) Droplet morphology change caused by enzymatic cleavage (scale bar 100μm). C) Total internal reflection in Janus emulsions. D) Our state-of-the art optical ratiometric readout.



# Structural and optical properties of (2+1)D colloidal crystals produced by a layer-by-layer approach

Lukas J. Roemling[1], Eric S. A. Goerlitzer[1], Gudrun Bleyer[1] and Nicolas Vogel[1]

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In the natural world, some of the most fascinating colors – i.e. the blue wings of the Morpho butterflies or the brilliant white of the Cyphochilus beetle – are based on tiny layers of complex, hierarchical micro- and nanostructured materials [1], [2]. To mimic these materials, self-assembly of colloidal particles with a few hundred nanometer in size is commonly used [3]. As a result of interactions between the particles, so called colloidal crystals can be formed which show a color based on Bragg diffraction. Commonly, these materials are produced by letting a suspension of colloids evaporate in a controlled manner. Finally, the structures will resemble an fcc lattice, as can be found in metals [3].

One drawback of this technique is the limited control over the colloidal crystal, i.e. controlling the number of layers precisely is difficult and the internal structure is mostly uniform. In this work, we entrap the colloids at the air/water-interface to assemble a monolayer – or 2D colloidal crystal – of particles and transfer it to a glass substrate via the Langmuir-Blodgett technique. By repeating this step, we can precisely control the number of layers. Additionally, it opens the possibility to incorporate absorbing or emitting species at specific positions in the crystal. One method reported in literature is a layer of absorbing material coated onto each particle [4]. But this also changes the parameters of the assembly and influences the order, which in turn has a great influence on the optical appearance [4].

We investigated the order of a layer-by-layer colloidal crystal by calculating the pair correlation function for every layer and compared it to a colloidal crystal produced by evaporative assembly. We found that the orientation of the particles does not translate between layers and the colloidal crystal can be referred to as a (2+1)D colloidal crystal instead of a 3D colloidal crystal [5]. The layer-by-layer colloidal crystal possesses multiple small defects and partial disorder in each monolayer, while the conventional colloidal crystal shows large cracks as grain boundaries. The optical analysis shows that the layer-by-layer colloidal crystal – despite its partial disorder – shows a higher reflection peak for a limited number of layers but the maximum achievable reflection with the layer-by-layer approach is limited due to the accumulation of defects.

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# Polyol-assisted synthesis of Copper microparticles and its size-dependent applications

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Colloidal copper particles exhibit excellent catalytic and optoelectronic characteristics, but their synthetic strategies are less common compared to other noble metal particles like gold, silver, or platinum. We proposed a simple additive-based polyol method to synthesize Cu microparticles.[1] Phthalonitrile employed as an additive, influenced the size and properties of the resulting copper particles.

Copper is known to have contraceptive properties and has been clinically used as a non-hormonal intrauterine contraceptive device (IUD) for decades. The spermicidal effect of copper has not been extensively explored and thus we studied the size, concentration, and time-dependent *in vitro* inhibition of bovine spermatozoa by these synthesized copper microparticles.[2]

Additionally, these particles were partially oxidized to $Cu_xO@Cu$ in low concentrations of peroxide. These synthesized colloids displayed outstanding photocatalytic properties and taking advantage of their distinct behavior we investigated the size-dependent (photo)catalytic degradation using rhodamine B (RhB) as a model organic pollutant. Further, followed by an asymmetrization step via deposition of a thin Au layer on one hemisphere, these particles demonstrated their applicability as a photocatalytic micromotor.[1]

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[2] P. Chattopadhyay, V. Magdanz, and K. B. L. Borchert, "Size dependent inhibition of sperm motility by copper particles as a path towards reversible male contraception," pp. 1–25.

The authors acknowledge a Freigeist grant (No 91619) from the Volkswagen foundation. P.C acknowledges the free state of Saxony represented by the state parliament for Saxony Fellowship.

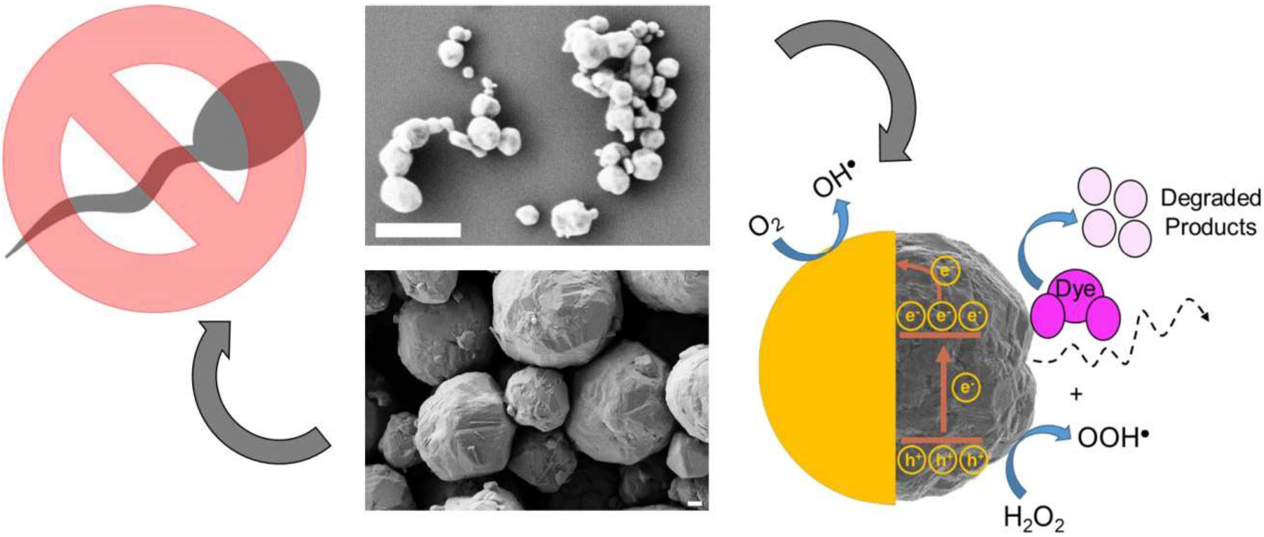

**Figure 1.** Two different sized copper particles synthesized by assisted polyol method and its application as photocatalytic micromotor and as sperm inhibitor. Scale bar: 1 µm.

# Ionization equilibria and swelling behaviour of weak polyampholyte core-shell microgels: A Monte Carlo study

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For polyampholyte microgels, their charge can be tuned by varying the pH and a charge reversal from a positively charged microgel at low pH to a negatively charged microgel at high pH can be achieved. Therefore, a swelling transition from a collapsed to a swollen state occurs when, starting from an average pH value and this value is increased or decreased. Experimental studies indicated an independent ionization of acidic and basic groups in a core-shell microgel, while in a random distribution, there is a mutual influence[1]. Building on our earlier work on alternating polyampholyte microgels, we now investigated the pH-dependent ionization and the swelling behaviour of polyampholyte core-shell microgels with Metropolis Monte Carlo simulations and using the constant-pH method in a bead-spring model[2,3].

As in our previous study on alternating microgels the width of the U-shaped transition in the swelling of the microgels depends on the relative dissociation constants of acid and base[2]. Due to the spatial separation of acid and base, the ionization is less enhanced compared to a microgel with an alternating distribution of the species. However, an independent ionization behaviour cannot be observed. Furthermore, we saw a shift of the isoelectric point towards higher pH caused by a higher charge distribution in the core. Added salt screens the charges within the network, and the U-shape transition becomes more narrow. Radial distribution functions show a clear core-shell structure at low and high pH and a complete interpenetration of the shell in the core at intermediate pH values[4].

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[3] C.Strauch, S. Schneider, *manuscript in progress*.
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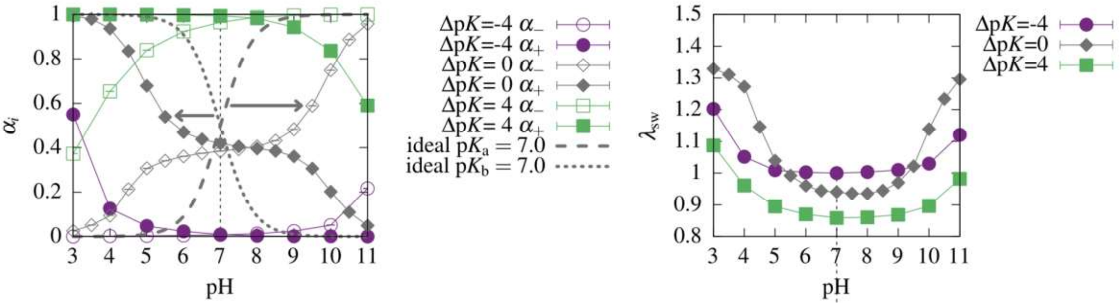

**Figure 1.** Degree of ionization as a function of pH and different $\Delta pK$ ($\Delta pK$=-4: p$K_a$ =9.0, p$K_b$=5.0; $\Delta pK$=0: p$K_a$ =7.0, p$K_b$=7.0; $\Delta pK$=+4: p$K_a$ =5.0, p$K_b$=9.0). Dotted lines represent the ionization of a system without interactions for p$K_a$=7.0 and p$K_b$=7.0 (left). Degree of swelling as a function of pH (right).

# Reversible structure formation by magnetic nanocubes

L. Rochels[1], R. Erkes[1], F. A. F. Mees[1], M. Kapuscinski[2], S. Sevitz[3], T. Plivelic[3], G. Salazar-Alvarez[2] and S. Disch[1]

[1] Universität zu Köln, Department für Chemie, Köln, Germany
[2] Uppsala University, Department of Materials Science and Engineering, Uppsala, Sweden
[3] Lund University, MAX IV Laboratory, Lund, Sweden

Superparamagnetic iron oxide nanoparticles find wide application in biomedicine [1,2] and materials science, including sensor technologies [3] or ferrofluids [4]. The self-organization of iron oxide nanocubes by evaporation-guided approaches typically leads to mesocrystals with a high structural diversity induced by particle size and shape [5-7]. Similar superstructure formation has been observed in dispersions of magnetic nanoparticles upon application of a magnetic field [8,9]. We have recently observed a clear indication of a reversible, field-induced aggregate formation by the magnetization behavior of concentrated dispersions of iron oxide nanocubes, depending on the particle size [10].

In this contribution we will present our recent SAXS study on the field-induced structure formation of these iron oxide nanocubes. Two different structure factors are revealed, indicating the presence of elongated aggregates and highly symmetric mesocrystals. We will emphasize the field- and time-resolved evolution of the mesocrystal structure and its orientation towards the applied magnetic field [11].

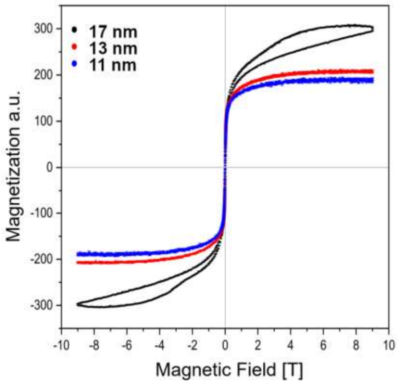

**Figure 1.** Field-dependent magnetization behavior of highly concentrated nanocube dispersions.

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# In situ and ex situ characterization of self assembled colloidal monolayers at air-water interfaces

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Self-assembly at interfaces is an effective and versatile strategy for the fabrication of highly ordered two dimensional colloidal films. Studies on the self-assembly of hard colloidal spheres are typically done with silica and polystyrene particles as building blocks, where the film formation is assisted by various techniques such as a Langmuir-Blodgett trough, spin-coating or self-assembly during solvent evaporation [1-2]. In general, rigid spheres tend to self-assemble into close-packed particle films due to capillary forces at the interface and therefore have only one length scale in interparticle distance [3]. In contrast to that, soft colloidal spheres such as microgels can have a range of interparticle distances due to their deformable nature [4]. In the past few years, core-shell hybrid microgels have received a lot of attentions as they possess properties from both hard and soft spheres [5-6]. However, not much is known about binary systems containing hard and soft spheres. Mixing both types of colloids could introduce controllable defects in assembled colloidal films.

In this study, we investigate binary mixtures of hard and soft colloids at the air-water interface. Previously, we observed strong attractive interactions between both types of colloids in bulk, which led to clustering and gelation of the dispersion. This attraction, already reported in the literature, is a challenge that must be overcome [7]. We tackled this by introducing a thin polymer layer covering the surface of the hard sphere colloids. By means of light microscopy and Langmuir-Blodgett deposition the system was investigated in terms of number ratio under various surface pressures both in and ex situ.

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# Direct Measurement of the Forces Acting Between Colloidal Silica Particles

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Natural colloidal dispersions have accompanied mankind in the form of blood or milk ever since. Besides this, artificial systems have gained a significant importance for our daily life during the last decades. From the production of many cosmetics or the water purification and sewage water treatment to the medical field, colloidal systems are widely used nowadays.

For all these applications, it is of special interest to gain an understanding of which interparticle forces govern the stability of colloidal dispersions and how this stability can be tailored. In electrolyte solutions, the classical DLVO theory describes these interactions as a superposition of van der Waals and electrostatic double layer forces. While the simplest description based on the Debye-Hückel superposition approximation provides a good agreement with experimental data for low concentrations and 1:1 electrolytes, larger deviations appear for systems of higher valency [1,2]. For a detailed examination of the van der Waals and electrostatically dominated regimes, we directly measure the forces between a colloidal silica particle and a flat substrate in aqueous solutions by the colloidal probe AFM (atomic force microscopy) technique (Fig. 1 A).

Varying the concentration of sodium chloride solutions allows us to demonstrate the transition from the double layer to the van der Waals dominated regime and the good agreement with the predictions of the DLVO theory for a simple 1:1 electrolyte. Similar measurements for phosphotungstic acid (a 1:3 system with a nanometer-sized anion of the Keggin type) can still be described with the DLVO theory, but reveal significant deviations between the calculated and measured ionic strength (Fig. 1 B). These might be attributed to the decomposition of PTA at pH values above 1.5 described in literature and to the large size of the Keggin ions [3].

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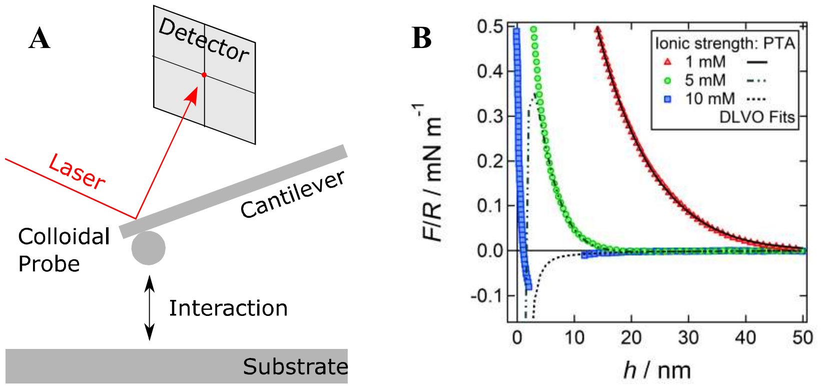

**Figure 1. A)** Schematic depiction of the colloidal probe technique, where a reflected laser beam records the bending of a cantilever with a colloidal silica sphere attached to it. **B)** Force versus separation curves for phosphotungstic acid (PTA, ionic strength calculated assuming a full dissociation) with the corresponding fits according to the DLVO theory.

# Evolution of Magnetization in Sequentially Grown Ferrite Nanoparticles

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Magnetic nanoparticles are technologically relevant for catalysis, high density magnetic data storage, ferrofluids and medical applications [1-2]. A drastically reduced magnetization to the bulk material is commonly observed and attributed to spin disorder in magnetic nanoparticles. Such spin disorder is typically considered confined to the nanoparticle surface but has also been observed in the nanoparticle interior as a result of atomic scale structural defects [3]. Structural defects and the associated spin disorder in nanoparticles have recently been suggested to be beneficial for magnetic heating such as in intracellular magnetic hyperthermia [4]. A key challenge in magnetic nanoparticle research is therefore in the quantitative description and control of the nanoscale distribution of magnetization and spin disorder. Magnetic SANS provides the nanoscale spatial sensitivity to monitor the intraparticle distribution of magnetization and spin disorder [5-6].

In this contribution, we will present our approach to the systematic variation of spin disorder in ferrite nanoparticles upon sequential growth. Our aim is to follow the surface near spin disorder in nanoparticles when the initial surface becomes the interior of the grown particle. Cobalt ferrite and manganese ferrite nanoparticles of varying growth stages are synthesized following an optimized thermal decomposition method involving a seeded growth technique [7]. Structural and magnetic characterization using electron microscopy, SAXS, and magnetization measurements confirms a systematic particle growth (Figure 1) that is accompanied by a significant evolution of the nanoparticle magnetization upon the first growth stages. In the long term, the sequential growth technique might contribute to the engineering of nanoparticles with a tunable surface spin disorder thickness [8].

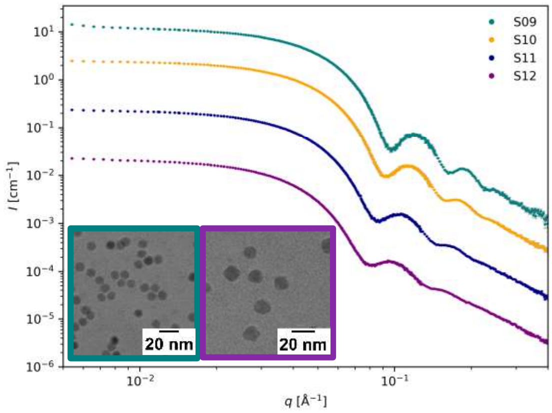

**Figure 1.** TEM and SAXS by sequentially grown cobalt ferrite nanoparticles.

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# How to make a surface act as a micropump

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In this work we investigated the phenomenon of *local* light driven diffusioosmotic (*l*-LDDO) long-range attractive[1] and repulsive[2] interactions between micro-sized objects trapped near a solid wall. The range of the DO flow extends several times the size of microparticles and can be adjusted to point towards or away of the particle by varying irradiation parameters such as intensity or wavelength of light. The "fuel" of the light driven DO flow is a photosensitive surfactant (Figure 1a) which can be photo-isomerized from a more hydrophobic *trans*-state to a rather hydrophilic *cis*-state.[3] The *trans*-isomer tends to accumulate at the interface, while the *cis*-isomer prefers to stay in solution. In combination with a dissimilar photo-isomerization rate at the interface[4] and in bulk solution[5] (Figure 1b), this yields into a concentration gradient of the isomers around single particles resulting in generation of *l*-LDDO flow (Figure 1c).[6] Here we present the extended analysis of the *l*-LDDO flow as a function of irradiation parameters by introducing time dependent development of the concentration excess of isomers near the particle surface and bulk solution. With this we demonstrate that the *l*-LDDO can be generated at any solid/liquid interface being more pronounced in the case of strongly absorbing material likewise human hair and dust particles (Figure 1d,e). This phenomenon has plenty of potential applications since it makes any type of surface to act as a micropump under right illumination conditions.

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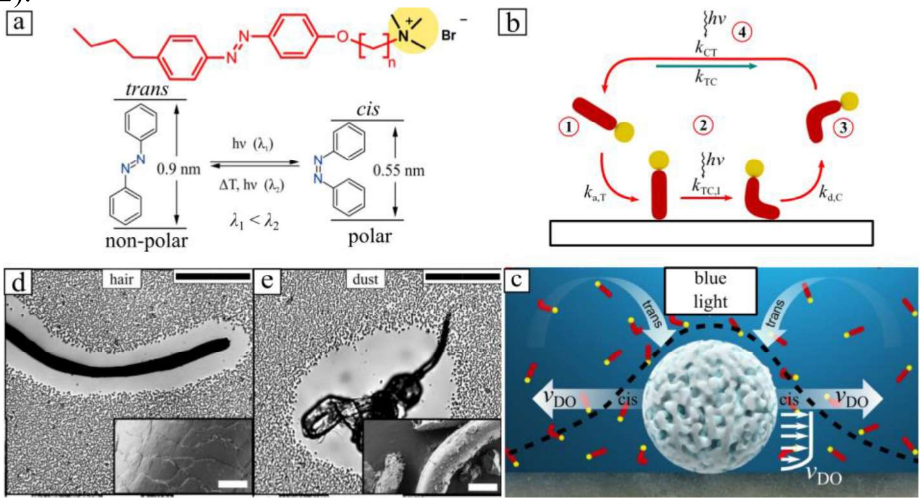

**Figure 1.** (a) Chemical structure of the photo-sensitive surfactant and the two isomers of the azobenzene group. (b) Cartoon of effective dynamic exchange of both isomers under illumination at bulk and interface, which induces a gradient and a local light driven diffusioosmotic flow illustrated in (c). Optical micrographs of human hair (d) and dust (e) mixed with tracer particles under irradiation with blue light. SEM micrographs of the corresponding surfaces are inserted. Black scale bar is 100 µm, white scale bar is 2 µm.

# Impact of ionic strength in the melting temperature of DNA coated colloids

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Microparticles can assemble into superstructures creating colloidal materials with unique properties arising from this structuration [1]. Surface functionalization is an appealing route to program the assembly pathways because it provides a way to encode affinity, specificity and directionality through selection of suitable motifs onto the colloids. A particularly powerful surface functionalization is DNA. Both the affinity and selectivity of hybridization of complementary single DNA strands is modular and to a large extent predictable, such that it can be used to program particles to assemble into a wide range of superstructures [2]. It has been shown that the total coverage of DNA on the particles will determine if particles can roll over each other to anneal into crystalline structures or not [3,4]. Thus, to be able to form crystalline structures and circumvent kinetic traps in assembly pathways the DNA coverage should be maximized. Here, we studied to what extent salt concentration/ionic strength can be used as control parameter to modulate the density of DNA strands covalently attached to polymer-coated polystyrene particles through click chemistry (see cartoon Figure 1). We check the DNA coverage via the melting temperature (Tm), as it has been shown that Tm of the colloidal suspension is a good indicators of DNA coverage [2]. We find that as more salt is added to the click chemistry step, Tm shift to higher values (Figure 1), thus indicating that more DNA is grafted onto the particles and salt is a crucial parameter in controlling DNA coverage of a particle.

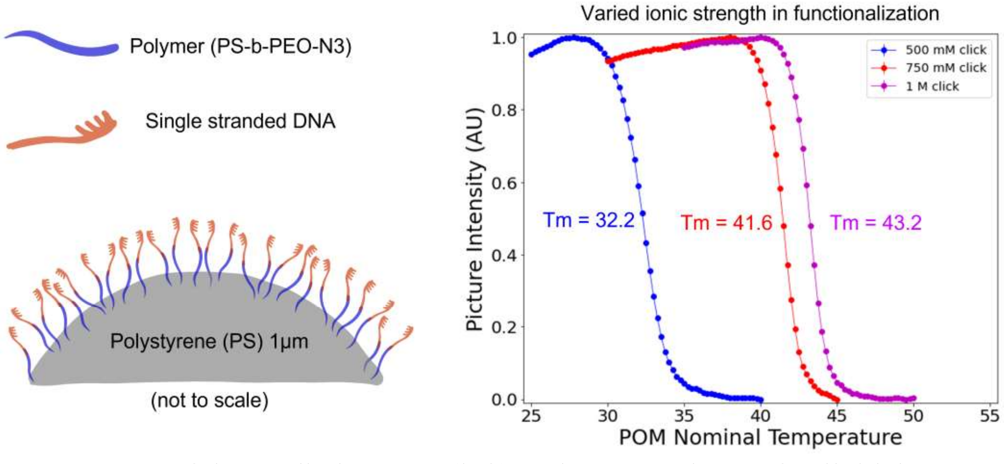

**Figure 1.** Cartoon of the studied system (left) and measured Tm of colloidal suspensions functionalized at varied ionic strength (right).

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The authors acknowledge funding from the European Union's Horizon 2020 research and innovation programme SuperCol under the Marie Skłodowska-Curie grant agreement No. 860914.

# Study on the Mechanical Properties of Interfacial Nanobubbles and Their Interaction with Different Hydrophobic Surfaces

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Due to the unique physical and chemical properties, interfacial nanobubbles (INBs) are widely used in minerals flotation, aquaculture oxygen enrichment, medicine delivery, etc. It is of great significance to understand the special physicochemical characteristics of INBs and the interaction with hydrophilic and hydrophobic surfaces. The morphology of INBs and the interaction between INBs and solid surfaces were investigated by AFM probe tips with different wettability. With hydrophilic probes, it is found that the distance between the first inflection point and the zero point of the approach force curve is equal to the vertical height of the nanobubble [1,2]. There is a positive correlation between the INBs vertical height and the applied force of the tip, i.e., the higher the position of the INBs, the greater is the applied force when reaching the bottom of the INBs. For instance, point a (7.4 nm) and point d (65.4 nm) require 0.7 nN and 6.5 nN, respectively (Figure 1 (a)) [3]. The shapes of INBs are deformed by the medium hydrophobic probe in the horizontal direction, but seriously deformed by the strongly hydrophobic probe. Moreover, the characteristics of the approach force curve show that the dimensions of INBs are underestimated by the medium hydrophobic probe (Figure 1 (b)), however, it cannot be calculated from the force curve tested by the strong hydrophobic probe (Figure 1 (c)). Besides, the maximum attraction and adhesion obtained by the strongly hydrophobic probes are significantly higher than those obtained with the hydrophilic and medium hydrophobic probes.

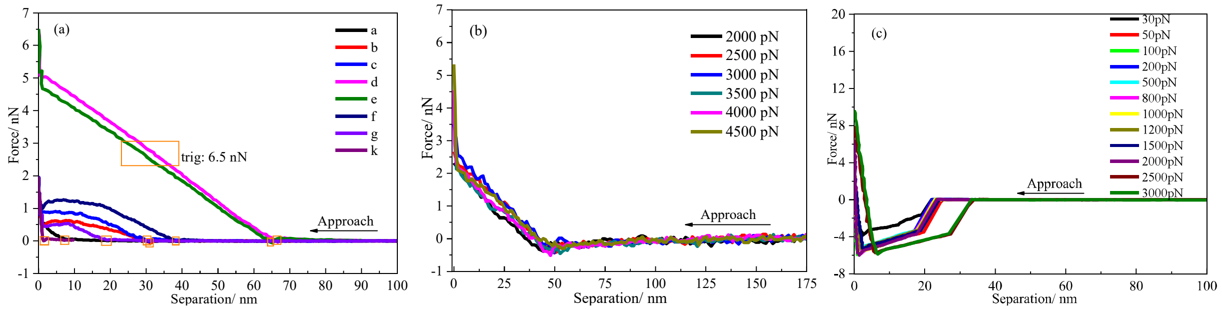

**Figure 1.** Interaction between INBs and AFM probes with different wettability: (a) interaction of an INB with the hydrophilic probe at its different positions; (b) interaction of an INB with the medium hydrophobic probe at its center; (c) interaction of an INB with the strong hydrophobic probe.

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# Microcube Self-Assembly at the Water / Air Interface to Fabricate Multifunctional Microwells for Cell Studies

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Self-assembled objects have been recently identified as an important subclass of smart materials [1]. Unlike the self–assembly of homogenous spherical particles, which possess only one orientation at e.g., the liquid/air interface, the self-assembly of anisotropic, e.g., cubic particles may lead to different structures of aggregates due to different particle orientations at the liquid/air interface [2-5]. Concomitantly, the structure of the aggregates obtained by the self-assembly of cubes (Fig. 1) opens interesting possibility to form combinatorial 3D microwells for systematic cell-environment studies. In particular, the hexagonal aggregates generated by cubes possess different surface properties in an individual microwell. Here we discuss recent progress in the assembly process and the engineering novel 3D microenvironments, which are rendered functional by introducing versatile poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) brushes for controlling the interfacial functionalities. Such microenvironments are beneficial to better understand the interactions of individual cells and cell clusters with their surroundings in 3D.

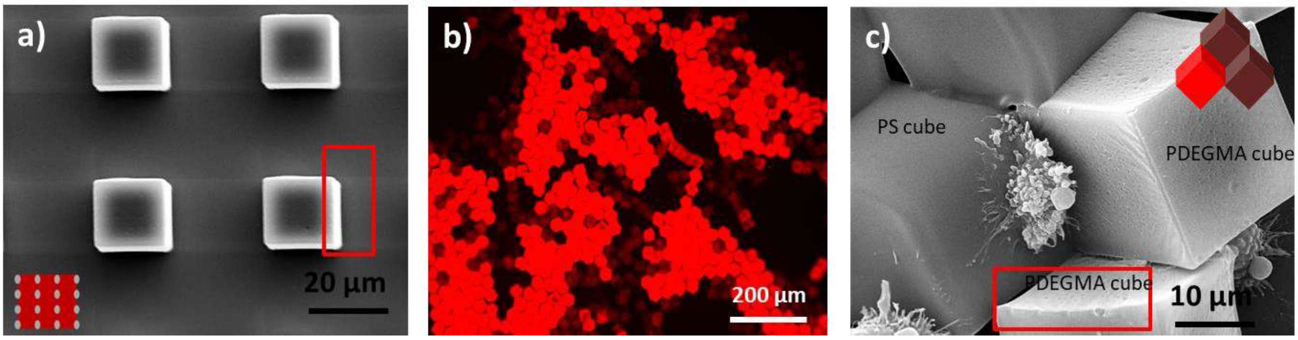

**Figure 1.** a) Scanning electron microscopy (SEM) image hydrophobic cubes fabricated by the hot embossing technique (top surface labeled with nanopoint patterns), the cube surfaces were pre-modified with a ~30 nm thin Au layer. b) Fluorescence microscope image of co-assembly of non-coated PS cubes and functionalized cubes at the water/air interface (all the cubes were labelled with Nile red). The dark red cubes represent the functionalized cubes and the bright red cubes represent the non-coated polystyrene cubes. c) SEM image of PaTu 8988t cells cultured inside the multifunctional microwells, consisting of 25 nm thick PDEGMA brush and non-coated PS surfaces.

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# Generation of local diffusioosmotic flow by light responsive microgels

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Our study shows that microgels trapped at a solid wall can issue liquid flow and transport over distances several times larger than the particle size. The microgel consists of crosslinked poly(*N*-isopropylacrylamide-co-acrylic acid) (PNIPAM-AA) polymer chains loaded with cationic azobenzene-containing photosensitive surfactant, which can assume either a *trans*- or a *cis*-state depending on the wavelength of the applied irradiation.

The microgel, being a selective absorber of *trans*-isomers, responds by changing its volume under irradiation with light of appropriate wavelength at which the *cis*-isomers of the surfactant molecules diffuse out of the particle interior [1]. Together with the change in particle size, the expelled *cis*-isomers form an excess of the concentration and subsequent gradient in osmotic pressure generating a halo of local light-driven diffusioosmotic (*l*-LDDO) flow. The direction and the strength of the *l*-LDDO depends on the intensity and irradiation wavelength, as well as on amount of surfactant absorbed by the microgel. The flow pattern around a microgel is directed radially outward and can be maintained quasi-indefinitely under exposure to blue light when the *trans-/cis-* ratio is 2/1, establishing a photo-stationary state. Irradiation with UV light, on the other hand, generates a radially transient flow pattern, which inverts from inwards to outwards over time at low intensities. By measuring the displacement of tracer particles around neutral microgels during a temperature-induced collapse, we can exclude that a change in particle shape itself causes the flow, i.e., just by expulsion or uptake of water. Ultimately, it is its ability to selectively absorb two isomers of photo-sensitive surfactant under different irradiation conditions that leads to an effective pumping caused by a self-induced diffusioosmotic flow [2].

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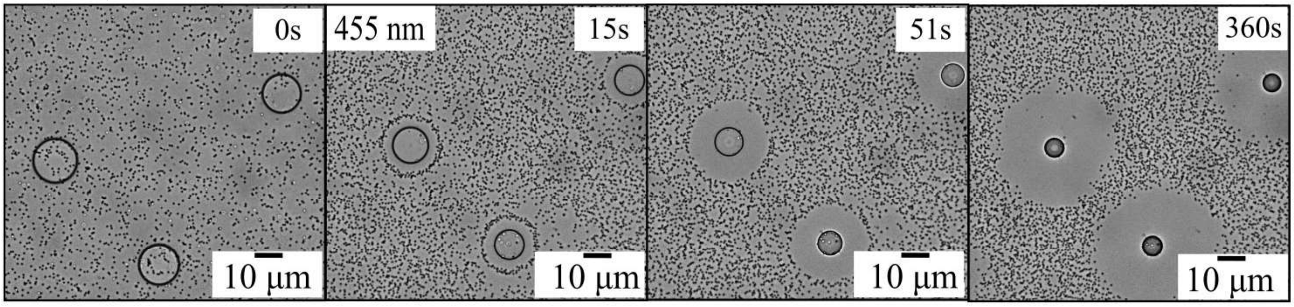

**Figure 1.** Optical micrographs of the microgel and the tracer particles before irradiation (at 0s) and during exposure to blue light (irradiation time is indicated on the micrographs).

# Thermo- and pH-responsive Pickering-emulsions stabilized by NnPAM and NIPMAM core-shell-microgels

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Using thermoresponsive microgels as an emulgator for Pickering-emulsions results in an emulsion that can be broken on demand by varying the temperature. By copolymerizing an acid-function, the emulsion gains an additional pH-responsiveness and can be destabilized by lowering the pH-value.[1] Therefore, these emulsions represent an interesting medium for chemical reactions that involve both water and organic soluble components.[2]

The stabilizing effect of microgels differs from that of rigid particles that are conventionally used to stabilize Pickering-emulsions. Microgels strongly deform at the liquid-liquid-interface to cover a wider area while they adsorb irreversibly. Therefore, the deformability of the microgel is a key parameter for the stabilizing effect.[3]

Usually *N*-isopropylacrylamide (NIPAM) or *N*-isopropylmethacrylamide (NIPMAM) based microgels are used as an emulgator for these emulsions. In this work *N*-*n*-propylacrylamide (NnPAM) and NIPMAM based core-shell microgels copolymerized with methacrylicacid (MAA) containing an NnPAM-co-MAA core, an NIPMAM shell and an additional layer of non-crosslinked NIPMAM dangling ends were used to stabilize emulsions that can by broken by varying the pH and the temperature. By varying the organic phase, it was possible to stabilize both water in oil and oil in water emulsions.

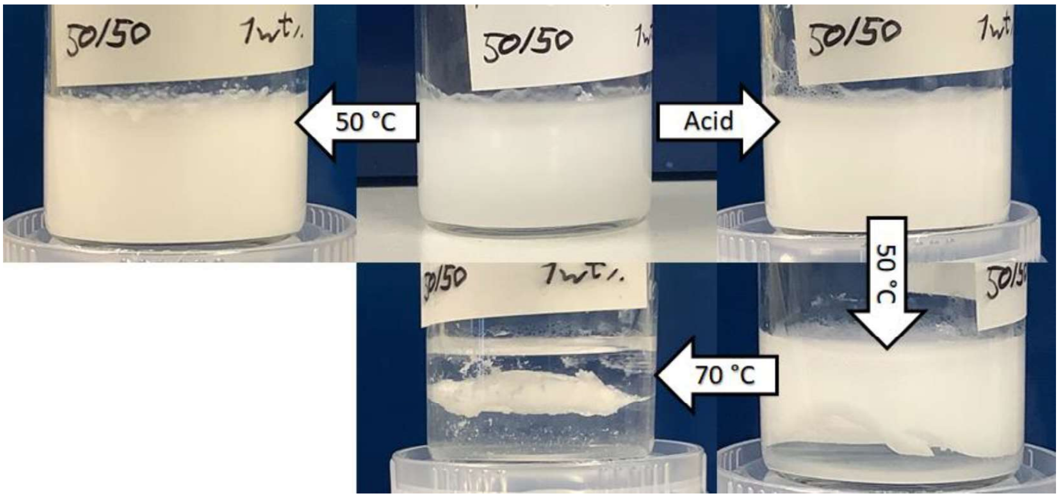

**Figure 1.** Phase separation behavior of an microgel based Pickering-emulsion under variation of the temperature and the pH-Value.

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# Hierarchical Self-Assembly of Triblock Terpolymers into Water-Soluble Multicompartment Micelles[1]

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In nature, compartmentalization into operating regions often functions as a barrier in order to increase efficiency and selectivity of biological reactions. Inspired by that, many scientists focus on the design of multicompartment micelle (MCM) architectures with phase separated nanodomains with applications in cascade catalysis,[2] in nanomedicine as nanocarriers,[3] or to receive stimuli-responsivity. For the design of complex nanostructured MCMs we chose triblock terpolymers as material and a hierarchical self-assembly process as method. Consecutively, in this work we demonstrate the synthesis of amphiphilic PEO-*b*-PS-*b*-PMA triblock terpolymers and their self-assembly into water-soluble spherically patched MCMs on the nanoscale. The synthesis of the triblock terpolymers was achieved by ATRP to receive different degrees of polymerization of the PS and PMA blocks. With control over the block chain length, we obtained terpolymers with systematically varied block weight fractions to research the transformation of the MCMs patch and core morphology. Hierarchical self-assembly was achieved by a stepwise dialysis process using different solvent mixtures. Firstly, spherical Janus precursor micelles were formed, which assemble in a further step to water-soluble MCMs equipped with spherical patches on the surface (**Figure 1**). By means of this strategy, we selectively achieved spheres-on-sphere, spheres-on-cylinder, spheres-on-sheet, and spheres-on-vesicle morphologies, which were confirmed by cryo-TEM.

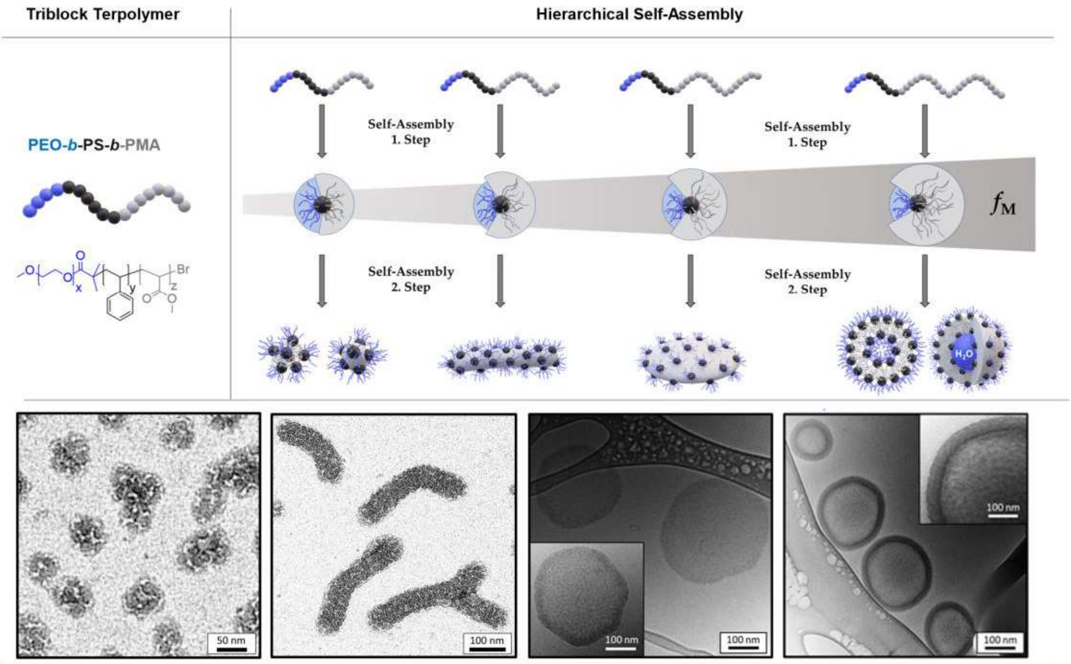

**Figure 1.** (A) Assembly of triblock terpolymers to spherical Janus precursor micelles followed by the formation to diverse MCMs. PEO (blue), PS (black), PMA (grey).[1]

[1] D. Coban, O. Gridina, M. Karg, A. H. Gröschel, *Macromolecules* **2022**, *55*, 1354–1364.
[2] T. L. Nghiem, D. Coban, S. Tjaberings, A. H. Gröschel, *Polymers (Basel).* **2020**, *12*, 2190.
[3] Y. Sun, F. Gao, Y. Yao, H. Jin, X. Li, S. Lin, *ACS Macro Lett.* **2021**, *10*, 525–530.

# Pre-programmed rod-shaped microgels to create multi-directional Anisogels for 3D tissue engineering.

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Microscale anisotropic building blocks have been receiving increasing attention in respect to their use as model systems to study complex phase diagrams, dynamics and self-assembly processes and for their biomedical applications. Tissue engineering is one of them, where rod-like magnetic microgels loaded with superparamagnetic iron oxide nanoparticles (SPIONs) were found to direct cell growth when aligned under a homogeneous magnetic field [1].

We are currently aiming at controlling the magnetic orientation and actuation of such microgels using ferrimagnetic maghemite spindles as anisotropic magnetic fillers instead of SPIONS [2]. Polyethyleneglycol based rod-shaped microgels were designed produced using particle replication in non-wetting templates (PRINT). The maghemite spindles were pre-aligned and self-assembled into dipolar chains during the microgel synthesis as evidenced by the examination of the resulting composite microgels by scanning electron microscopy (SEM) (Figure 1A). This procedure allows us to pre-program the orientation of the composite microgels parallel or perpendicular to the applied magnetic field as shown in Fig. 1B,C. The actuation of these systems by an external rotating magnetic field further offers the possibility to dynamically align the microgels rods with an orthogonal magnetic moment in the third dimension (Figure 1D). When embedded in Anisogels for cell culture, cell growth can be directed in the direction of the pre-programmed microgel rods. (Figure 1E).

[1] J.C. Rose , M. Cámara-Torres, K. Rahimi, J. Köhler; M. Möller; L. De Laporte, Nano Letters, 2017, 17, 3782.

[2] V. Malik, A. Pal, O. Pravaz, J.J. Crassous, S. Granville, B. Grobety, A.M. Hirt, H. Dietsch, P. Schurtenberger, Nanoscale, 2017, 9, 14405.

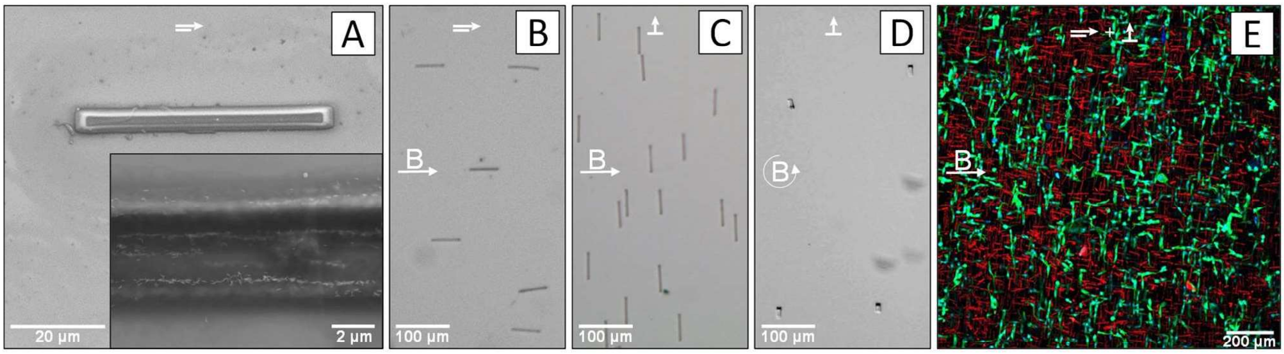

**Figure 1.** (A) SEM image of incorporated maghemite nanoparticles inside a rod-like microgel. (B,C) Bright field micrographs of the composite microgel alignment parallel and perpendicular to the applied magnetic field. (D) Vertical alignment of the composite microgels with an orthogonal magnetic moment under rotating field (70 mT, 10 rpm). (E) Mouse fibroblast cells growing along parallelly and perpendicularly aligned rod-shaped microgels.

# Percolation in binary colloidal systems – introducing direction-dependent thermal properties

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Predicting the properties of a binary mixture of colloids is essential to design new materials for various applications selectively. Several studies exist investigating the behavior of such particle mixtures, investigating full spheres, hollow spheres, and different arrangements of the particles. With these findings, it is possible to predict the thermal and mechanical properties of a material concerning the volume content of its components[1]. The results can be attributed to percolation effects. For particular systems consisting of two particles with various volume fractions, percolation occurs when a continuous connection between the components of one type is formed. Predicting the so-called percolation threshold can be challenging, as it is influenced by the arrangement of the particles and their individual properties. For homogeneous systems, the challenge has been extensively met. But what happens when introducing particles with non-homogenous properties? Does the percolation threshold shift to a higher or lower amount of the anisotropic particles? How does the introduction of direction-dependent properties influence the network behavior?

To study this effect systematically, COMSOL Multiphysics simulations are the tool of choice. This enables the investigation of a vast amount of particle arrangements while changing the particle's properties and vice versa. Furthermore, different particle structures (ordered, disordered) and particle shapes are accessible for statistical analysis. The presented study focuses on the thermal properties of binary mixtures, which can be extended to other mixtures' properties. Therefore, the property of choice to introduce direction-dependency in the system is the thermal conductivity of the single particles. Evaluating the resulting heat flux of the binary colloidal mixture opens the way to establish correlations between structure and the number of anisotropic particles. The final goal is to predict the resulting thermal properties of binary colloidal assemblies containing one or two species of thermally anisotropic components[2].

[1] P. Ruckdeschel, A. Philipp, B. A. F. Kopera, F. Bitterlich, M. Dulle, N. W. Pech-May and M. Retsch, Physical Review E, 97 (2018).

[2] This project was supported by the Bavarian Center for Battery Technology (BayBatt).

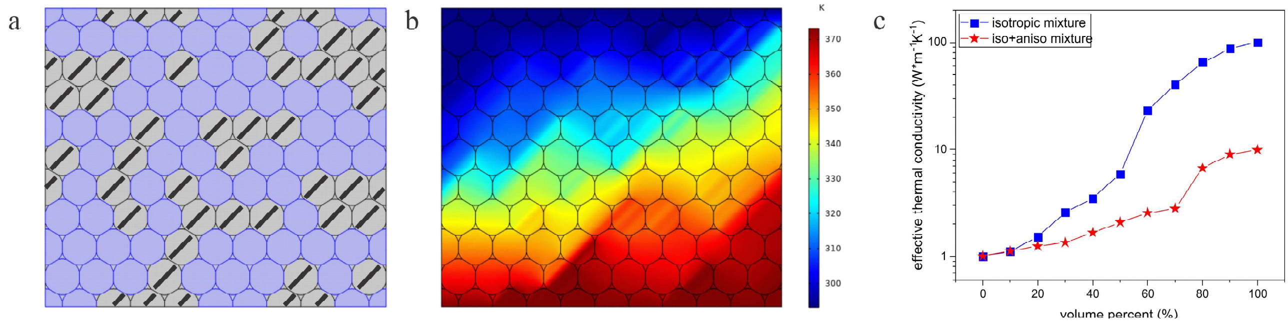

**Figure 1.** a) 2D-view of a mixture of 50 % isotropic particles (blue) and 50 % thermally anisotropic particles (grey). The preferred way of heat conduction is given by the black lines. b) Resulting steady-state temperature distribution for a temperature gradient of 80 K from bottom to top. c) Effective thermal conductivities for different mixing ratios of a system consisting of two isotropic materials (blue) and a system like in a) (red).

# Phase behaviour and percolation of Red Blood Cells

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In the mixture of colloidal particles and polymers, the range and magnitude of the interaction potential can be tuned by the size and volume fraction of the polymers. Depending on the volume fraction of the particles and the interaction potential, colloidal particles and polymers can form a percolated gel-like network.

Similar to colloidal particles, Red Blood Cells (RBCs) exhibit a transition to a solid phase at a sufficiently high enough volume fraction and strong attraction. Depletion and bridging interactions are the two mechanisms for RBC aggregation, underlying the formation of a 3-D network of rouleaux similar to a weak physical gel. Understanding the dynamics of formation and break-up of the 3-D network of RBCs plays an important role in different phenomena, such as RBCs sedimentation or increased hydrodynamic resistance at low shear rates.

In this project, we induce the attraction between RBCs by adding rod-like particles with a high length-to-diameter ratio, as well as small Dextran polymers. The different nature of interaction results in different percolated networks of RBCs. We investigated the phase diagram of the mixture of RBCs and these macromolecules from the gas phase up to percolation using confocal images. To this end, we developed an algorithm to directly determine percolation in 3 dimensions from confocal images of RBCs.

# Control of the light-driven flow direction by the irradiation intensity

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We report on interplay of two surface bound flows emanating from thermo-osmotic and diffusio-osmotic mechanisms. The orthogonally directed flows are generated at the gold surface immersed into an aqueous solution containing photo-sensitive surfactant during irradiation with focused light. At low power of incoming UV light, the diffusio-osmotic mechanism generated due to local photo-isomerization of the surfactant dominates resulting in the flow directed out of the irradiated area (**Figure 1a**).[1,2] While at larger power thermo-osmotic flow takes over due to local heating of the gold surface and the flow points towards the hot spot.[3] To image flows, we utilize colloids as tracer particles which can be visualized in an optical microscope.
By simple turning the power one can reversibly sweep the liquid flow between outwards and inwards with an intermittent range of zero flow at which tracer particles undergo only thermal motion (**Figure 1b**). Our work demonstrates an optofluidic type of flow generation enabling a high degree of the net motion control necessary to transport particles precisely on desired locations, which opens a new possibility to generate novel and advanced microfluidic applications.

[1] D. Feldmann, S.R. Maduar, M. Santer, N. Lomadze, O.I. Vinogradova and S. Santer, Sci. Rep. 6 (2016), p. 36443.
[2] P. Arya, J. Jelken, N. Lomadze, S. Santer and M. Bekir, J. Chem. Phys. 152 (2020), p. 024904.
[3] B. Ciraulo, J. Garcia-Guirado, I. de Miguel, J. Ortega Arroyo and R. Quidant, Nat. Commun. 12 (2021), p. 2001.

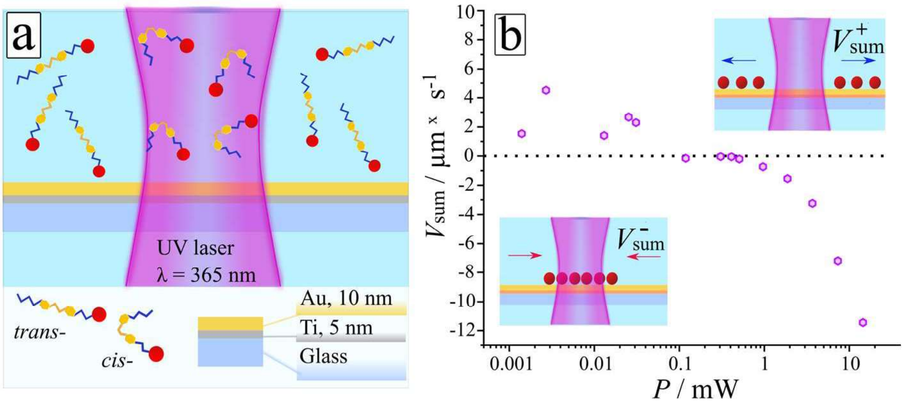

**Figure 1.** (a) Schemes of the sample: a glass surface is covered by gold layer; the solution above contains tracer particles (red spheres) and photo-sensitive surfactant (cis- and trans- isomers). (b) The average velocity of silica particles as a function of the laser intensity. Inset in the upper right corner representing positive velocities are related to outwards flow, while the negative velocities are assigned to flows pointing towards the laser beam. The laser (λ=375nm) is focused at the Au/liquid interface.

# Near-infrared reflective coatings

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[2] Department of Civil Engineering-Construction Materials, Institute of Science, Akdeniz University, Antalya, Turkey

The sun's rays hitting the Earth's have a wide spectrum of wavelengths, from ultraviolet to infrared. The absorption of near-infrared (NIR) rays, which constitute 53% of the sun's total rays, is responsible for the heating of objects [1, 2]. The amount of NIR rays increases during the summer season, causing the walls and roofs of buildings to overheat. To reduce the discomfort felt in warm buildings, the usage of air conditioning increased. Buildings coated with a NIR reflective paint absorb less energy, resulting in a 20% - 40% energy savaging through reduced use of air conditioning systems [3, 4].

In this study, different NIR reflective coatings have been prepared by sol-gel reaction of tetraethoxysilane, methyltrimethoxysilane, and $TiO_2$ based inorganic NIR reflective pigments. The coatings morphology and spectral reflectance were investigated by SEM and UV-VIS-NIR spectrophotometry, respectively. NIR solar reflectance (%) performance of coatings was calculated to examine the effect of pigment concentration on reflectance performance. The coatings showed a maximum of 89% NIR solar reflectance.

[1]Levinson, R., P. Berdahl, and H. Akbari, Solar spectral optical properties of pigments—Part I: model for deriving scattering and absorption coefficients from transmittance and reflectance measurements. Solar Energy Materials and Solar Cells, 2005. 89(4): p. 319-349.
[2]Kaur, B., et al., Near-infrared reflective properties of perylene derivatives. Dyes and Pigments, 2012. 92(3): p. 1108-1113.
[3]Parker, D.S. and S.F.B. Jr., Roof Solar Reflectance and Cooling Energy Use Field Research Results From Florida. Energy and Buildings, 1997. 25(2): p. 105-115.
[4]Synnefa, A., M. Saliari, and M. Santamouris, Experimental and numerical assessment of the impact of increased roof reflectance on a school building in Athens. Energy and Buildings, 2012. 55: p. 7-15.

# Poly (ionic liquids) templated molybdenum nitride nanoparticles

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The incoming novel approach of hybrid materials has made possible to fulfill various function in a nanoscale range. Among them, molybdenum-based hybrid materials are highly desired for their tunable crystal structure, tunable composition, high temperature and pressure window usage [1-2]. Herein, it is reported a facile method to synthesize templated molybdenum nanoparticles (Mo-NPs) within poly(ionic liquids) (PILs) as main carbon source. Poly(3-*n*-Decyl-1-vinylimidazolium Bromide) was coated with polydopamine (PDA), subsequently coordinated with ammonium orthomolybdate ($(NH_4)_2MoO_4$), followed by calcination in argon atmosphere at 600 °C. Overall, the morphology of PILs after calcination resembles that of porous particles formed by the absorbed Mo-crystal, according to TEM images (Figure 1 a-b). In addition, $Mo_2N$ nanoparticles have been successfully obtained and confirmed by X-ray diffraction (XRD) (Figure 1 c). [3]

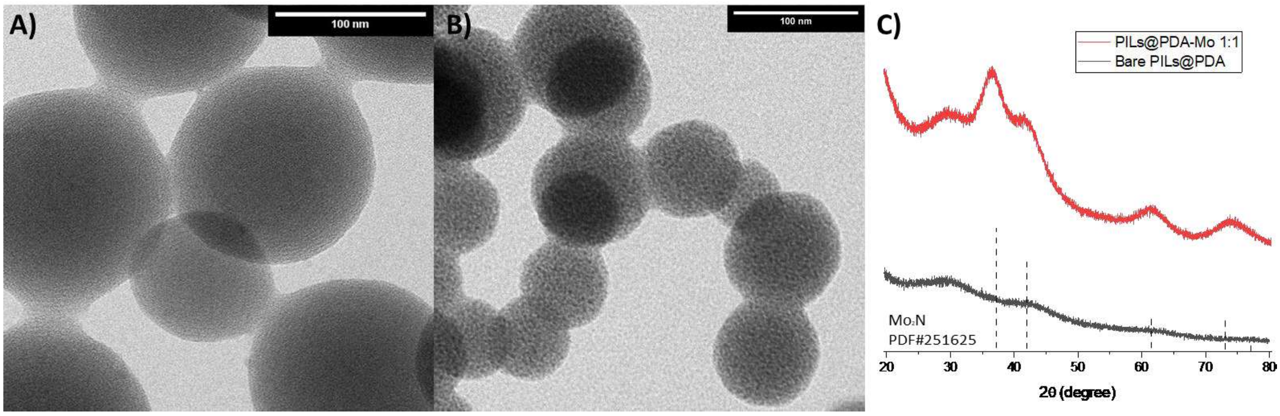

**Figure 1.** PILs template TEM images, a) after $(NH_4)_2MoO_4$ coordination, b) after calcination, and c) XRD of templated Mo-NPs after calcination

[1] Henghan Dai, Lumin Wang, Yue Zhao, Jialu Xue, Ruicong Zhou, Chenyang Yu, Jianing An, Jinyuan Zhou, Qiang Chen, Gengzhi Sun, Wei Huang, , Research, vol. 2021.
[2] Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu, and H. J. Fan, Advanced Science, vol. 3, no. 5, 2016.
[3] The authors acknowledge Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for financial support.

# Towards rapid prototyping of graded macroporous polymer foams

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Graded polymer foams (GPFs) confer substantial mechanical stability in a lightweight form to various natural and technical materials. Their versatile properties are particularly sought after in applications such as energy absorption, insulation, or tissue engineering. For example, ideal bone mimics for tissue engineering recapitulate the solid skin as well as the density gradient towards its center in a way that allows cells and fluids to move freely within. GPFs can be produced using microfluidics (MFs), 3D printing or reaction injection molding. The resulting polymer foam properties can be tuned by using different polymers or by varying their morphology.

Foam templating using microfluidics allows one to adjust GPF parameters like the pore size, the degree of polydispersity and even the window size of the interconnection between pores with ease. Moreover, it can be scaled to liter per hour production rates [1-3]. However, attainable bubble sizes remain usually limited to roughly 100 – 1000 µm and only spherical structures can be produced. Costantini et al. [4] introduced a PDMS chip to formulate gradient foams (Fig. 1 (left)) with controlled bubble sizes spanning one order of magnitude in real time. Conversely, additive manufacturing of GPFs using two-photon-polymerization (2PP) or stereolithography (SLA) offers tantalizing avenues. Fused filament deposition molding allowed Bates et al. [5] to create density gradient scaffolds of ~1 cm honeycombs (Fig. 1 (right)). Improved energy absorption and damping profiles were observed for the graded honeycombs compared to their uniform counterparts. While freeform additive manufacturing usually covers extensive design space freedom, their sequential fabrication puts stringent limits on suitable fabrication volumes, especially for highest resolutions.

This work seeks to establish a combined microfluidic SLA 3D-printing approach for the synthesis of GPFs to combine the advantages of both techniques. For this purpose, ultracompact 3D microfluidic engineering [6] will be tailored for rapid foam production rates, increased bubble size ranges, as well as precise local foam property control. The morphology and the mechanical properties of the resulting GPFs are studied and compared. Our approach will expand the scope of designing innovative gradient and graded materials for tissue engineering, energy absorption, or insulation applications in the future.

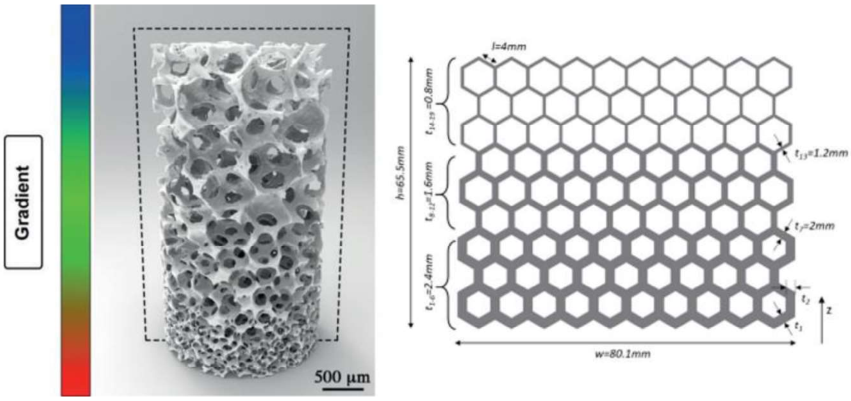

Figure 1: (left) 3D reconstruction of graded porous material [4]. (right) Density graded honeycombs [5].

[1] C. Stubenrauch et al., Angew. Chem. Int. Ed. 57 (2018), 10024 -10032. [2] S. Andrieux, A. Quell, C. Stubenrauch, W. Drenckhan, *Adv. Colloid Interf. Sci.*, 2018, *256*, 276-290. [3] F. Dehli et al., Journal of Colloid and Interface Science 588 (2021), 326-335. [4] M. Costantini, et al., Angew. Chem. Int. Ed. 58 (2019), 7620 -7625. [5] S. R.G. Bates et al., Materials and Design 162 (2019), 130-142. [6] J.L. Sanchez Noriega et al., Nat Commun 12 (2021), 5509.

# Synthesis of Plasmonic Silver Nanowires and Their Surface Modification with Organic Emitters

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Hybrid inorganic-organic plasmonic nanostructures coupled to organic emitters are interesting building blocks for future nanophotonic devices. For example, dye-modified silver nanowires can be used for sub diffractional waveguides (to localise light to nanoscale and guide them to a certain direction) and for chiral sensing (where the organic dyes facilitate detection of the directional, propagating plasmons) [1]. Here I show recent works on our hybrid nanostructure, which consists of modified perylene diimide (mPDI) embedded in a thin silica shell (~8 nm) around the colloidal silver nanowires. I will cover the synthesis of these nanowires and their surface modification [1]. Then I will briefly discuss their use as a chiral sensor and share our latest findings on the photobleaching process of the embedded emitters.

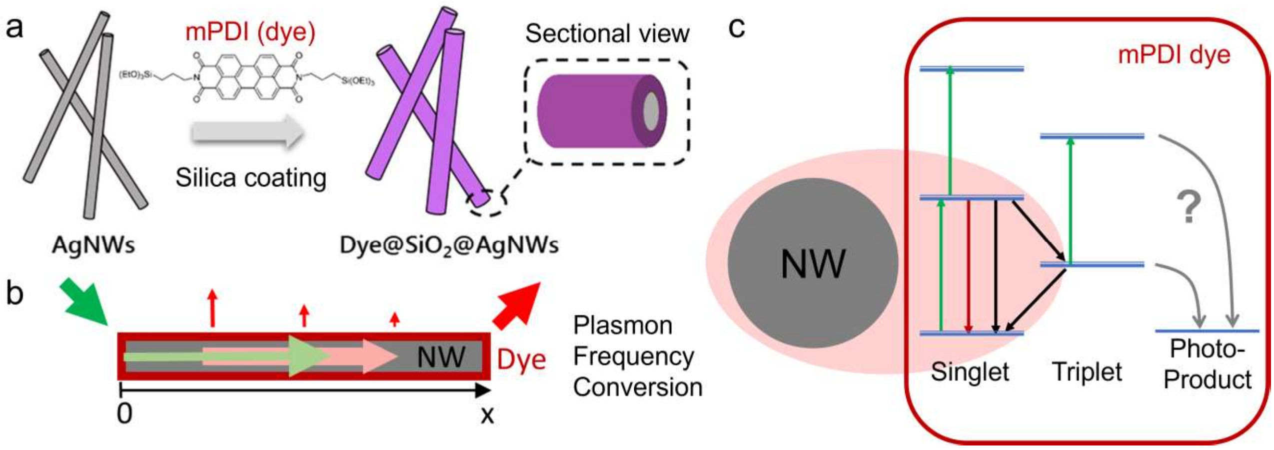

**Figure 1.** a) Schematic of embedding organic dyes to the silica shell of silver nanowires (NW) to form the metal-organic plasmon converter [1]. b) Schematic of the photobleaching experiment [2]. A single nanowire is excited by a 532 nm continuous wave laser on one end (green arrow). The energy from the laser excites the propagating plasmons (light green arrow) and is also frequency converted (light red arrow). The fluorescence emitted from the dyes are measured (red arrows). c) Simplified Jablonski diagram of the embedded mPDI dye molecules. Green arrows represent excitation, red arrow fluorescence, black arrows non-radiative decay and grey arrows as the irreversible bleaching of the mPDI.

[1] M. Rothe et al. *ACS Nano* **2021** *15* (1), 351-361
[2] M. Rothe et al. *Optics Express* **2022** *submitted*
[3] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG), Sonderforschungsbereich 951 (SFB 951), Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS)

# Duo-stimuli microgels for the control of cell adhesion

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One of the major difficulties in the treatment of cancer is the formation of metastases. Since metastases are often caused by circulating tumor cells (CTCs), their early detection is of great importance. Strategies to isolate and detect CTCs include specific targeting via ligand-receptor interactions, e.g. by using cancer-related receptors like CD44 and their natural ligand hyaluronic acid [1, 2]. Our aim was to create a gentle isolation method for CTCs with hyaluronic acid -functionalized switchable microgels.

For this purpose, HA-functionalized thermoresponsive microgels based on poly-(N-isopropylacrylamide) were prepared and coated on glass surfaces. The prepared microgels were evaluated for size, degree of swelling, surface charge, and ligand functionalization, all parameters that were shown to affect cell attachment. We expected that when the temperature was increased above the lower critical solution temperature (LCST) of 32°C, the cells would show increased binding to the microgels due to an increase in hyaluronic acid density at the microgel surface. When the temperature was lowered below the LCST, the cells would detach due to the lower hyaluronic acid density and the brush-like conformation of the microgels. Therefore, extensive cell adhesion studies were performed on the microgel surfaces at 37°C and 20°C using microscopy and automated cell counting. To enable even more effective detachment of adhered cells, a dual-switchable microgel surface was developed. For this purpose, the hyaluronic acid was coupled to the microgel via a UV-labile linker, which was cleaved off under UV irradiation. Overall, moderately selective adhesion of cells to hyaluronic acid -functionalized microgels was observed, and detachment of cells below LCST was demonstrated as intended. Additionally, it was shown that the adhered cancer cells could be released more efficiently when the UV-labile linker was used. [3]

[1] M. Wang, Y. Xiao, L. Lin, X. Zhu, L. Du, X. Shi, *Bioconjugate chemistry*, **2018**, *4*, 1081–1090.
[2] S. Martin, H. Wang, T. Rathke, U. Anderegg, S. Möller, M. Schnabelrauch, T. Pompe, S. Schmidt, *Polymer*, **2016**, 342–349.
[3] Schmidt M, Franken A, Wilms D, Fehm T, Neubauer HJ, Schmidt S, *ACS Applied Bio Materials* **2021**

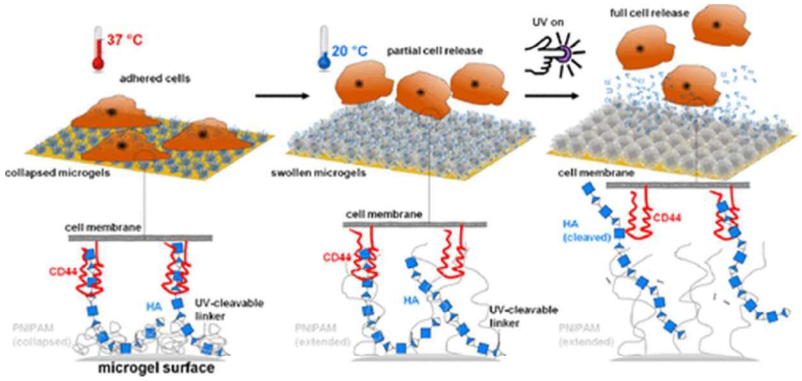

**Figure 1.** Illustration of the surfaces coated with dual-stimuli responsive HA-functionalized microgels and the expected cell release by temperature and light stimulus.

# Effect of surface conductivity on zeta potential of latices in electroacoustic measurements.

Matthias Frangenberg[1], Prof. Dr. Annette M. Schmidt[2] and Prof. Dr. Jan Wilkens[1]

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The measurement of electroacoustic colloidal vibration current (CVI) can be used to determine zeta potential of particles even in highly concentrated dispersions without dilution [1]. Most publications analyzing zeta potential with the CVI method have studied concentrated inorganic dispersions. Publications dealing with concentrated polymer latices are quite rare [2].

Surface conductivity effects can often be neglected for the evaluation of CVI experiments. This has considerable advantage because the evaluation of CVI results is associated with significantly less effort. However, our current results indicate that for most of the latex samples we have studied, the consideration of surface conductivity effects is mandatory. Neglecting this would lead to measurement errors of nearly up to 50% in case of very high particle volume fractions, as can be seen in Fig. 1 right side. Surface conductivity effects can be taken into account by determining the Dukhin number $Du = K^{\sigma}/(a \cdot K_{\mathrm{m}})$, which relates surface conductivity $K^{\sigma}$ to conductivity of the medium $K_{\mathrm{m}}$ and particle radius $a$ [3]. The Dukhin number itself was determined by measuring the conductivities of dispersion and medium, $K_{\mathrm{s}}$ and $K_{\mathrm{m}}$ respectively at different particle volume fractions $\varphi$. For this purpose, relative conductivity $K_{\mathrm{s}} \cdot K_{\mathrm{m}}^{-1}$at different particle volume fractions has to be fitted by means of Maxwell-Wagner-O'Konski theory (Eq.1) [4].

$$\frac{K_{\mathrm{s}}}{K_{\mathrm{m}}} = \frac{1 + Du - \varphi(1 - 2Du)}{1 + Du + 0{,}5\varphi(1 - 2Du)} \tag{1}$$

[1] A. S. Dukhin et al., *Langmuir* 15, (1999) p. 6692–6706.
[2] Y. Ishikawa et al., *Colloids Surf. B.* 46 (2005) p.147–151.
[3] J. Lyklema and M. Minor, *Colloids Surf. A* 140 (1998) p. 33–41.
[4] A. S. Dukhin and P. J. Goetz in "Characterization of Liquids, Dispersions, Emulsions, and porous Materials Using Ultrasound - 3rd. Edition" ed. A. S. Dukhin (Elsevier, Amsterdam) p. 19–83

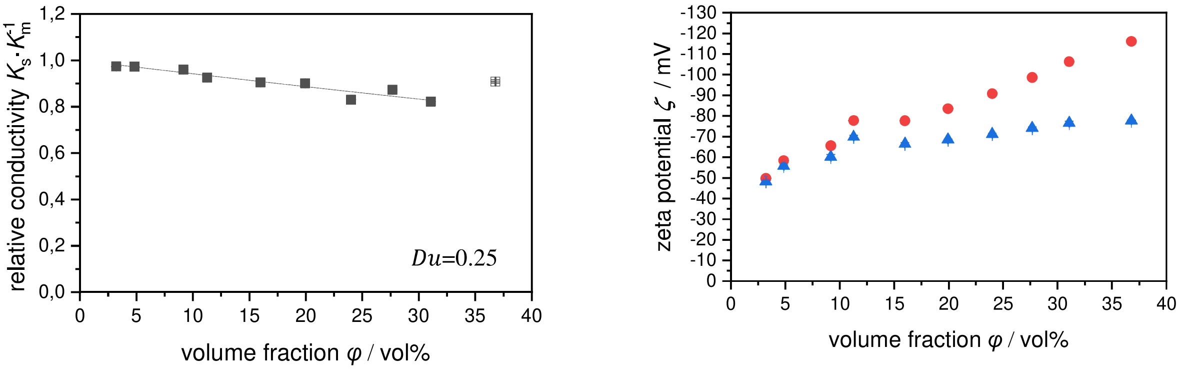

**Figure 1.** Results of an PVC latex with a $d_{50}$=0,79 µm. Left side diagram shows relative conductivity data (■). By fitting data to Maxwell-Wagner-O'Konski theory, a Dukhin number of 0.25 was obtained (solid line). The diagram on the right shows the zeta potential without taking surface conductivity into account (●) and taking surface conductivity into account (▲).

# Interface Driven Atomically Oriented 2D Assembly of Colloidal Gold Nanodisks Leads to Tunable Plasmonic Resonance

Santanu Maiti[1,2,3], Milan K. Sanyal[1], Andrei Chumakov[4], Oleg Konovalov[4], Ali Hossain Khan[5], Subrata Maji[5], and Somobrata Acharya[5]

[1]Surface Physics and Materials Science Division, Saha Institute of Nuclear Physics, Kolkata, India
[2]Institute of Applied Physics, University of Tübingen, Tübingen, Germany
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[4]ID10, The European Synchrotron (ESRF), 38000 Grenoble, France
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Colloidal Nanoparticles (NPs) are broadly used to produce self-assembled superstructures, however, a little have been achieved on the 2D assembly of NPs with anisotropic shapes[1]. A key challenge with the anisotropic NPs is to assemble them into long-range positional and orientational order. We synthesize disk-shaped colloidal gold nanocrystals (AuNDs) and assemble them into two-dimensional iso-oriented ordered superlattices at the air-liquid interface using Langmuir method[2-3]. *In-situ* structural and optical properties of the ND assemblies have been monitored using grazing incidence small-angle X-ray scattering (GISAXS), X-ray reflectivity (XRR), grazing incidence X-ray diffraction (GIXD) and UV-vis spectroscopy. Au NDs assemble into a highly ordered 2D hexagonal superlattice and align preferentially with a specific atomic orientation at the air-liquid interface. A continuous blue shift of the plasmonic peak has been observed from the coherent ND assembles with increasing surface pressure[4]. Such preferentially oriented anisotropic NCs is expected to lead to novel optoelectronic properties, which have promising prospects for future applications.

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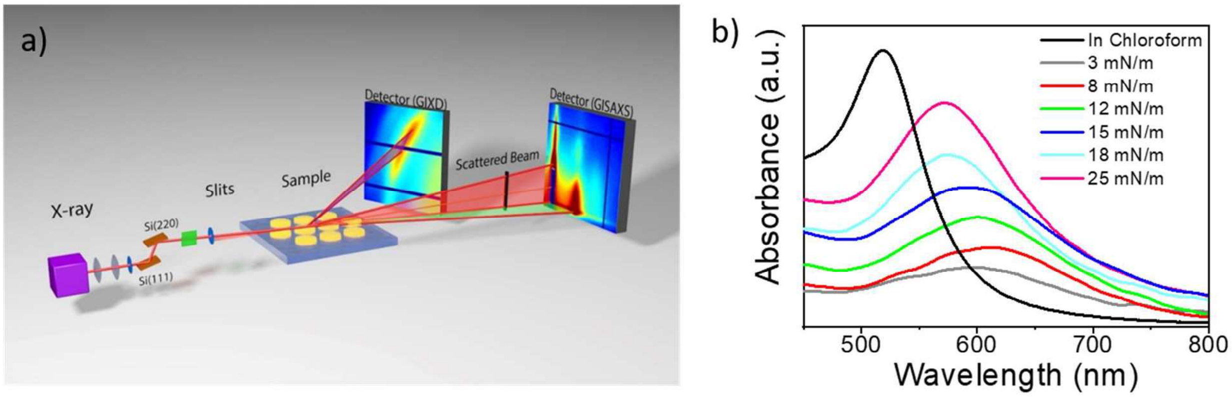

**Figure 1.** a) A schematic of simultaneous GISAXS, GIXD geometry to study *in-situ* self-assembly at the air-water interface. b) UV-vis absorption spectra of AuND superstructure films.

# Cloud point, auto-coacervation, and nematic ordering of micelles formed by ethylene oxide containing carboxylate surfactants

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Independently of temperature and concentration, only spherical or slightly prolate micelles are formed in binary solutions of octyl ether octaethylene oxide carboxylic acid ($[H^+][C_8E_8c^-]$, Akypo™ LF2) in acidic, sodium and calcium forms, due to the surfactant's strong packing constraint. In the presence of sodium or calcium ions, the micelles cannot only be negatively charged, but also intermicellar cross-linking is made feasible by divalent calcium ions or by two monovalent sodium ions. Even in the presence of multivalent ions, the micelles are stable only in two morphologies: the classical core-shell state ($L_1$) and the water-poor state with partially interdigitated head-groups ($L_1^{'}$). At the borderline of these two regimes, the 'flocculated' micellar regime ($L_1/L_1^{'}$), probably a new wormlike hexagonal (WH) phase made from linear chains of charged prolate micelles is found. The peak shift in SAXS/SANS suggests that the WH phase is an unusual lyotropic liquid crystalline phase because the hydrocarbon cores have the same shape as in the micelles. The WH phase of $[X^+][C_8E_8c^-]$ shares some characteristics with a proposed transition from a classical hexagonal phase of infinite cylinders ($H_1$) to a cubic Im3m phase by Sakya et al. [1] in binary mixtures of $C_{12}E_{12}OH$ and water. Sakya et al. proposed that undulations form in the hexagonally packed cylinders with the cylinders subsequently being 'pinched' at regular intervals to form the isotropic cubic phase made of spherical micelles. In the case of $[X^+][C_8E_8c^-]$, however, neither a $H_1$ nor a cubic phase are observed. Instead of a cubic phase made of spherical micelles, a hexagonal phase made of prolate micelles is found. An increase in temperature leads to a decrease of the average number of micelles per chain, 'melting' the hexagonal phase into a nematic phase (N) and eventually into an isotropic micellar phase. While there are some examples of nematic phases made of prolate or oblate micelles made of charged surfactants and a co-surfactant in literature [2,3], they always involve a micellar shape transition through the right ratio between surfactant and co-surfactant. Thus, they are intermediate states between lamellar or $H_1$ phases and do not form a hexagonal phase made of the same prolate or oblate micelles but have a shape transition to cylinders. In the present case, there is no shape transition involved and all phases are made of the same prolate micelles. The presence or absence of a lower critical solution temperature (LCST) located on the clouding line is related to intermicellar interactions between small spherical or prolate micelles. Clouding is driven by intermicellar attraction and impeded by electrostatic repulsion. If electrostatics are screened, ion bridging can enhance intermicellar attraction especially well at higher concentrations (in the $L_1/L_1^{'}$ phase), thus lowering the LCST and shifting it to higher concentrations. Auto-coacervation triggered by polar head-group heterogeneity occurs as equilibrium between a sub-critical micelle concentration bulk phase and small quantities of a coacervate that is made of macroscopically observable droplets formed by flocculated, partially head-group interdigitated micelles.

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# Multicompartment Micelles and Cubosomes from Redispersion of Triblock Terpolymer Bulk Films

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Compartmentalization is ubiquitous in nature, considering for example the working principle of cells and organelles. Despite nature complexity, synthetic counterparts, that could mimic their compartmentalized character, represent an emerging trend. ABC triblock terpolymers are the ideal candidates for the formation of multicompartment micelles (MCMs), due to the possibility to synthesize building blocks, with different chemistries, which can microphase separate in nanocompartments.

In the present work, we investigate the formation of MCMs out of ABC triblock terpolymers, *i.e.,* through redispersion of polymeric bulk films in selective solvents. In particular, we employ polystyrene-*block*-polybutadiene-*block*-poly(*tert* butyl methacrylate) (SBT) triblock terpolymers in acetone/isopropanol solvent mixtures of varying composition (). The largely different block compositions result in diverse morphologies, including spheres-on-spheres, -cylinders, -bilayer sheets and -vesicles, helix-on-cylinders, striped sheets and vesicles, as well as sheets and vesicles with a bicontinuous membrane. Interestingly, below a critical PT corona length ($f_{\mathrm{PT}}$ = 5-7 wt%), we were able to identify the first reported example of a multicompartment cubosome (MCC), which in our case consist of a lamella-lamella membrane morphology. We modified these MCCs for catalytical applications by first crosslinking of the PB middle block (outer wall of the membrane) followed by loading with catalysts (*e.g.*, metal nanoparticles such as Pt NPs). Hydrolysis of the PT corona block further converts the MCCs into water-soluble and porous catalyst scaffolds, while the PS inner walls maintain structural stability. Hybrid MCCs loaded with Pt NPs (MCC@Pt) were employed for reduction of methylene blue (MB) to leuco MB, which resulted in enhancement of reaction time. We foresee that such MCCs will serve as platform for catalytical applications due to their larger surface area, porous structure, and overall chemical and mechanical stability.

GQ and AHG are grateful for financial support from the DFG through the Emmy Noether Program (GR5075/2-1). SA is grateful for Evonik foundation for doctoral fellowship.

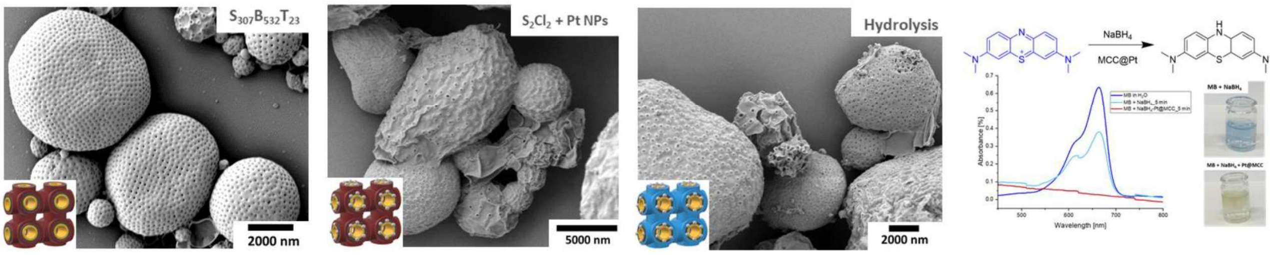

**Figure 1. Multicompartment Cubosomes (MCCs) for catalysis application.** a) Schematic of formation of water soluble MCCs@Pt; b) $S_{307}B_{532}T_{23}$ in acetone/isopropanol 30:70 v/v; c) MCCs crosslinked with $S_2Cl_2$ and loaded with Pt NPs; d) Hydrolysis and redispersion in $H_2O$; e) Reduction of methylene blue to leuco methylene blue catalysed by MCC@Pt.

# Janus particles: Challenges in the preparation process and self-thermophoretic propulsion

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Inspired by biological microswimmers (e.g., sperm or flagellated bacteria), scientists began creating artificial microswimmers in the early 21st century. Active colloidal particles with different functionalities at their opposite sides are named Janus particles - motivated by the Roman mythological god. The anisotropy in the particle architecture enables them to generate an out of equilibrium condition around the particle under the right environment, which is a precondition to induce self-propulsion. One possible propulsion mechanism is thermophoretic self-propulsion. When laser light ($\lambda$ = 532 nm) illuminates a gold-capped particle, a local temperature gradient is generated along the particle surface due to surface plasmon excitation of the gold cap. This gradient perturbs the equilibrium conditions of the surrounding medium and finally leads to particle self-propulsion.

This contribution focuses on various preparation processes of self-thermophoretic gold-polystyrene (Au-PS) microswimmers. The influence of the preparation technique on the gold cap size and the resulting self-thermophoretic behavior of the Janus particle will be presented. For this purpose, Janus particles are prepared either by metal sputtering or thermal evaporation or by a combination of gel trapping technique and metal sputtering. With scanning electron microscopy (SEM), the dimension of the gold cap was investigated. Dark-field microscopy (DFM) combined with a LabView program enables real-time tracking of the Janus particles. The study shows that the preparation method of the Janus particle has a strong effect on the size of the gold cap.

[1] The SEM images were recorded in the materials department at GSI Helmholtzzentrum für Schwerionenforschung GmbH.

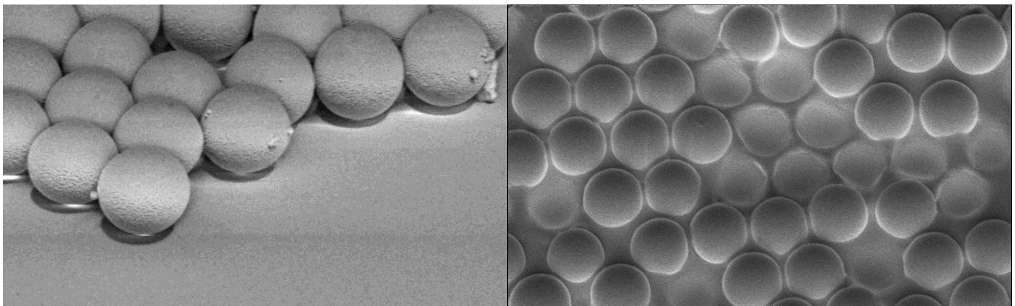

**Figure 1.** SEM images of Au-PS Janus particles after thermal evaporation (left) and particle embedding + metal sputtering (right). The scale bar represents a length of 1 µm in both images [1].

# Mesoporous multicompartment microparticles consisting of semi-crystalline polystyrene-*block*-polybutadiene-*block*-poly(*L*-lactide) (SBL) triblock terpolymers

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Confinement-Assembly of block copolymers (BCPs) are a powerful tool to design a variety of diverse internal structures of multicompartment microparticles (MMs). In particular, mesoporous MMs are highly beneficial and provide promising applications in catalysis, nanomedicine, or energy storage [1]. Nevertheless, less knowledge is gathered about degradation of individual microdomains domains in order to generate mesoporous microparticles with highly complex morphology.

In this contribution, we show the formation of MMs from SBL triblock terpolymers with a semi-crystalline and degradable P*L*LA block. First, SBL triblock terpolymers with different block compositions were synthesized by anionic vinyl and ring-opening polymerization before transformation into MMs *via* evaporation-induced confinement assembly (EICA). After EICA process, we dominantly achieved hexagonally-packed cylinders with a PS matrix, a P*L*LA core and a PB shell. To obtain control about particle size and narrow distribution, the MMs were fabricated through *Shirasu Porous Glass* (SPG) membrane emulsification technique. Furthermore, the variation of the block composition and the affect of the crystallinity exhibit influence on the inner morphology. Degradation studies were performed under basic conditions for selective removal of the P*L*LA domain and reveal mesoporous SBL MMs with clear surface roughness.

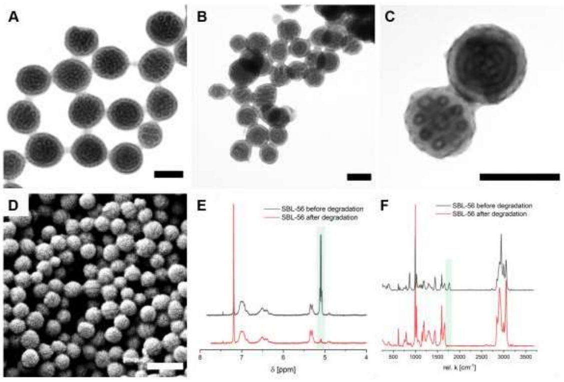

**Figure 1. Degradation study of the smallest SBL-56 MMs ($\mathbf{d_{pore} = 0.3\mu m}$) under basic conditions in a course of 5 days**. TEM overview before (A) and after (B) degradation experiment (scale bars: 200 nm), C) TEM close-up image and D) SEM images after degradation (scale bars: 500 nm), E) $^1$H-NMR and F) Raman analysis before (black) and after degradation (red) [2].

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# Influence of the hardness on the crystallization behavior of binary polystyrene microgel systems

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Polystyrene (PS) microgel colloids can be used as model systems for hard spheres (HS). Binary mixtures of dispersed small (S) and large (L) PS particles with diameter ratios of S to L close to $\Gamma = 0.8$ have been widely used to investigate glass formation [1]. In purely hard sphere $\Gamma = 0.8$ mixtures the crystallization was found to be kinetically suppressed around the eutectic composition [1,2]. In contrast, simultaneous formation of single component fcc crystals of both components could be enforced at a volume fraction slightly below the glass transition upon addition of a critical amount of free (depletion) PS polymer [3].

Recent investigations of a binary PS microgel system revealed crystallization near the glass transition volume fraction already in case of purely repulsive interactions [4]. Hynninen et al. predicted the so called Laves phases in the investigated region [5]. Static light scattering revealed the crystal structure of the binary system to be $MgZn_2$, a Laves phase of the type $AB_2$, with an axial ratio consistent with the ideal axial ratio of $c/a = 1.633$. Such Laves phases are of great interest as precursors for the preparation of photonic band gap materials [6,7]. To investigate the crystallization behavior further, we varied the hardness of the PS particles via crosslinking [8]. LaCour et al. predicted that softer particles have a broader region for Laves phases which decreases with higher particle hardness [9]. We prepared and analyzed bimodal systems with different hardness of L and S. By analyzing the crystallization behavior of the different compositions, we found that Laves phases can only be observed if L is the hard and S is the soft component.

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# Control of Gold Nanoparticle Suspension Stability by Salt Concentration, Ion-Type and Aging

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Nanocomposite materials based on inorganic inclusions inside an organic matrix are employed in various fields: medical technology, catalysis, materials engineering. Combining the properties of both material classes facilitates high versatility of mechanical, optical and chemical properties, while simultaneously covering obvious drawbacks, e.g. toxicity of many inorganic compounds. One prominent sub-class features gold nanoparticles (AuNPs) in an arbitrary organic matrix (e.g. a polymer brush), since gold provides a distinct set of properties: easy synthesis with variable, well-defined size; versatile surface functionalization via gold-thiol chemistry; antimicrobial behaviour; display of localized surface plasmon resonance (poss. in the visible spectrum) that is sensitive to AuNP parameters (size, shape) and the environment (solvent, neighbouring AuNPs).

To provide the wide range of applications, nanocomposite materials usually require a specific internal structure. Yet, the understanding of the formation of internal structure and control over formation process is still lacking. Therefore, the long-term goal of our project aims to provide an approach to manufacture nanocomposite materials with controlled structure. The model system utilizes salt concentration and ion-specific effects as stimulus to guide the assembly process, since the stimulus is variable and already proven to work [1]. Prior to structure control of the composite materials, the effect of the stimulus on the pure AuNP suspension is necessary. Thus, we investigate AuNP (citrate capping) suspensions with two particles sizes (5 nm, 13 nm) by monitoring their optical response to different sodium salts (anion: $F^-$, $Cl^-$, $Br^-$, $I^-$, $SCN^-$) of different concentration over time. Figure 1 shows photos of AuNP (5 nm) suspensions at various parameter sets [2].

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[2] We acknowledge funding through the Deutsche Forschungsgemeinschaft (DFG) through GRK2516 (Grant No. 405552959).

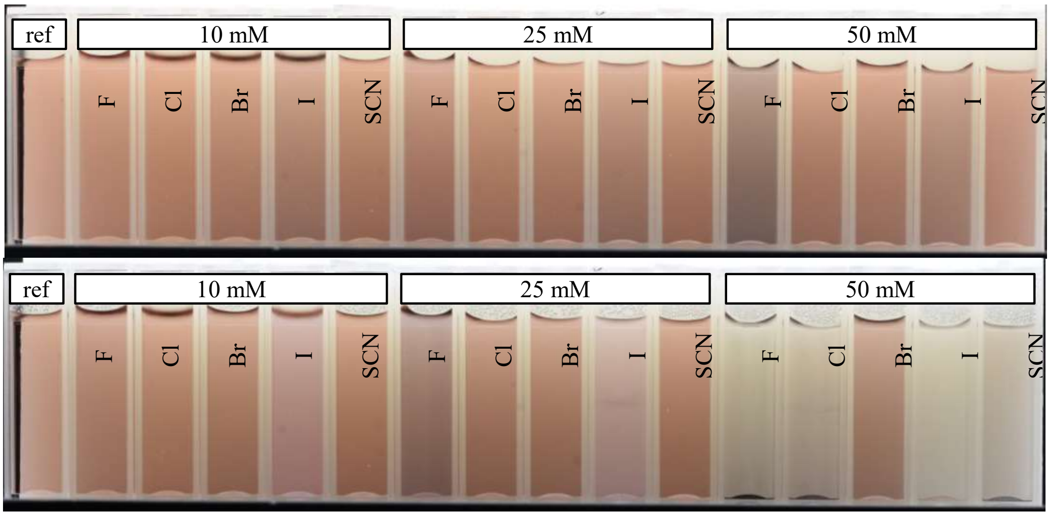

**Figure 1:** AuNP (5 nm) suspensions with varying salt type and concentration: directly after mixing (upper) and 12 h later (lower). The samples are ordered from left to right with increasing salt concentration and ion size of the sodium salt (F, Cl, Br, I, SCN).

# Influence of systematically varied aromatic additive isomers on the phase transition behavior of thermoresponsive Poly(N-isopropylacrylamide) microgels with different cross-linker content

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Thermoresponsive polymers bear a large potential for drug delivery applications, however, the influence of small molecules on the phase transition is a critical issue. Our work investigates the effects of different additives such as benzene derivatives, employed as model drugs, on the phase transition behavior of differently crosslinked Poly(N-isopropylacrylamide)/*N*,*N′*-methylenebis-acrylamide (μ-PNiPAM/x-BIS) microgels. While the homopolymer PNiPAM already has been studied earlier in the presence of aromatic additives, the present work concentrates on a systematic variation of additive isomers and their influence on the phase transition behavior of differently crosslinked microgels[1]. NMR Spectroscopy, Differential Scanning Calorimetry (DSC) and Dynamic Light Scattering (DLS) are employed to determine the Volume Phase Transition Temperatures (VPTT) of polymers in absence and presence of additives. Insights into local dynamics and additive distribution are gained by measuring one dimensional $^1$H-NMR spectra and transversal relaxation times $T_2$ in temperature series.

All additives investigated induce a shift $\Delta T$ of the VPTT to lower temperatures, consistently determined by all applied methods. It is observed that this shift is depending on the type, position and number of functional groups attached to the aromatic ring. In addition, the crosslinker content influences the sensitivity of the microgel particles towards model drugs considering the same additive in a crosslinker-variation series.. The VPTT depression in dependence on crosslinker content varies somewhat for different parameters considered, which is interpreted as the influence of the network structure.

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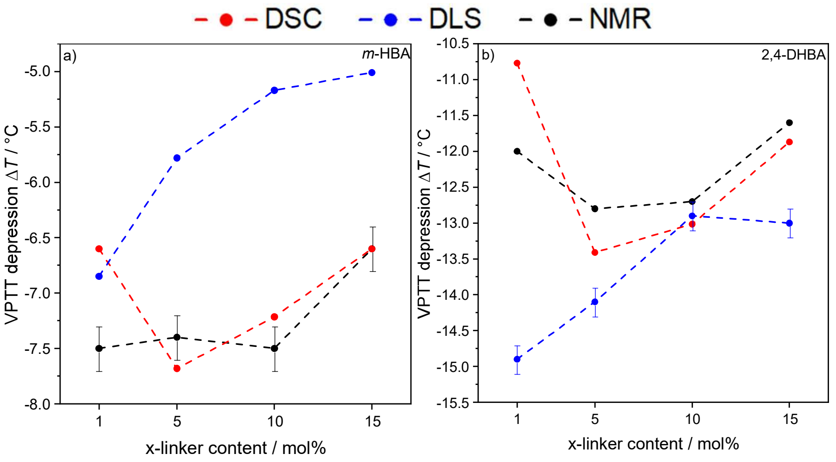

**Figure 1.** VPTT shifts $\Delta T$ of microgels in aqueous solutions with 20 mM *meta*-hydroxy-benzaldehyde (*m*-HBA; (a)) and 20 mM 2,4-Dihydroxybenzaldehyde (2,4-DHBA; (b)) obtained from different methods.

# Solid-phase microcontact printing for the preparation of precisely functionalized multi-patch $SiO_2$ particles

Pinar Akarsu[1,2], Richard Grobe[1], Martin Reifarth[1,2], Marcel Sperling[1], Matthias Hartlieb[2] and Alexander Böker[1,2]

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[2]Chair of Polymer Materials and Polymer Technologies, University Potsdam, D-14476 Potsdam-Golm, Germany

We present a microcontact printing routine suitable to introduce multiple patches, which are precisely localized at the surface of silicon dioxide ($SiO_2$) microparticles, and exhibit a well-defined chemical functionality. This method holds great potential for the attachment of functional molecules to up to four different faces at the particles. As a feature of this method, recently introduced solid phase microcontact printing, which contains polymer brush-modified polydimethylsiloxane (PDMS),[1] is adapted in a way to enable addressing $SiO_2$ particles from multiple sites with certain geometries. Implementing stamps with dimensions, which match the particle size, well-defined particle geometries can be obtained. The presented routine should, therefore, allow the surface modification of particles with the target molecules by keeping the current topography of the aforementioned substrate substantially constant. We anticipate that the advances might stimulate further interest in the anisotropically functionalized particles in the field of directing self-assembly of patchy particles system, or other application fields.[2-4]

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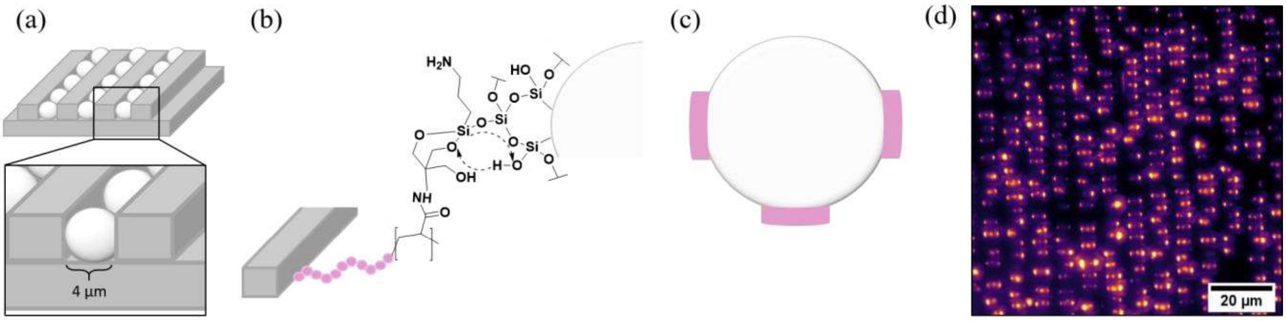

**Figure 1.** Schematic representation of the microcontact printing process used for the preparation of precisely functionalized multi-patch $SiO_2$ particles: (a) $SiO_2$ particles aligned inside the micro channels of PDMS stamp; (b) the transfer of patch material from polymer modified stamp surface to the contact area of the $SiO_2$ particle; (c) multi-patch $SiO_2$ particle after microcontact printing; (d) fluorescence microscopy image of the multi-patch $SiO_2$ particles

**Acknowledgement:** The authors acknowledge financial support of the European Research Council (ERC) in the framework of the research project Replicoll (Project 648365).

# Interaction of microgels with the biomimetic surface

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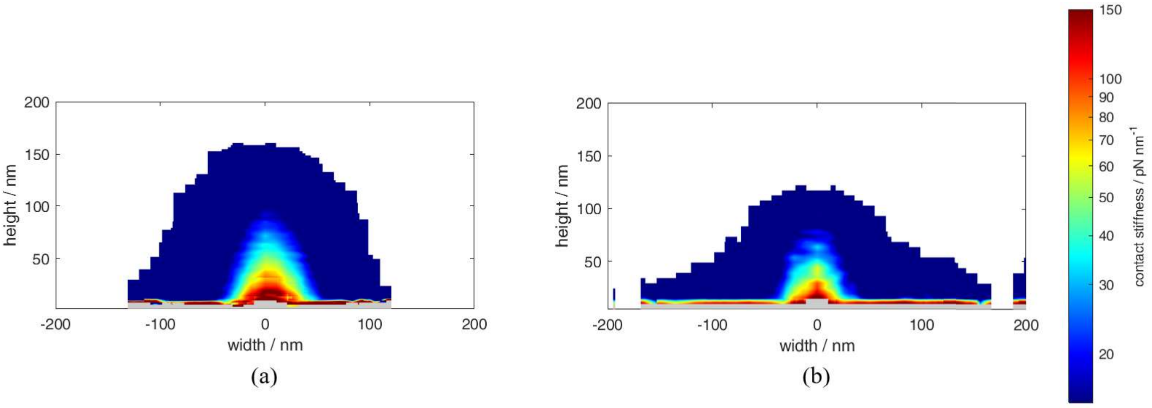
PNIPAM and PNIPMAM microgels are promising agents for various biomedical applications. Though some articles studied how some physicochemical properties of microgels influence their interaction with cells, a detailed understanding is still needed. Important parameters for translocation are microgel softness and its internal structure [1]. Recently it was shown that stiffness and size of the microgels strongly influence their cellular uptake and impact the uptake pathway. [2]. In this work, we investigated how mechanical properties of microgels affect interaction with lipid bilayer.

Atomic force microscopy is a powerful method that allows investigation of mechanical properties, that are related to the internal structure of the material. With this technique we can determine how microgels deform on the interface. Moreover, Force Volume measurements allow determining the stiffness as a function of the three-dimensional position and could be used even for ultra-soft materials [3].

Previously in our group was shown the interaction of microgels with solid-air and solid-liquid interfaces. To continue those findings, we made a first step to the cell membrane surface. We used the simplistic model of the cell surface – supported lipid bilayer (SLB). We prepared SLB based on 1,2-dioleoyl-sn-glycero-3-phosphatidylcholine (DOPC) as model systems for biomimetic surfaces. Then we quantified microgels deformation upon the adsorption to the bilayers (Fig. 1).



(a)

(b)

**Figure 1.** Average contact stiffness profile of microgels on glass (a) and SLB (b) in water at 27 °C

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# Free-Radical Polymerizations in Surfactant-Free Microemulsions

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Today, several systems for polymerizations are known, but especially polymerizations in (micro)emulsion and (micro)suspension comprise an attractive technique. By using microemulsions it is possible to tune the polymer size and morphology, while yields are usually good and temperature control is not a problem. However, the surfactants or auxiliary colloids might have an impact on the latter polymer properties. For example, surfactants have been shown to accelerate the release of small molecules (plasticizers) from a polymeric workpiece into the environment. [1]

Surfactant-free microemulsions (SFME) are ternary, mesostructured liquids consisting of an oil, water, and a hydrotrope. SFMEs were firstly postulated in the late 1970s and found their way to applications as mesostructured reaction systems in the context of enzymatic reactions in the 1980s [2,3]. However, it took until the last two decades that SFMEs were investigated in more detail. [4] In terms of polymerizations, only a limited number of studies in SFME were presented in the last years. All of them present quite special applications. [5,6]

We present a simple system composed of water, the monomer methyl methacrylate as the oil phase, and simple alcohols (iso-propanol, n-propanol, tert-butyl alcohol) as hydrotropes. The alcohols were chosen, as they can be separated simply by distillation after polymerization, if dry polymers are of interest. Polymerizations can be performed using commercial thermal initiators such as peroxodicarbonates, redox-activated systems or UV-activated initiators. By the choice of the exact position to polymerize in the phase diagram, which should be preferably in the pre-Ouzo region close to the phase-border left-hand of the critical point, it is possible to affect the polymer morphology, yield, and mean molar mass. [7]

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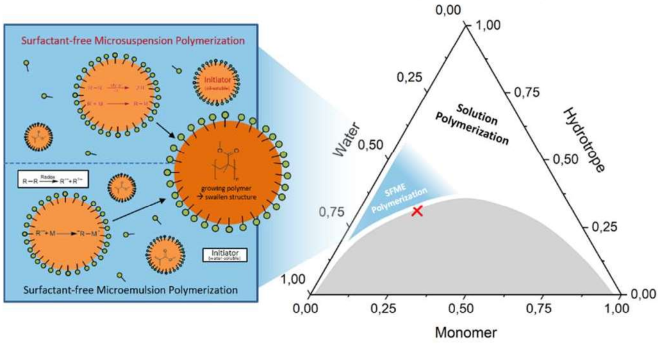

**Figure 1.** Water – alcohol (as iso-Propanol or tert-Butanol) – (vinyl) monomer structured mixtures (SFME), for which polymerization can be fined-tuned, concerning morphology, yield, and mean molar mass.

# Molecular Handedness Detection with Induced Chirality in Plasmonic Lattice Modes

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Plasmonic nanoparticles placed in lattices enable the localised plasmonic resonances (LSPR) to couple to Bragg modes leading to the appearance of surface lattice resonances (SLR). Such resonances can mitigate losses from individual structures and thus show spectrally narrower features (see e.g. white arrows in **Figure 1**, right top inset).[1]
We recently reported the first excitation of surface lattice resonances in arrays of the intrinsic chiral nanocrescent building blocks. These chiral SLRs show the same preference and sign of circular dichroism (CD) as the localised resonances of the metamolecules, while exhibiting a similar narrowing as non-chiral lattice modes.[2] Here, we complete the scene and extend chirality transfer from metamolecules (chiral nanocrescents) to an actual molecular-induced chirality transfer to lattices modes of arrays of achiral gold nanoparticles. We use the synthesis and self-assembly of core-shell gold nanoparticles (AuNPs@PNiPAm) to allow a uniform coverage of substrates over large areas (> cm²) with hexagonal particle monolayers that have tuneable lattice parameters. The achiral arrays of AuNPs are homogenously covered with randomly oriented chiral molecules of one enaniomer. Illumination with circularly polarized light shows that the chirality of the molecules is not only transferred to LSPRs[3], but also to the lattice modes of the AuNP arrays as revealed by a circular dichroism signal at the wavelength of the SLR (**Figure 1**).[4] This allows to reveal the handedness of a molecule by SLRs. We extend our experiments by numerical and theoretical calculations to examine the underlying transfer mechanism from molecules to plasmonic lattice resonances. Chirality transfer to lattice modes has, to the best of our knowledge, not been observed before.[4]

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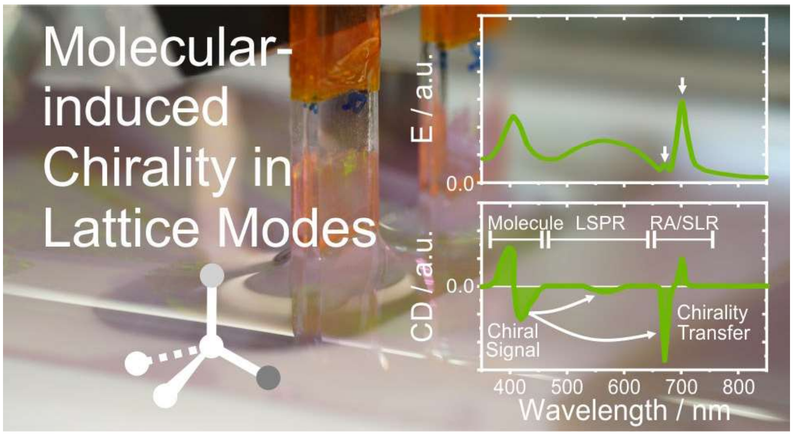

**Figure 1.** Self-assembly of core-shell AuNPs@PNiPAm) at the air-water interface with a langmuir blodgett trough. Arrays of well-defined AuNPs can reveal the handedness of chiral molecules via induced chirality. This transfers a CD signal from the molecular region to the lattice modes (arrows) of the array, allowing an easy detection in the visible range.

# Grain boundary conductivity in hybrid perovskite crystallite clusters

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Hybrid organic-inorganic perovskite semiconductors, based on the prototype compound methylammonium lead iodide ($MAPbI_3$), are successfully applied as absorber materials in photovoltaic devices reaching power conversion efficiencies of 25.7% as of 2022 [1]. Prepared from solution, perovskite solar cells allow for an inexpensive, low-temperature fabrication. The crystallization of the polycrystalline perovskite thin films ensues from a precursor solution that is viewed as a colloidal dispersion. The colloid chemistry of this dispersion can affect the film morphology by changing the crystal size, orientation and density of the resulting perovskite layer [2]. In this study, we investigated the influence of the film morphology on the electrical transport properties between adjacent $MAPbI_3$ crystallites: By contacting an interconnected crystallite cluster with a gold electrode, we were able to determine the current flow between crystallites via conductive atomic force microscopy (cAFM) and directly correlate the conductivity to the respective grain boundary morphology. While the contact area between adjacent crystallites appeared to have a negligible impact, the grain boundary morphology strongly affected its conductivity. Therefore, a more controlled crystallization from the precursor dispersion could minimize current losses at grain boundaries by increasing crystallite size, orientation and density.

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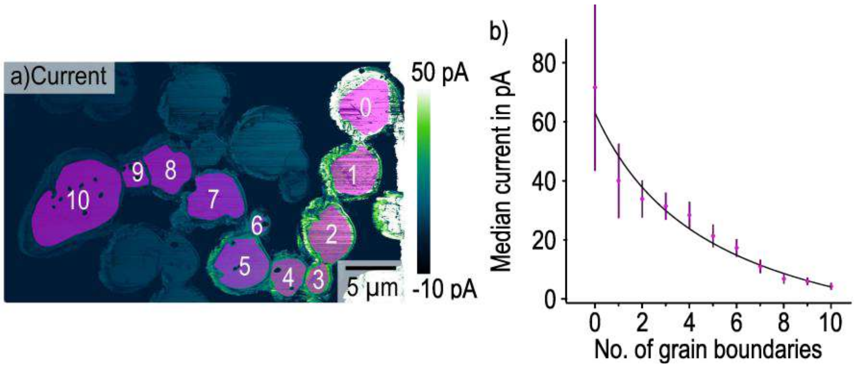

**Figure 1.** a) CAFM measurement on interconnected $MAPbI_3$ crystallite cluster in contact with gold electrode on the right side of the image. All crystallites are numbered according to the amount of grain boundaries between the gold electrode and the current detection via the conductive AFM tip. b) Median current measured on each of the numbered crystallites.

# $Cu^{2+}$ and temperature dual-responsive microgels for smart foams preparation

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Smart foams that can be stabilized and destabilized at will are highly desirable especially for the industrial use of froth flotation in recovering heavy metal ions (e.g. $Cu^{2+}$) from polluted aqueous environment[1-2]. This study was aimed to developing a $Cu^{2+}$ sensitive foam stabilized by microgels, targeting for selective recovery of $Cu^{2+}$ from competitive ions.

Firstly, a $Cu^{2+}$-responsive thermo-sensitive poly (N-Isopropylacrylamide-co-Vinyl imidazole) (PNV) microgel was synthesized, and $Cu^{2+}$-imidazole complexation was demonstrated to enhance the microgel swelling with a softer and more homogenous microstructure and a significant volume phase transition temperature (VPTT) shift to higher temperatures, and the swelling/deswelling was tuneable by $Cu^{2+}$ concentration.

Secondly, temperature responsive foams with a ultra-stability below VPTT of the microgel and a rapid collapse above the VPTT were readily produced based on PNV microgels. $Cu^{2+}$ complexation enabled a modulation of temperature responsiveness of the foams, able to maintain a good foam stability above a critical temperature where foams collapsed for other cations (e.g. $Na^+$, $Mg^{2+}$, $Zn^{2+}$), showing significance for selective recovery of $Cu^{2+}$ from competitive ions.

Furthermore, an interfacial study revealed a better surface activity of $Cu^{2+}$ -complexed PNV microgel with a less temperature dependence, and the responsive foam destabilization was dominated by an abrupt reduction of surface shear viscoelasticity that was avoidable by entanglements between $Cu^{2+}$-complexed PNV microgels[3].

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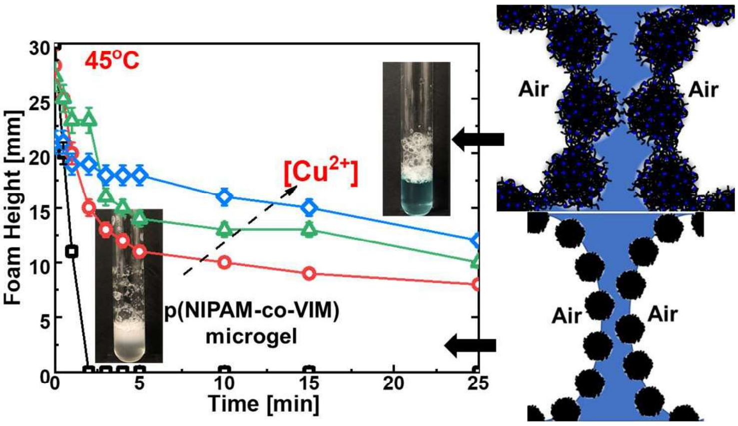

**Figure 1.** Foam height versus time for PNV microgels with varied $Cu^{2+}$ concentrations and schematics of possible response of the microgel laden air-water interfaces.

# Binding of biotin-functionalized and mannose-functionalized, thermosensitive microgels on receptor surfaces: Effect of the volume phase transition

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Almost all biological processes on the cellular scale are mediated by ligand-receptor interactions between biomolecules such as proteins and carbohydrates e.g. cell-cell communication, pathogen invasion, or cell development. To study and mimic these interactions, microgels can be functionalized with bioligands, thus binding of these ligand-presenting polymer scaffolds to receptor systems can be achieved in order to control biological functions. Responsive "smart" microgels could enable a more profound control of these functions. For example, by undergoing a phase transition upon external stimuli, the biomolecular interactions of the ligand-functionalized microgels can be activated and deactivated [1].

Thermoresponsive microgels based on poly *N*-isopropylacrylamide P(NIPAM) exhibit a volume phase transition in a biologically applicable range near the temperature of 32 °C [2]. Two different microgel systems were characterized in terms of their binding properties above and below the volume phase transition temperature (VPTT). For this purpose, mannose- and biotin-functionalized P(NIPAM) microgels and corresponding protein-receptor surfaces were prepared. Inhibition assays were performed below and above the VPTT and the binding of the microgels to the protein surfaces was measured at different inhibitor concentrations by detecting their presence on the receptor surfaces via fluorescence spectroscopy and microscopy. It was found that the biotin-functionalized microgels bind to the avidin surface at temperatures below the VPTT, whereas they do not bind to the surface at 40 °C. We assume that the hydrophobic biotin ligands are located within the polymer network above the VPTT and are thus not available for the specific binding to the surface. In contrast, the mannose-functionalized microgels bind to the ConA surfaces at temperatures above the VPTT. This is presumably due to a higher density of hydrophilic mannose ligands at the microgel-water interface above the VPTT.

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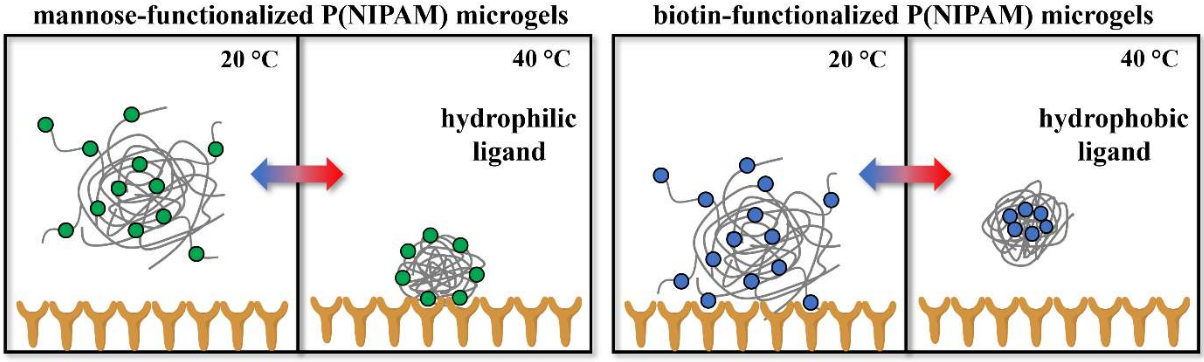

**Figure 1.** An illustration of mannose- and biotin-functionalized microgels on receptor surfaces. The change in microgel adhesion upon varying the temperature below and above the VPTT is shown. The biotin-functionalized microgels bind to the avidin surface at temperatures below the VPTT, whereas they do not bind to the surface at 40 °C (right). In contrast, the mannose-functionalized microgels bind to the ConA surfaces at temperatures above the VPTT (left).

# Buckling and Interfacial Deformation of Fluorescent Poly(*N*-Isopropylacrylamide) Microgel Capsules

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Hollow microgels are fascinating model systems at the crossover be-tween polymer vesicles, emulsions and colloids as they deform, interpenetrate and eventually shrink at higher volume fraction or when subjected to an external stress. Furthermore, their hollow architecture makes them ideal candidates as nanocarriers. Here, we introduce a new system consisting of micron-sized microgels with a large micron-sized cavity enabling a straightforward characterization in situ using fluorescence microscopy techniques. These capsules are found to reversibly buckle above a critical osmotic pressure, conversely to smaller hollow microgels, which were previously reported to deswell at high volume fraction. Simulations performed on monomer-resolved in silico microgel capsules confirm the buckling transition and that the presented capsules can be described with a thin shell model theory leading to a direct estimation of their elasticity. The latter refers to a Young modulus that is experimentally determined to be lower than that of usual polymeric capsules. When brought to the air-water or oil-water interfaces, these microgel capsules strongly deform and we thus propose to utilize them to locally probe interfacial properties within a soft capsule model adapted from the JKR theory.

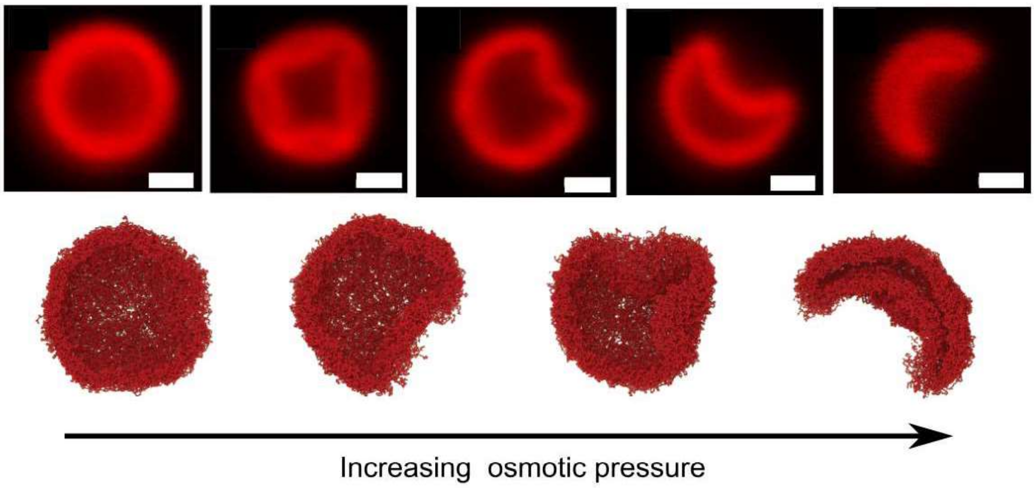

**Figure 1.** (Top) CLSM micrographs of the microgel capsules obtained from the maximum intensity projection of z-stack highlighting typical configurations observed upon increasing osmotic pressure by addition of PEG 8000. Scale bars: 500 nm. (Bottom) Simulation snapshots of the hollow microgel across the buckling transition.

# State Diagram of Soft Dipolar Ellipsoids

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[2] *Institute for Theoretical Physics, Technical University Vienna, Vienna, Austria*
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Dispersions of anisotropic ellipsoidal particles are investigated using confocal laser scanning microscopy (CLSM). The particles were obtained by post-processing spherical particles into prolates with an aspect ratio of by mechanical stretching and consist of a polystyrene core surrounded by fluorescent microgel shell [1]. Their phase behavior is explored as function of the volume fraction across the glass transition under deionized conditions at 20 °C. We study the structure and dynamics of dispersions at various volume fractions, the influence of an external electric field on the phase diagram and the metastability of the resulting phases. Our results, supported by Monte Carlo simulations, evidence the organization of the polarized ellipsoids into columnar phases or a face center tetragonal (FCT) crystals with increasing dipolar coupling at high volume fractions with a persisting nematic ordering when the field is turned off at the highest volume fraction.

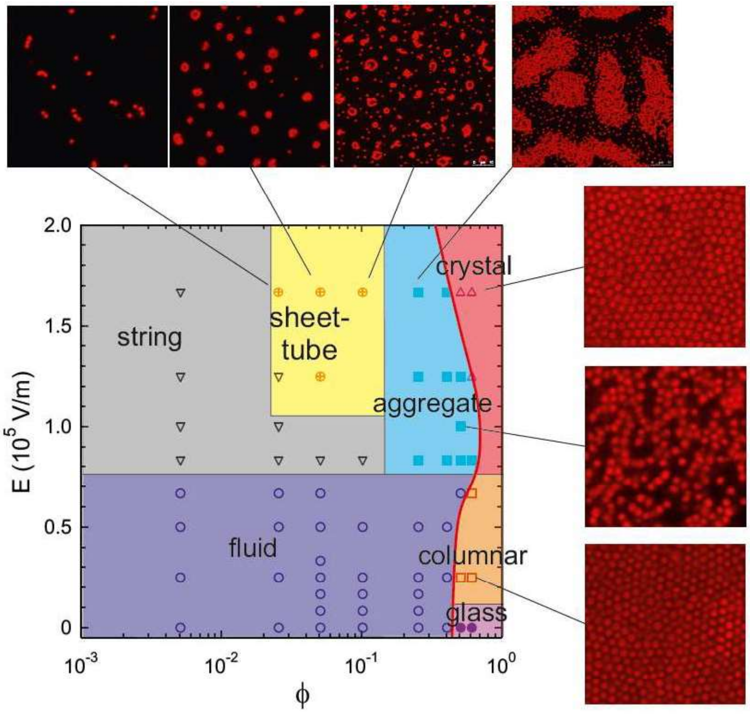

**Figure 1.** Experimental state diagram of dipolar ellipsoids with an aspect ratio of 3.3 polarized by an alternating electric field determined via confocal microscopy.

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# Drying of Responsive Microgels

Nabanita Hazra[1], Hichame Ait El Mallali[1], Fan Rong[1], Kevin Roger[2] and Jérôme J. Crassous[1]

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*[2] Laboratoire de Génie Chimique, Université de Toulouse, CNRS, Institut National Polytechnique de Toulouse, Université Paul Sabatier, France*

At higher volume fractions, depending on their degree of crosslinking, such soft microgels may further interpenetrate, deform and facet with direct consequences on their collective properties. We discuss how the interplay of molecular and colloidal scales controls drying of microgel dispersions. This is achieved by monitoring the drying at the end of a capillary exposed to a controlled humidity with constant particle feeding ensures by its connection to a reservoir. Hereby, the water evaporation and diffusion set a flow driving the particles at the drying front where they build up crystals. Whether or not the particles are interpenetrable is characterized by the difference of scaling law in the time evolution of the drying front. We evidence an original drying behavior intermediate between colloidal and solution drying, in which a diffusional scaling is observed together with a weak dependence on the air relative humidity. Mapping composition and structuration gradients using Raman spectroscopy and small-angle scattering techniques, we show that this behavior stems from the ability of microgels to both interpenetrate and compact. As a result, water activity and transport is drastically decreased in the vicinity of the air/liquid interface [1]. We further present the influence of the microgel degree of crosslinking down to so-called ultralow crosslinked microgels (ULC) and temperature on the drying process. The described mechanism will be at play in a large diversity of complex colloidal systems and is pivotal for the mastering of drying processes.

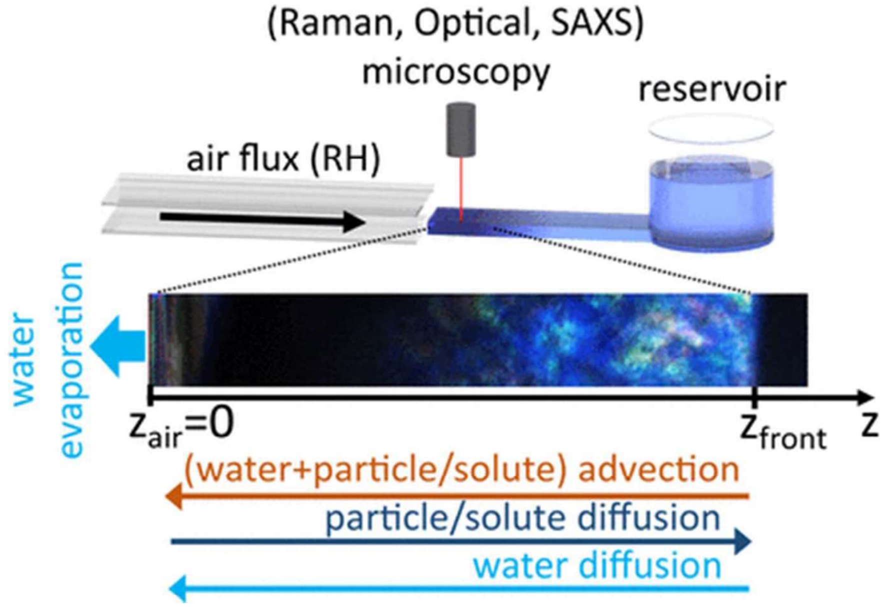

**Figure 1.** Schematic view of the millifluidic setup, which consists of a rectangular capillary connected on one end to a reservoir containing the microgel dispersion and exposed on its other end to an air flux of controlled RH.

## Reference

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# Working with Nanoparticles and other Hazardous Substances: Challenges for Safety Products

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[2] DermaPurge GmbH, Dresden.

Although Nanotechnology has been used for centuries and concerns of adverse effects of nanoparticles on human health continue, standard work safety is still not ensured.
In this work we will show the problems that arise from nanoparticle-skin contact and inform about measures that ensure work safety.

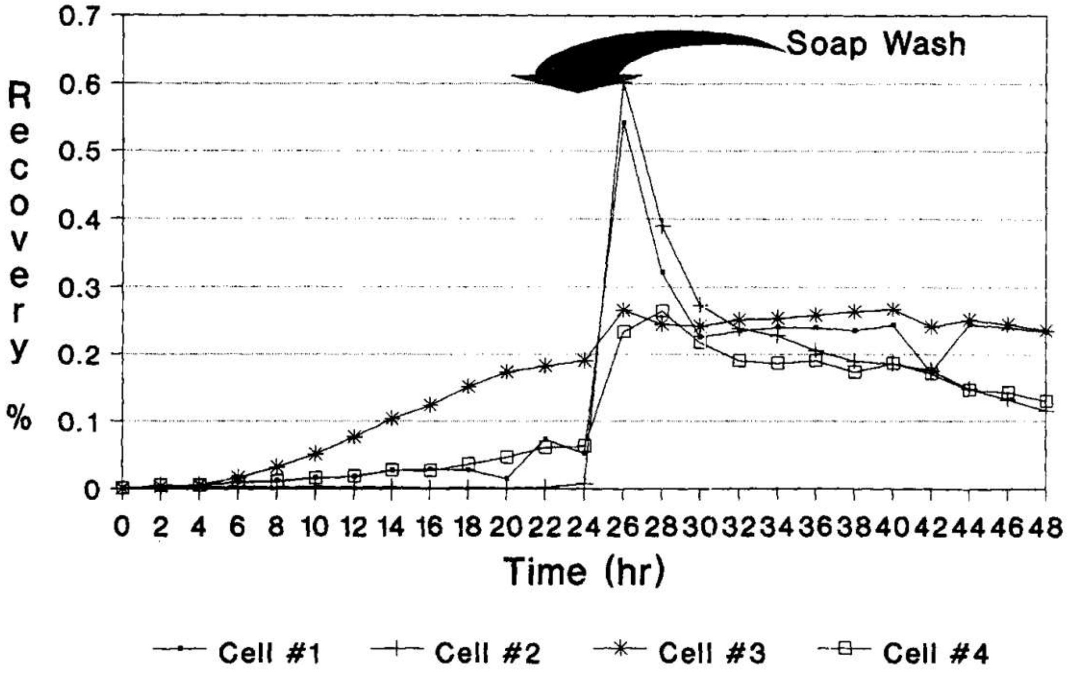

**Figure 1.** In vitro analysis of "C-B[a]P permeating 32-year-old Q human skin. The % recovery in the receiver solution is shown versus time for each of the four replicate Bronaugh cells. The onset of the 24-h skin wash with Radiac soap and water is shown.

We will concentrate on the problems of the so-called wash-in effect and the ingestion via carry-over contamination. Here a new classification of nanoparticles is shown and how this helps to identify the personal risks. A solution is presented how this risk can be mitigated by modern safety equipment. Finally new insights in the removal of soot particles and the removal of the cancerogenic polycyclic aromatic hydrocarbons will be presented. Firefighters and chimney sweeps are just two groups who constantly work with these hazardous substances. Thus, in the longrun, many suffer from so called chimney sweep cancer. A solution to this problem has long been required. It will be presented in our talk.

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# Colloidal graphene-based inks for screen printed stretchable conductors

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Screen printing presents a suitable manufacturing technique for electronic components, as it is flexible, scalable, cost-effective and prints thick layers, enabling relatively low resistances [1]. Graphene is an ideal conductive component of these inks as it is skin-compatible [2]. We have previously developed conductive inks containing colloidal graphene nanoplatelets (GNPs) for screen printing of flexible conductive tracks [1] and are currently extending their formulation to inks suitable for printing of *stretchable*, skin-compatible conductors combining high conductivity with a high durability over many strain cycles.

We have developed an ink based on colloidal GNPs utilizing a skin-compatible thermoplastic polyurethane (TPU) binder with adjustable rheology. We are currently employing small-angle X-ray scattering (SAXS), dynamic light scattering (DLS) and rheological measurements to gain fundamental insights into these complex systems and formulate colloidally stable inks suitable for high resolution printing. Screen printing was used to print stretchable conductors on TPU substrates with high conductivity and excellent feature definition down to 200 µm line width. The conductors tolerate strains up to at least 100% and demonstrate high fatigue resistance to cyclic strains of 20–50%. Post-processing was employed to further reduce the resistances while preserving stretchability and cyclic durability. Its tunable viscosity makes the ink potentially suitable to printing techniques beyond screen printing. This opens a route towards the scalable production of printed sensors, heart rate monitors, athletic garments and artificial skin.

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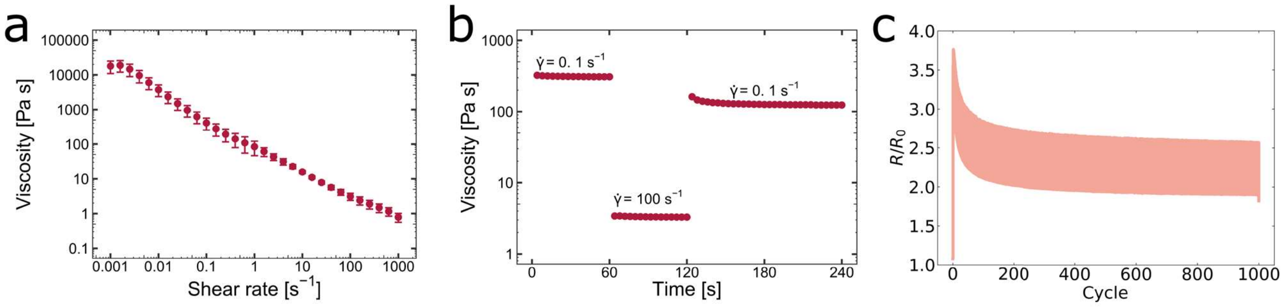

**Figure 1.** a-b) Ink rheology; a) Flow ramp b) Peak-hold test emulating the screen printing process; c) Electrical resistance response of printed linear tracks submitted to 1000 cycles of 20% strain.

# Phase behavior and morphology of cationic/anionic surfactant mixtures

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Cationic surfactants show promising effects in laundry applications, such as an antimicrobial or care effect. However, in such applications anionic surfactants are widely used. Due to their different charge mixtures of cationic and anionic surfactants will not only show a strongly altered phase behavior but can also suffer from aggregation and precipitation of non-soluble complexes. Therefore, there is a great interest in understanding the phase behavior of cationic/anionic mixed systems.

In this study, the phase behavior of the technical, anionic surfactants sodium laureth sulfate (SLES) and sodium dodecylbenzene sulfonate (LAS) and the cationic surfactant didecyldimethylammonium chloride (DDAC) were investigated. Based on turbidity measurements, different aggregates were suspected depending on the mixing ratio. This is in line with changes in conductivity. The charge of the formed objects was characterized through zeta-potential measurements. To identify the morphology of the aggregates, dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS & cryo-TEM) measurements were used.

The figure below shows that mixed micelles can be found at low ratio of oppositely charged surfactant followed by vesicle phases (uni- and multilamellar). Close to stochiometric ratio phase separation occurs and precipitates are formed.

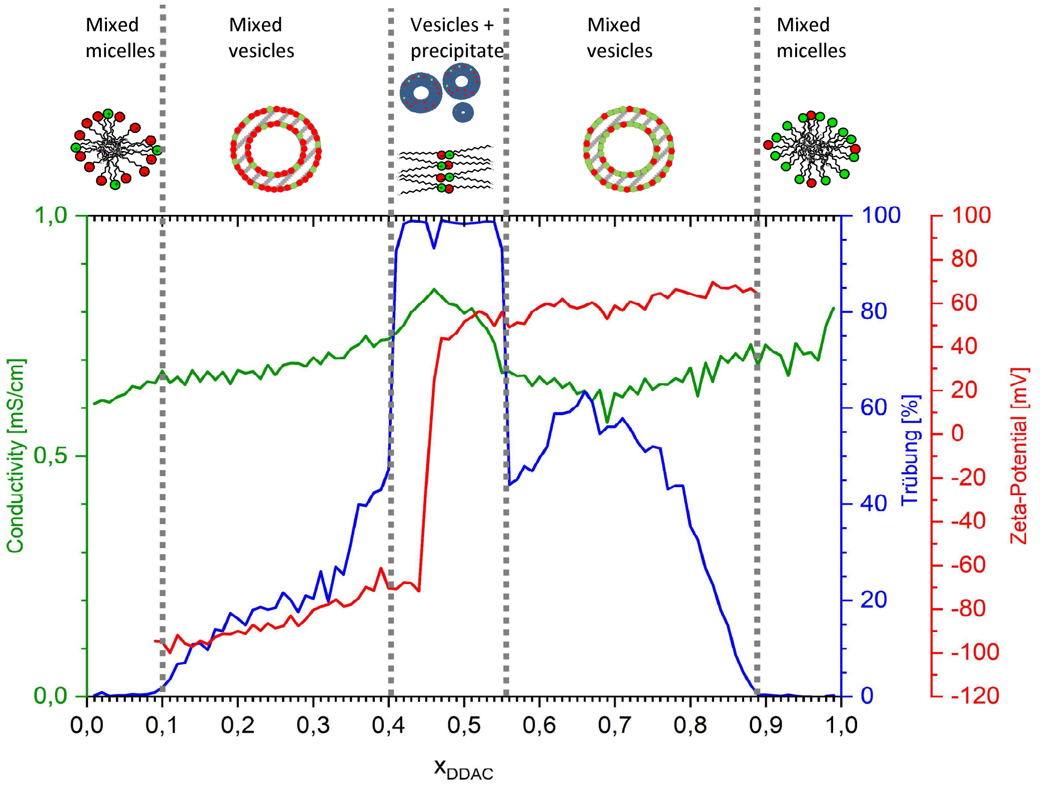

**Figure 1.** Phase behavior of SLES/DDAC mixtures with the DDAC to SLES molar ratio $x_{DDAC}$ followed by conductivity (green), turbidity (blue) and zeta-potential (red).

# Inducing defects in colloidal crystals

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Crystal defects are imperfections that can occur in any crystalline material and can crucially influence the mechanical, structural, and optical properties of the material. Colloidal crystals are useful model systems to study defect phenomena due to their similarities with atomic/molecular crystal systems. Although defect structures in colloidal crystals have been addressed, little is known about how (point) defects interact and the mechanisms of their diffusion in 3D, due to the lack of experimental control over the defect formation.

The aim of this project is to develop a colloidal system in which defect formation in 3D crystals can be controlled *in-situ*. For this the aim was to embed thermo-responsive colloids in a crystal of non-responsive particles. By heating or cooling, the defect particles can collapse or swell, which will induce vacancy-like defects or interstitials, respectively (Figure 1a). To realize this system, we synthesized thermo-responsive colloids with a poly(N-isopropyl acrylamide) microgel shell and non-responsive poly(2,2,2-trifluoroethyl methacrylate) (pFEMA) core [1], and non-responsive core-shell pFEMA particles of the same size that can be refractive index matched. Using a confocal microscope equipped with a temperature-controlled stage, the mixed system can be visualized on a single particle level (Figure 1b) and the dynamical properties of the defects upon switching can be studied. By adopting existing particle tracking and image analysis procedures, local stress- and strain-fields around crystal defects can be visualized [2]. Ultimately, this project will yield fundamental insight into the formation and dynamics of defects in colloidal crystals and in crystalline materials in general.

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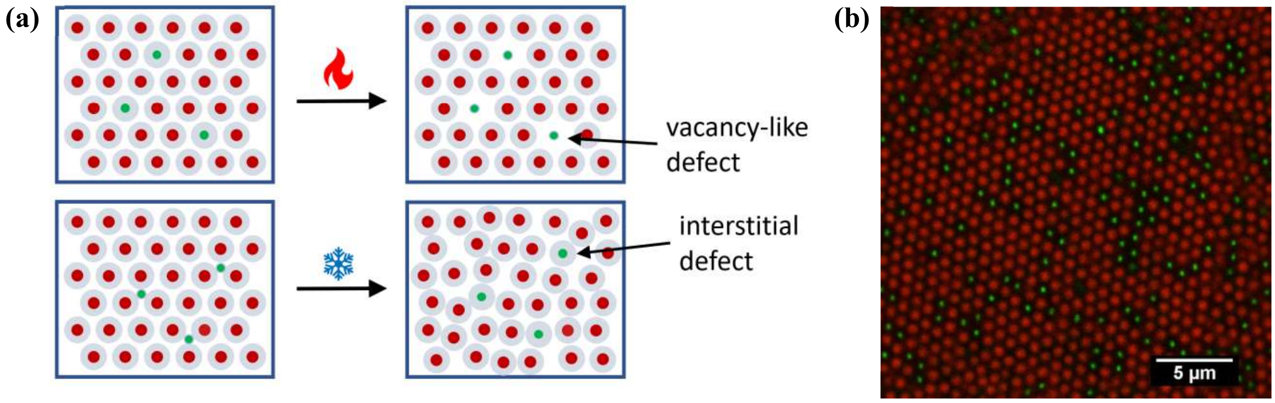

**Figure 1. (a)** Conceptual visualization of inducing vacancy-like and interstitial defects using thermo-responsive particles. **(b)** Confocal image showing swollen thermo-responsive microgels (green) embedded in a crystal of non-responsive particles (red) at 20 °C.

# In-situ Investigation of $Ca^{2+}$-involved Flocculation of Natural Organic Matter (NOM) with Modified Chitosan

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Natural organic matter (NOM) exists ubiquitously in aquatic environments and can negatively affect the quality of drinking water. Its removal typically proceeds via coagulation by means of adding hydrolysing metal cations and cationic polyelectrolytes.[1] To develop a more environmental-friendly and effective chemical regime to remove NOM, natural origin chitosan was chemically modified in our lab and then studied with respect to its interaction with humic acid (HA), which was selected as well-defined model as it is the main component of NOM.[2, 3] In our investigation we concentrated on the phase behavior and the colloidal structures in the dispersed and precipitated state.

The principal aim of our investigation is to understand the interaction of HA (as example for NOM) under different ion conditions with modified chitosan and their formation of larger aggregates that ultimately results in the formation of flocs and precipitates. To gaining comprehensive knowledge about the structural properties. systems with various charge ratio Z, defined here as $Z= [+]_{\text{modified chitosan}} / [-]_{\text{humic acid}}$ were investigated via a series of characterization techniques, such as UV-Vis, static and dynamic light scattering (SLS, DLS), small-angle X-ray scattering (SAXS), and confocal microscopy. In this context we also focused on the role of $Ca^{2+}$ in HA removal in our study to mimic the real condition **(Figure 1)**, and it finally showed the capability to prompt and aid the precipitation process by forming larger/denser complexes. It is worth to mention that in-situ observation via UV-Vis and SAXS were achieved to monitor the transformation of aggregates during the whole process of precipitation of humic acid. With the insights gained on the HA flocculation mechanism, this study is promising in optimizing parameters for NOM water treatment, based on a fundamental colloid chemical investigation.[4]

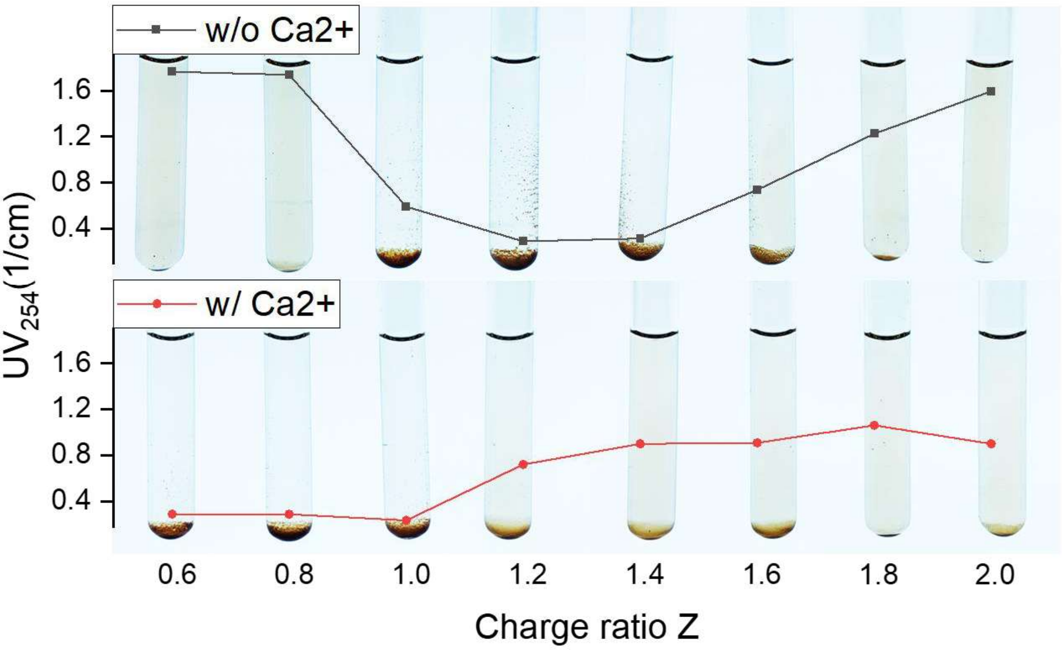

**Figure 1**. UV absorbance at 254 nm (UV 254) for HA-modified chitosan complexes with charge ratio ranging from 0.6 to 2.0 with the presence of 0 and 75 mg/L $Ca^{2+}$, respectively.

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# Capillary Driven Self-Assembly of Ellipsoidal Composite Microgels at the Air/Water Interface

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In this study, we explored the spontaneous capillary driven self-assembly of composite prolate shaped microgels at air-water interface. The core-shell microgels contain a polystyrene (PS) core surrounded with a cross-linked fluorescently labelled poly(*N*-isopropylmethylacrylamide) (PNIPMAM) shell. The aspect ratios of the composite microgels can be finely adjusted upon uniaxial stretching the particles embedded into polyvinyl alcohol films [1]. The ellipsoidal particles obtain an aspect ratio range ρ varying from 1 to 8.8, measured from confocal laser microscopy (CLSM) in their swollen conformation at 20°C. Using inverted fluorescence microscopy, we investigated their spontaneous interfacial self-assembly at the air-water interface. Comparing with spherical particle (ρ=1) with small assembly having weak capillary forces to an apparently random trigonal assembly for ρ=2.1 to highly elongated particle (ρ=8.8) with a side-to-side assembly into long chains transition is observed. The transition occurs between ρ=2.6 and 3.3 for which a trigonal and trigonal/side to side coexistence assembly are respectively identified. The influence of the microgel anisotropy and softness on their interfacial deformation and is further discussed supported by computer simulations.

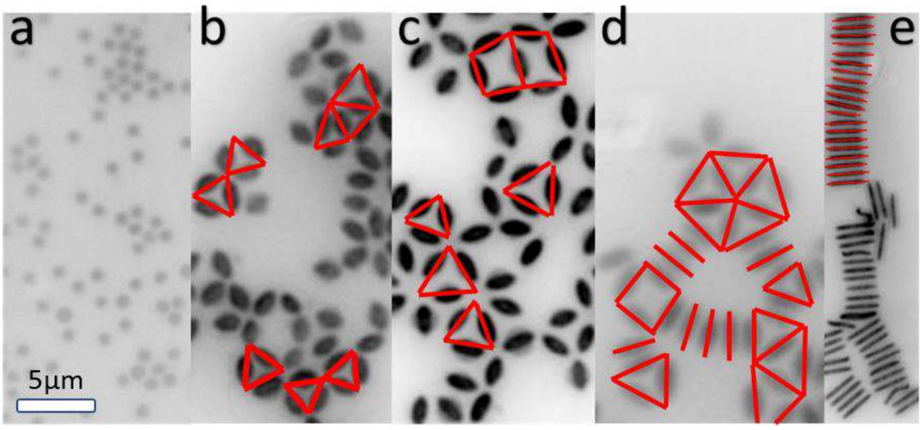

**Figure 1.** Colour inverted fluorescence micrographs of spherical composite microgels (a) and ellipsoidal composite microgels with an aspect ratio ρ equal to 2.1 (b), 2.6 (c), 3.3 (d) and 8.8 (e) assembled at the air-water interface at 20°C. Some of the typical assemblies are highlighted with red lines.

**References**

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# Colloidal black gold with broadband absorption for plasmon-driven catalysis and surface-enhanced Raman scattering

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Broadband light absorbers are very attractive for many applications including solar energy, photothermal therapy, and plasmonic nanocatalysis. Colloidal black gold works as an excellent example of the broadband light absorbers in the visible and near-infrared ranges; however, their synthesis procedure typically requires multi-step deposition and/or high temperatures [1-2].

In this study, we report the synthesis of black gold nanowires via a facile, one-step green method using commonly known precursors (chloroauric acid and sodium citrate) performed at room temperature. The formation of the black gold particles is driven by self-assembly of in-situ formed small nanoparticles (~ 5 nm) followed by a fusion step forming extensive networks of nanowires (Figure 1). These assemblies form intense hotspots for enhancing the electric field as well as the local heat. Thus, the nanowires exhibited a strong photothermal effect as well as surface-enhanced Raman scattering (SERS) performance. Upon NIR irradiation, a high temperature up to 47 ºC was recorded in the colloidal solution. While the high SERS signal enhancement is used to monitor the plasmon-driven dimerization reaction of 4-nitrothiophenol (4-NTP) in real timescale (milliseconds to seconds).

This work presents the colloidal black gold as a promising candidate for many photo-based applications, as the broadband light absorption enables the use of excitation sources with different wavelengths.

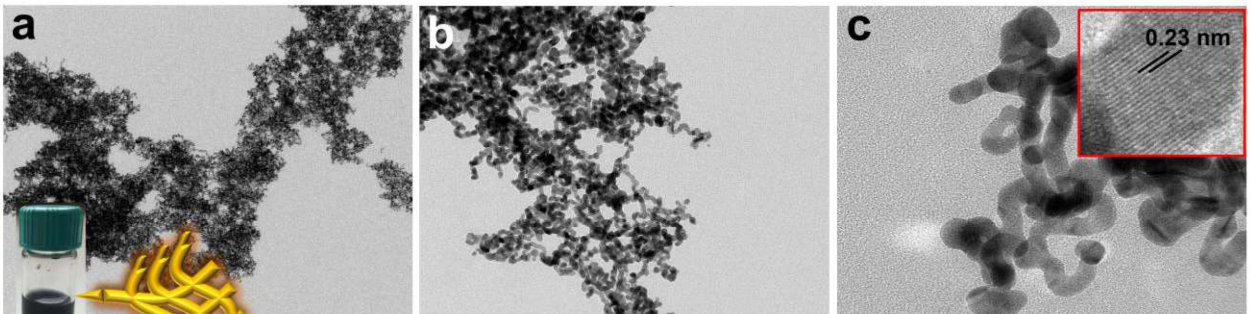

**Figure 1**. TEM and photo images of the as-prepared black gold showing the network-like morphology of the obtained gold nanowires.

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# Gradual, selective, and reversible ionic transport at nanopores by ligand-binding

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Selective binding between different metal ions and their receptors at the cell membranes is essential for the immune reactions, signaling and opening/closing the ion channels.[1] In recent years, such ligand-binding-based pore activities inspired scientists to build ordered and metal-ion-responsive mesoporous films that interact selectively with the metal ions to tune the ionic pore transport. For instance, a chelation reaction between $Ca^{2+}$ ions and phosphate groups of the pH-responsive polymer brushes at the mesopores was recently used to control the transport of anions in on/off states (Fig. 1).[2] For using such mesoporous materials in catalysis, drug release, sensing, and separation applications, their ligand-binding-triggered ionic pore transport needs to be investigated under different application scenarios, such as applications requiring gradual (beyond on/off) transport of both cations and anions under the presence of different amounts and types of metal ions.

Here we show how $Ca^{2+}$ ions interact with phosphate-bearing metal-ion responsive polymer brushes in silica mesopores under different conditions to gradually control the transport of both anions and cations at the pores. First, we explain the growth mechanism of our responsive polymer brushes at silica mesopores in a controlled pore filling. Then we discuss the polymer presence and amount effects on the gradual ionic transport controlled by $Ca^{2+}$ ion amount. Second, we introduce the metal-ion valency number ($Ca^{2+}$ or Al3+) selectivity and reversibility of the $Ca^{2+}$ ion attachment at our (non)functional nanopores and their role on gradual ionic pore transport. We anticipate that the results of our work will be a starting point for the application of hybrid mesoporous films with ligand-binding-triggered ionic pore transport. With (i) reversible and (ii) valency number selective metal-binding and (iii) the detection capability of $Ca^{2+}$ ions even at sub-µM concentrations, the presented hybrid pores will be a suitable platform in challenging nanopore applications.[3]

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[3] The authors acknowledge funding from ERC: European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement No 803758).

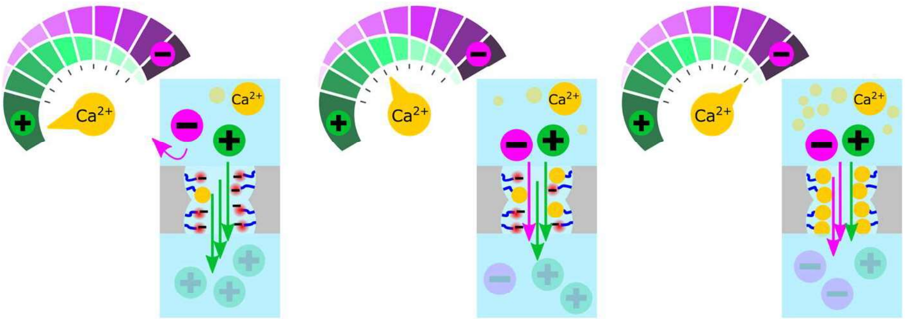

**Figure 1.** At a fixed pH, transport of anionic (purple) and cationic (green) cargoes gradually be tuned by the Ca2+ ion (ligand) binding at our silica mesopores (grey) functionalized by metal-ion-responsive polymer brushes (curved blue lines).

# Multicompartment Polymeric Particles from Functional Precursor Microgel: Synthesis in Continuous Process

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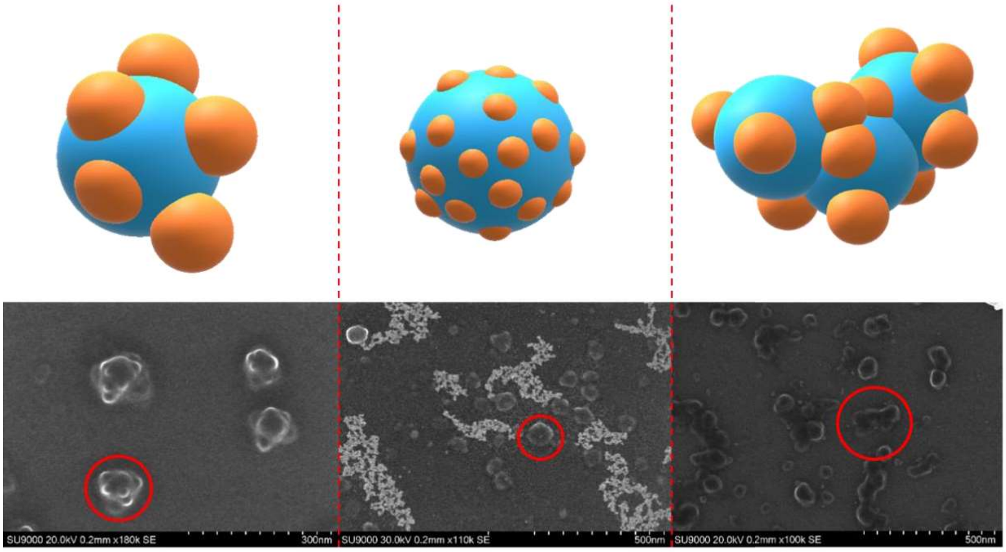
**ABSTRACT:** Raspberry-like poly(oligoethylene methacrylate-*b*-*N*-vinylcaprolactam)/polystyrene (POEGMA-*b*-PVCL/PS) Janus particles (JPs) and complex colloidal particle clusters (CCPCs) were fabricated in two-, and one-step (cascade) flow process. Surfactant-free, photo-initiated RAFT precipitation polymerization was used to develop internally cross-linked POEGMA-*b*-PVCL microgels with narrow size distribution. Resulting microgel particles were then used to stabilize styrene seed droplets in water, producing raspberry-like JPs. In the cascade process, different hydrophobicity between microgel and PS induced the self-assembly of the first formed raspberry particles that then polymerized continuously in a Pickering emulsion to form the CCPCs. The internal structure as well as the surface morphology of JPs and CCPCs were studied as a function of polymerization conditions such as flow rate/retention time (RT), temperature and the amount of used cross-linker. By performing Photo-PISA in tubular flow-reactor we were able to gained advantages over heat dissipation and homogeneous light distribution in relation to thermally-, and photo-initiated bulk polymerizations. Tubular reactor also enabled detailed studies over morphological evolution of formed particles as a function of flow rate/retention time.



JP: Raspberry - rough JP: Raspberry - smooth CCPC

**Figure 1.** Resulting raspberry-like JPs and CCPCs with different surface roughness.

# High yield synthesis of water-processable donor:acceptor Janus nanoparticles with tuned internal morphology and highly efficient charge separation/transfer

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Here we report, for the first time, high yield (87.6%) robust and facile synthesis of donor-acceptor, water-processable, Janus nano-particles (JNP), that are of high potential for optoelectronic applications. The water-processable JNPs have easily controlled Janus ratios and are of excellent quality, that is shown by energy-filtered transmission electron microscopy (EFTEM). The JNPs exhibit improved charge separation and transfer properties compared to the conventional donor-acceptor nanoparticles that is characterized via both steady-state and transient photoluminescence spectroscopy. The Janus character of particles allows the combination of two materials into one composite and programs morphology of structures, which can be formed on the basis of the particles. Finally, we show outstanding performance of JNP based photovoltaic cells with 53% improvement of efficiency.[1]

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[2] The authors acknowledge Anja Caspari and Martina Priebs for electrokinetic measurements, Fupeng Wu for steady-state photoluminescence measurements. Y.D. acknowledges the financial support from the China Scholarship Council (CSC). The authors thank Benjamin Kohn for language polishing. This project was financially supported by the Volkswagen Foundation through a Freigeist Fellowship to T.A.F.K. The Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) − 404818834 funded the project for O.A. and T.A.F.K.

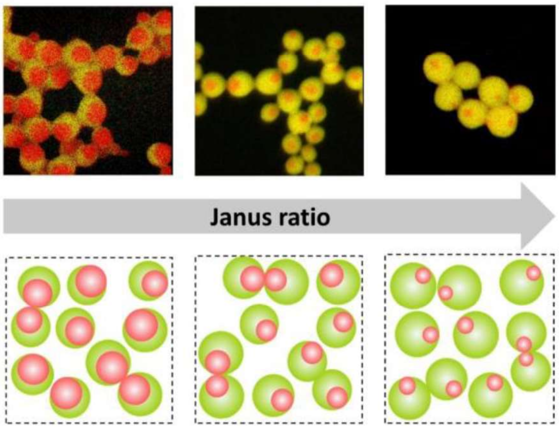

**Figure 1.** The internal structure of aqueous D:A nanoparticles can be well controlled through a facile route. This strategy is successfully applied to synthesize high-yield and high-quality environmentally friendly D:A Janus nanoparticles with tuned internal morphology. These obtained Janus nanoparticles exhibit efficient charge separation and effective charge transfer properties, that exhibits significant enhancement than traditional core-shell structures in photovoltaics devices.

# A Platform for Stop Flow Gradient Generation to Investigate Chemotaxis

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The ability of artificial microswimmers to respond to external stimuli and the mechanistical details of their origins belong to the most disputed challenges in interdisciplinary science [1]. Therein, the creation of chemical gradients is technically challenging, because they quickly level out due to diffusion [2]. Inspired by pivotal stopped flow experiments in chemical kinetics, we show that microfluidics gradient generation combined with a pressure feedback loop for precisely controlling the stop of the flows, can enable us to study mechanistical details of chemotaxis of artificial Janus micromotors, based on a catalytic reaction. We find that these copper Janus particles display a chemotactic motion along the concentration gradient in both, positive and negative direction and we demonstrate the mechanical reaction of the particles to unbalanced drag forces, explaining this behavior [3].

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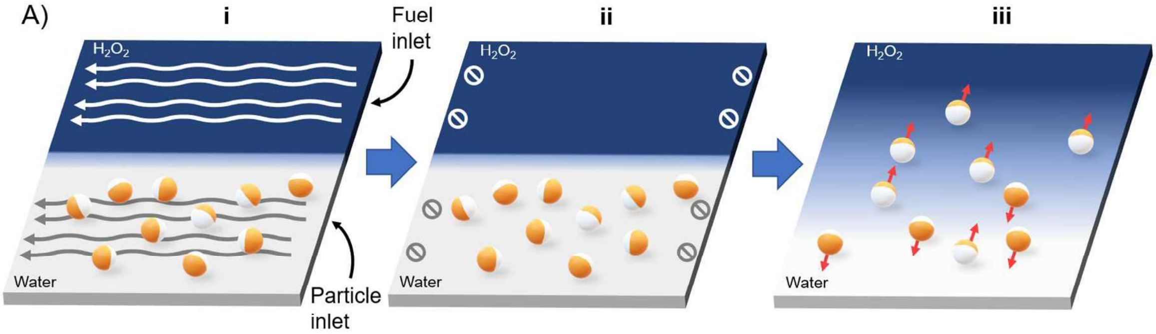

**Figure 1.** Operating principles of the positive and negative chemotaxis of Cu@$SiO_2$ micromotors: i sdadas; ii dasdad; iii dadasdas.

# Phase behaviour and percolation of Red Blood Cells

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[2] Laboratory for Soft Matter and Biophysics, KU Leuven, Leuven, Belgium

In the mixture of colloidal particles and polymers, the range and magnitude of the interaction potential can be tuned by the size and volume fraction of the polymers. Depending on the volume fraction of the particles and the interaction potential, colloidal particles and polymers can form a percolated gel-like network [1].
Similar to colloidal particles, Red Blood Cells (RBCs) exhibit a transition to a solid phase at a sufficiently high enough volume fraction and strong attraction. Depletion and bridging interactions are the two mechanisms for RBC aggregation, underlying the formation of a 3-D network of rouleaux similar to a weak physical gel. Understanding the dynamics of formation and break-up of the 3-D network of RBCs plays an important role in different phenomena, such as RBCs sedimentation or increased hydrodynamic resistance at low shear rates [2, 3].
In this project, we induce the attraction between RBCs by adding rod-like particles with a high length-to-diameter ratio, as well as small Dextran polymers. The different nature of interaction results in different percolated networks of RBCs. We investigated the phase diagram of the mixture of RBCs and these macromolecules from the gas phase up to percolation using confocal images. To this end, we developed an algorithm to directly determine percolation in 3 dimensions from confocal images of RBCs.

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# Crystallization of hollow microgels assisted by regular ones

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Microgels are crosslinked polymer networks in the colloidal size domain swollen in a good solvent. Their swelling degree can be reversibly modified by external stimuli, such as temperature or pH. Advanced synthesis protocols allow for complex architectures, such as hollow microgels with a solvent-filled cavity in the center [1]. The soft and responsive nature of microgels, as well as the variety of internal architectures, makes them an excellent model system to study phase transitions and the behavior of complex fluids.

Here, we focus on mixtures of regular ‘neutral’ microgels with hollow ‘neutral’ microgels of the same size. Although the former are well-known to form colloidal crystals similar to hard incompressible colloids, it has been recently shown that hollow microgels fail to do so [2]. The reason for the absence of crystals is that hollow microgels increase their configurational entropy by rearranging the polymer chains into the solvent-filled cavity. By systematically realizing binary mixtures of regular and hollow microgels, we explore the role of hollow microgels as possible ‘defects’ that suppress the formation of crystals because of a different internal architecture, rather than size mismatch.

First, we confirm the absence of size mismatch and a sufficiently low polydispersity of single microgels using dynamic light scattering, small angle X-ray, and small angle neutron scattering in diluted conditions. In the concentrated binary mixtures, we observe colloidal crystals at fractions of hollow microgels up to 50%, whereby the width of the crystalline region gradually decreases. Small angle X-ray scattering is used to verify the crystal structure of the solutions and to obtain average nearest-neighbor distances in them. We speculate that below this threshold value of 50%, regular microgels can serve as a ‘template’ that assists the incorporation of hollow microgels into an ordered structure [3].

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[3] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft within the SFB 985 Functional Microgels and Microgel Systems.

# Paradigms for Directional Self-Assembly of Polymer-Functionalized Nanoparticles

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Inorganic Nanoparticles may feature unique size-, shape-, and composition-dependent plasmonic, excitonic, or magnetig properties. From the assembly of these nanoscale entities into ordered supracolloidal clusters, these properties may be further enhanced or completely new phenomena may emerge, as a result of interparticle coupling effects. Therefore, controlling nanoparticle self-assembly is of utmost importance.

This presentation will highlight approaches toward nanoparticle patterning through the recently established approach of constrained de-wetting in polymer grafted nanoparticles.[1] It will be shown how adaptive polymer ligands can be used to achieve surface patterning through distinct stimuli (like solvent environment, temperature, chemical triggers).[2,3] Building on that, it will be demonstrated how diblock copolymers can be employed to achieve colloidally stable, asymmetrical polymer-coated nanoparticles, and their directional self-assembly into supracolloidal clusters (see Figure 1).[3]

Finally, an alternative paradigm for directional nanoparticle self-assembly that does not rely on prior surface patterning with polymer ligands will be discussed. It will be shown that polystyrene-coated gold nanorods can undergo directional tip-to-tip self-assembly, even when they are uniformly coated with a polymer ligand layer.[4] The importance of electrostatic forces for the observed directional colloidal interactions will be discussed.[5]

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[2] C. Rossner, I. Letofsky-Papst, A. Fery, A. Lederer, G. Kothleitner, *Langmuir* 34 (2018) p. 8622.
[3] C. Rossner, E.B. Zhulina, E. Kumacheva, *Angew. Chem. Int. Ed.* 58 (2019), p. 9269.
[4] S. Vazirieh Lenjani, M. Mayer, R. Wang, A. Fery, J.-U. Sommer, C. Rossner *(submitted).*
[5] The authors acknowledge funding by a Liebig fellowship (Fonds der Chemischen Industrie.)

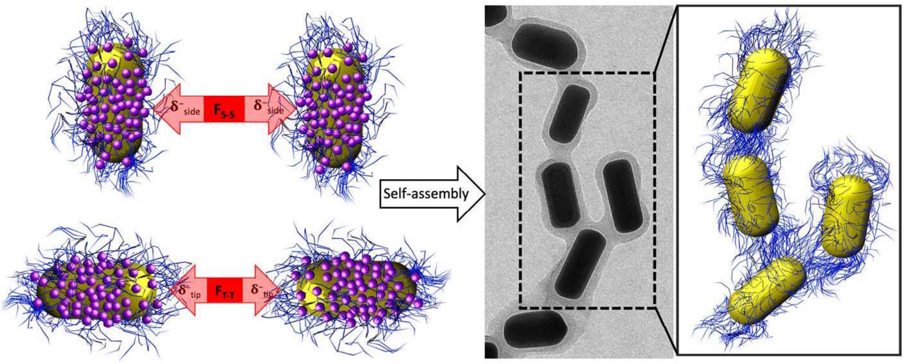

**Figure 1.** Tip-to-tip self-assembly of gold nanorods coated with a homogeneous polystyrene layer.

# Small angle X-ray (SAXS) study of bicontinuous non-ionic microemulsions in confined space

René Haverkamp[1], Margarethe Dahl[2], Stefan Wellert[2] and Thomas Hellweg[1]

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The widespread use of surfactants in tertiary oil recovery, enabling the recovery of otherwise unreachable oil in porous rock, requires a deeper knowledge of the properties of microemulsions under confinement in pores. Our approach to this problem is to study the phase behaviour of a non-ionic surfactant $L_3$ phase microemulsion consisting of n-decyltetraoxyethylene($C_{10}E_4$), water, and octane in a controlled porous glass (CPG) as a model system. CPGs are isotropic porous glasses with a bicontinuous pore network.

The stabilising effect of confinement on the single-phase range of a binary liquid from 20°C to lower temperatures has been shown previously [1]. The characterisation of a more complex ternary system, namely the $L_3$ phase of a $C_{10}E_4$/water/octane microemulsion (CE), is challenging. A theoretical model, together with experimental data, has shown that this system forms a lamellar layer at the solid-liquid interface of a planar glass [2,3]. It is important to note that the thickness of the lamellar layer in this case is equal to the domain size d of the corresponding bulk microemulsion.

To study this system under confinement, the bicontinuous liquid is soaked in a powder of controlled porous glass (CPG) with variable pore diameters. Thus, the confined system can be studied by small angle X-ray scattering (SAXS) to determine the domain size d. Measurements were performed at temperatures from 5°C to 55°C in CPGs with a nominal pore diameter of the CPG from 75 Å to 1000 Å. The SAXS data show a strong temperature-dependent shift in domain sizes of the confined microemulsion in large pore diameters while this shift is suppressed in small pore diameters.

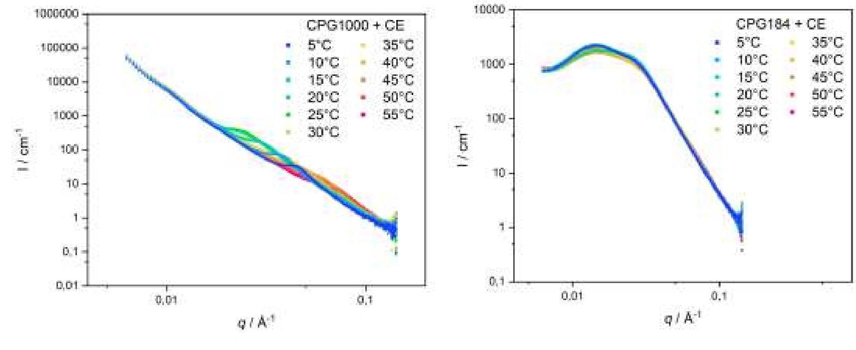

**Figure 1.** SAXS Graphs of a confined microemulsion in CPG with nominal pore diameter of 1000 Å on the left and 184 Å on the right side.

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[4] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG), Project number 455432427

# Crown ether-functionalized complex emulsions as an artificial adaptive material platform

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In this contribution, we present a material platform based on biphasic, anisotropic double emulsion droplets that can autonomously and reversibly adapt to their chemical environment through different supramolecular recognition events. The recognition mechanism is achieved by the selective assembly of synthetic crown ether surfactants on one hemisphere of the emulsion droplets. [1] The dynamic and reversible host-guest complexation of the crown ether surfactants with different analytes, such as metal and ammonium ions or amino acids, leads to interfacial tension changes at the droplet surface, which in turn results in morphological reconfiguration of the complex emulsion droplets. The newly developed adaptive soft material platform has been used for biomimetic recognition of biomolecules, including amino acids, carbohydrates and antibodies, and for triggered surface-encoded release of payloads, among other applications.
By using the crown ether-functionalized droplets, we observed that different supramolecular host-guest recognition events at the interface can lead to two opposite morphological transitions. After the addition of inorganic metal salts, such as potassium acetate, the droplets transitioned from their initial Janus configuration to an encapsulated double emulsion morphology ($\theta = 0°$). It is known that crown ether units form hydrophobic complexes when coordinated with suitable metal ions, leading to a phase transfer of the metal salts into the organic phase. The reduced effectiveness of the crown ether surfactants thus led to an increase in the interfacial tension between hydrocarbon and water. In contrast, the addition of a hydrophilic ammonium compound, was followed by a further 'opening up' of the Janus droplet morphology towards contact angles of $\theta > 90°$, which corresponds to a decrease of the HC-W interfacial tension. In this scenario, complexation of the hydrophilic ammonium compounds led to an increase of the hydrophilic-lipophilic balance of the surfactant, resulting in a more effective surfactant. Horizontal imaging allowed in-situ visualization of both morphological transitions evoked by the different molecular recognition events.

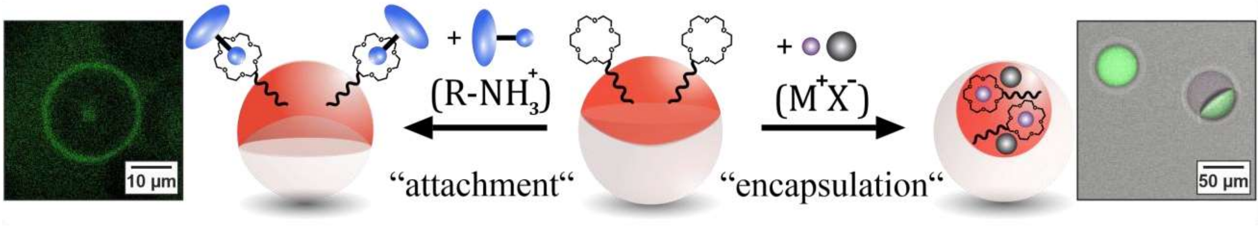

**Figure 1.** Crown ether-functionalized droplets that can undergo two opposite morphological transitions depending on the supramolecular host-guest recognition event at the interface of the droplets. Attachment of hydrophilic ammonium compounds left and encapsulation of metal ions right.

[1] S. Djalali et al., *Adv. Funct. Mater.* **2021**, 2107688.