CHIMIA 2021, Volume 75
ISSN 0009-4293
www.chimia.ch
Supplementa to Issue 7-8/2021

SCS
Swiss Chemical
Society

SCS Fall Meeting 2021 (online conference)
Lecture, Short Talk and Poster Abstracts

Session of Polymers, Colloids & Interfaces

September 10, 2021
University of Bern (online conference)
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Colour with a twist: from cellulose to large scale production of interference pigments

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The most brilliant colours in nature are obtained by structuring transparent materials on the scale of the wavelength of visible light. By designing the dimensions of such nanostructures, it is possible to achieve extremely intense colourations over the entire visible spectrum without using pigments or colorants. Colour obtained through structure, namely structural colour, is widespread in the animal and plant kingdom [1]. Such natural photonic nanostructures are generally synthesised in ambient conditions using a limited range of biopolymers. Given these limitations, an amazing range of optical structures exists: from very ordered photonic structures [2], to partially disordered [3], to completely random ones [4].

In this seminar, I will introduce some striking example of natural photonic structures [2-4] and share some insight on their development. Then I will review our recent advances to fabricate biomimetic photonic structures using the same material as nature. Developing biomimetic structures with cellulose enables us to fabricate novel photonic materials using low cost polymers in ambient conditions [6-7]. Importantly, it also allows us to understand the biological processes at work during the growth of these structures in plants.

[1] Kinoshita, S. et al. (2008). Physics of structural colors. Rep. Prog. Phys. 71(7), 076401.
[2] Vignolini, S. et al. (2012). Pointillist structural color in Pollia fruit. PNAS 109, 15712-15716.
[3] Moyroud, E. et al. (2017). Disorder in convergent floral nanostructures enhances signalling to bees. Nature 550, 469.
[4] Burresi M. et al. (2014) Bright-White Beetle Scales Optimise Multiple Scattering of Light. Sci. Rep. *4,* 727
[5] Parker R. et al. (2018) The Self-Assembly of Cellulose Nanocrystals: Hierarchical Design of Visual Appearance. Adv Mat 30, 1704477
[6] Parker R. et al. (2016). Hierarchical Self-Assembly of Cellulose Nanocrystals in a Confined Geometry. ACS Nano, 10 (9), 8443–8449
[7] Liang H-L. et al. (2018). Roll-to-roll fabrication of touch-responsive cellulose photonic laminates, Nat Com 9, 4632

Polymers, Colloids & Interfaces, Contributed Talk (15min) **PI-013**

Loop structures for strain sensing in elastomers

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Mechanophores that exploit non-covalent interactions have gained recent interest due to their high reversibility and variable interaction strength.[1] Taking advantage of this concept, we developed polymers containing a rotaxane mechanophore that shows highly sensitive and reversible fluorescence switch-on behavior and a cyclophane mechanophore that displays ratiometric fluorescence color changes when subjected to uniaxial tensile deformation.[2] However, the synthesis of these motifs is complex and requires a large number of steps. Simple loop structures are an attractive alternative, since they are much more accessible, and related efforts in polymers gels have reported promising results.[3] We now report a non-covalent loop mechanophore with two covalently linked perylene diimide chromophores that was accessed in only three synthetic steps.[4] The incorporation of small amounts of this motif in poly(methyl acrylate) (PMA) and elastomeric polyurethanes (PU) with different hard segments was pursued to obtain solid polymer films that display the orange excimer emission of associated perylenes. In response to temperature or uniaxial tensile deformation, disruption of the dye aggregates occurs and an increase in green monomer emission is observed (**Figure 1**). An in-situ spectroscopic characterization corroborates that the intramolecular loop structure efficiently responds to the mechanical stimuli translating the applied strain into a defined optical response. Moreover, we demonstrate how complex stress relaxation processes and loading/unloading cycles can be monitored in samples that feature the loop mechanophores.

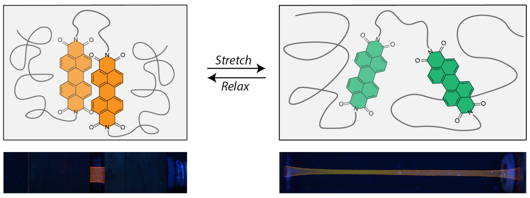

Figure 1 : Illustration of the working principle of a loop mechanophore (top) and photographs of polymer films bearing such loop mechanophores at 0 % and 1500 % strain (UV light illumination; λ_{ex} = 365 nm).

[1] Hanna Traeger, Derek J. Kiebala, Christoph Weder, Stephen Schrettl, *Macromolecular Rapid Communication* **2021**, *42*, 2000573

[2] a)Yoshimitsu Sagara**,** Marc Karman, Ester Verde-Seto, Kazuya Matsuo, Yuna Kim, Nobuyuki Tamaoki, Christoph Weder, *Journal of the American Chemical Society* **2018**, *140*, 1584; b) Yoshimitsu Sagara, Hanna Traeger, Jie Li, Yuji Okado, Stephen Schrettl, Nobuyuki Tamaoki, Christoph Weder, *Journal of the American Chemical Society.* **2021,** *143*, 5519–5525

[3] Jian Chen, Adam W. Ziegler, Baoming Zhao, Wei Wan, Alexander D. Q. Li, *Chemical Communications* **2017**, *53*, 4993

[4] Hanna Traeger, Yoshimitsu Sagara, Derek J. Kiebala, Stephen Schrettl, Christoph Weder, *Angewandte Chemie International Edition.* **2021**, https://doi.org/10.1002/anie.202105219

Thermoplastic Toughening of Semiaromatic Polyamides Using Amine-terminated Polyethylene

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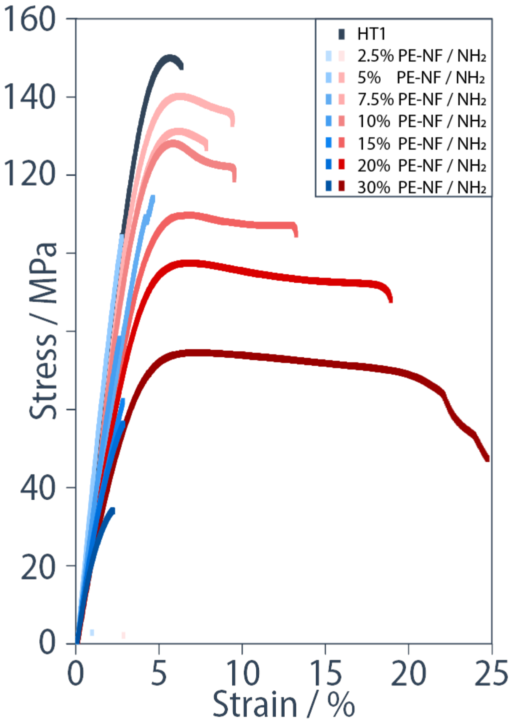
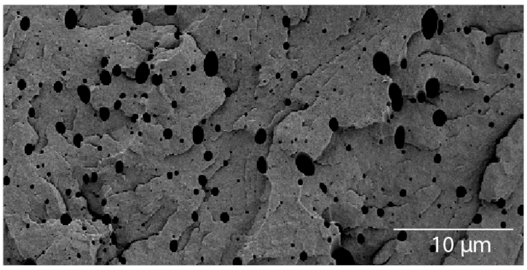
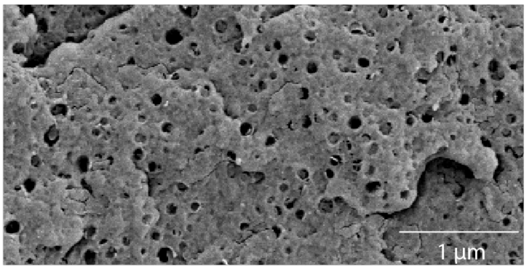
[1]Institute of Materials Science and Engineering, École polytechnique fédérale de Lausanne, Route Cantonale, Lausanne, Switzerland

Semiaromatic commercial polyamides can be used for metal replacement in advanced engineering applications, as a way to decrease total weight and improve efficiency. However, they often suffer from an inherent lack of ductility. Here, we have incorporated amine-terminated polyethylene (PE) into semiaromatic polyamide HT1 using high-temperature melt blending, which we have envisaged to serve as a thermoplastic toughener. We have investigated the resulting materials microstructure and properties in comparison to materials blended with non-functional PE or the commercial impact modifier styrene-ethylene-butylene-styrene (SEBS). This analysis shows that significantly smaller and more uniform PE domains are present in the amine-terminated composition, resulting in superior mechanical performance.





5% PE-NF



5% PE-NH$_2$

Glass fibers are widely used to reinforce polyamides when increasing stiffness and strength are required; for this reason, we have reinforced our PE/polyamide materials with glass fibers and have observed a similar property profile to the of aliphatic polyamide PA6 with glass fibers. The primary advantage of our composite materials over a reinforced PA6 is the thermal stability of the matrix due to a higher melting temperature.

Tuning Dispersity by Photoinduced Atom Transfer Radical Polymerisation: Monomodal Distributions with ppm Copper Concentration.

R. Whitfield [1], K. Parkatzidis[1], M. Rolland[1], N. P. Truong[1], A. Anastasaki[1]*

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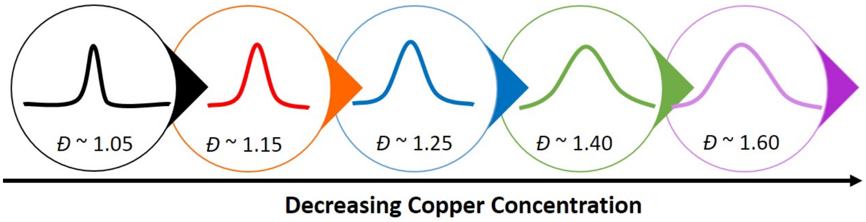
Dispersity significantly affects the properties of polymers. However, current methods for controlling polymer dispersity are limited to bimodal molecular weight distributions, adulterated polymer chains, or low end-group fidelity and rely on feeding reagents, flow-based, or multicomponent systems. To overcome these limitations, we report a simple batch system whereby photoinduced atom transfer radical polymerisation is exploited as a convenient and versatile technique to control dispersity of both homopolymers and block copolymers. By varying the concentration of the copper complex, a wide range of monomodal molecular weight distributions can be obtained ($Đ$ = 1.05–1.75). In all cases, high end-group fidelity was confirmed by MALDI-ToF-MS and exemplified by efficient block copolymer formation (monomodal, $Đ$ = 1.1–1.5). Importantly, our approach utilises ppm levels of copper (as low as 4 ppm), can be tolerant to oxygen and exhibits perfect temporal control, representing a major step forward in tuning polymer dispersity for various applications.



[1] Richard Whitfield, Kostas Parkatzidis, Manon Rolland, Nghia Truong, Athina Anastasaki, *Angew. Chem. Int. Ed.,* **2019,** 58, 13323-13328.

[2] Richard Whitfield, Nghia Truong, Daniel Messmer, Kostas Parkatzidis, Manon Rolland, Athina Anastasaki, *Chem. Sci,* **2019,** 10, 8724-8734.

Amphiphilic Polymer Conetworks – Wearable and High Energy Transfer Rate Luminescent Solar Concentrators

C. Huang[1,2], K. Jakubowski[1], S. Ulrich[1], S. Yakunin[2], L. F. Boesel[1]*, M. V. Kovalenko[2]*

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Luminescent solar concentrators (LSCs) have attracted considerable attention in recent years for their advantages in absorbing diffusive light and increasing the cost-effectiveness of solar cells; however, the compatibility with flexible photovoltaics and the energy transfer (ET) efficiency still require improvement. In our current work [1], amphiphilic polymer conetworks (APCNs) are employed as polymer matrices for wearable LSCs owing to their flexibility and wearability. Furthermore, with the assistance of APCNs' nanophase separated hydrophobic and hydrophilic domains, hydrophobic (Lumogen Red, acceptor) and hydrophilic (fluorescein, donor) luminescent materials are loaded in adjacent nanometer-separated domains. This results in high ET rates and broaden the acceptor's absorption range, rendering a more efficient down conversion emission. With this straightforward synthesis procedure, we could achieve high ET rates between dye pairs via FRET and photon recycling. This two energy transfer mechanisms were confirmed by steady-state and dynamic photoluminescence methods, showing a ~100% total ET between donors and acceptors.

Applying the loaded APCN as a coating, we were able to increase the efficiency of flat solar cells by matching its absorption profile with the emission range of the dye pairs (e.g. pc-Si PVs PCE increased of 14.5% in the excitation range of 375-550 nm). The developed nanostructure-assisted ET system is not limited to the dyes investigated here, but can be directly extended to a wide variety of dyes (Rhodamine B, HPTS, DCM, and Lumogen Yellow) and quantum dots (CsPbBr3 and CdSe/ZnS). Furthermore, the re-emitted photons are monitored via geometry photoluminescence measurement and Monte Carlo ray tracing simulation, indicating the APCNs LSC vertically-tandem attached to the flexible photovoltaics can effectively increase the light absorbing area and be beneficial to the optimal utilization of incident light. This novel APCN could find potential uses in the energy-harvesting field, serving as wearable LSCs for the next generation of flexible and wearable photovoltaics.

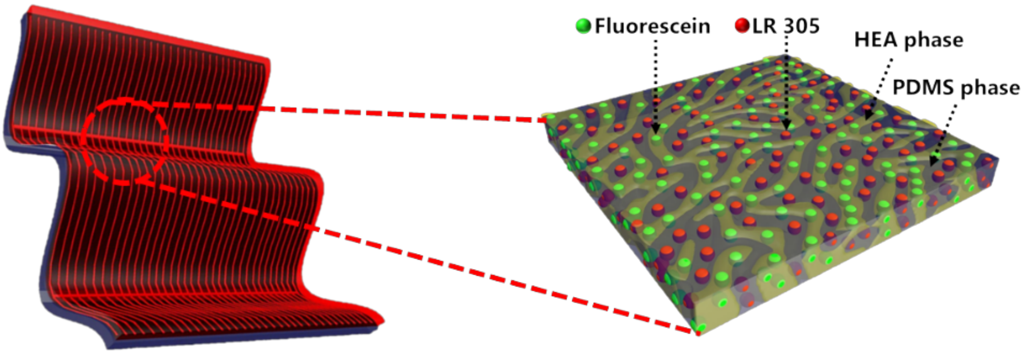

Figure 1. Scheme of flexible tandem LSC/PVs with APCN containing two dyes forming FRET pairs

[1] C.-S. Huang, K. Jakubowski, S. Ulrich, S. Yakunin, M. Clerc, C. Toncelli, R. M. Rossi, M. V. Kovalenko, and L. F. Boesel, *Nano Energy*, **2020**, 76, 105039

Bacteria-Induced Mineralization of 3D Printed Hydrogel Structures

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Despite recent advances in the field of hydrogel inks for 3D printing applications, the ability to precisely control their local composition remains unexplored. The introduction of particle-based inks enabled the possibility to engineer mechanical and chemical gradients within the printed constructs with unparalleled precision. However, the capability of homogeneously integrating inorganic components, such as biominerals, in the hydrogel ink, while maintaining good mechanical integrity, still remains a major challenge. Inspired by nature, we mimic the biomineralization process often observed in crustaceans and mussels, where inorganic crystals are precipitated in a gelatinous matrix. Here, we introduce a 3D printing approach to fabricate biomineralized hydrogel structures by encapsulating ureolytic bacteria in a granular bioink. The resulting printed structure can be easily stabilized with no harm to the bacteria, and the mineralization can be initiated simply by urea exposure. The final biomineral-gel composite is able to retain the initial shape and support its own weight. This new technique promises to further extend the field of 3D hydrogel printing enabling the fabrication of new hybrid materials for the production of next generation biomineral composites.

High-Performance Polyamides by EMS-GRIVORY

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Programming of Self-Assembly in Time with Chemical Clocks

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Living systems can grow bottom-up a huge variety of materials with the highest degree of sophistication, and an overall efficiency that remains largely unparalleled by artificial fabrication techniques. Moreover, living materials are adaptive *i.e.* are able to exist and perform autonomously under dissipative conditions. These features are possible thanks to the ability to control complex reactions networks, carefully organized in spatio-temporal sequences.

Filling the gap between state-of-art stimuli-responsive materials and living materials requires to combine materials science with systems chemistry. In this way, chemical curiosities such as clock and oscillating reactions become versatile tools to program in time the autonomous and transient self-assembly of organic as well as inorganic building blocks.

The design of such *ad hoc* reaction networks is at the core of my current research efforts. I will show how to “clock” molecules, polymers and metal cations into different structures (from nanoparticles to gels), without the need for external control, and how this approach can pave the way to the development of (almost) living artificial materials.

[1] Solenn Riedel, Thomas Schweizer, Katrina Smith-Mannschott, Eric R. Dufresne, Guido Panzarasa *Soft Matter* **2021**, *17*, 1189-1193.

[2] Guido Panzarasa, Eric R. Dufresne, *Chimia* **2020**, *74*, 612.

[3] Guido Panzarasa *ChemistrySelect* **2020**, *5*, 8074-8077.

[4] Alina Osypova, Matthias Dübner, Guido Panzarasa, *Materials* **2020**, *13*, 2957 (18 pp).

[5] Christian C. M. Sproncken, Berta Gumí-Audenis, Guido Panzarasa, Ilja K. Voets,

[6] Guido Panzarasa, Alexandre L. Torzynski, Tianqi Sai, Katrina Smith-Mannschott, Eric R. Dufresne, *Soft Matter* **2020**, *16*, 591-594.

[7] Guido Panzarasa, Tianqi Sai, Alexandre L. Torzynski, Katrina Smith-Mannschott, Eric R. Dufresne, *Mol. Syst. Des. Eng.* **2020**, *5*, 445-448.

[8] Guido Panzarasa, Eric R. Dufresne, *Chaos* **2019**, *29*, 071102 (5 pp).

[9] Guido Panzarasa, Alina Osypova, Alba Sicher, Arie Bruinink, Eric R. Dufresne, *Soft Matter* **2018**, *14*, 6415–6418.

Understanding the role of monomer-monomer interactions in the formation of semi-crystalline surface patterns from trimeric DNA macromolecules

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Adsorption of colloidal particles from a bulk solution onto a perfectly planar substrate has been extensively exploited as a way to obtain ordered two-dimensional (2D) phases, called 2D colloidal crystals (2DCC). Even if these crystals have plenty of applications in the fields of biology, biomedicine and materials science, many questions still remain regarding the dynamics of their formation, such as how monomer-monomer interactions affect the assembly dynamics and the final assembled structure.

To gain insights on the fundamental assembly mechanisms, we engineered blunt-end trimeric DNA macromolecules that are able to form extensive semi-crystalline surface networks through pi-pi stacking of terminal bases upon adsorption on a mica surface. We are able to track the early stages of nucleation and growth of these trimeric DNA macromolecules through images obtained by high-speed atomic force microscopy (HS-AFM) to derive the fundamental mechanisms behind the nucleation, growth and error-correction kinetics in 2DCCs.

Using the unique programmability provided by DNA-nanotechnology, we show we can tune the monomer-monomer interactions by modifying the end-group affinity and the flexibility of the particles and relate the molecular monomer design to changes in network formation. We then combined our observations with Monte Carlo simulations of trimeric patchy particles to further estimate the range of physical energies involved in the experiments. Our findings contribute to the understanding of the fundamental mechanisms behind the formation of 2DCC and provide insights on the design of molecular building blocks in bottom-up nanotechnology.

Self-Assembly of Polymeric Nanocapsules towards Multi-Functional Supracapsules

M. Hu[1], N. Reichholf[1], L. A. Frances[1], S. N. Ramakrishna[1], Y. Xia[2,3], X. Cao[2], S. Ma[3], A. J. deMello[2], L. Isa[1]*

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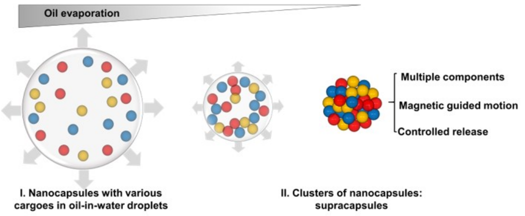
The assembly of nanomaterials offers the possibility of fabricating functional materials for various applications. Compared with a single nanomaterial exhibiting a single function, the co-assembly of different nanomaterials allows performing multiple tasks simultaneously or in sequence.[1-3] Usually, nanoparticles are the most commonly used building blocks in nanomaterials assembly. However, nanocapsules possess more functionality and versatility.[4,5] Herein, we use evaporation-guided assembly to produce controlled assemblies of polymeric nanocapsules, called supracapsules. We first synthesize dextran-based nanocapsules with fluorescent dyes and superparamagnetic nanoparticles, by interfacial polyaddition in a water-in-oil miniemulsion. Subsequently, we confine the synthesized nanocapsules within monodisperse oil droplets in an oil-in-water emulsion obtained by microfluidics. After evaporating the oil, the nanocapsules spontaneously assemble into a spherical cluster, which we term supracapsule. By controlling the size of the droplets and the concentration of nanocapsules, the size of supracapsules can be finely tuned. After assembly, the resulting supracapsules preserve the functions presented in the nanocapsules. In the case of the incorporation of magnetic nanocapsules, the magnetic properties of supracapsules are enhanced compared with single nanocapsules, resulting in an easily controllable motion. Interestingly, the supracapsules have unique release kinetics compared with single nanocapsules. The release profile of encapsulated cargos in supracapsules can be further programmed. We envision that this new generation of assembled materials could promote the development of supraparticle-based materials for a wide range of applications.



[1] Zhihong Nie, Alla Petukhova, Eugenia Kumacheva, *Nature Nanotechnology*, **2010**, 5, 15-25.

[2] Susanne Wintzheimer, Tim Granath, Maximilian Oppmann, Thomas Kister, Thibaut Thai, Tobias Kraus, Nicolas Vogel, Karl Mandel, *ACS Nano*, **2018**, 6, 5093-5120.

[3] Songbo Ni, Jessica Leemann, Ivo Buttinoni, Lucio Isa, Heiko Wolf, *Science Advances*, **2016**, 4, e1501779.

[4] Banu Iyisan, Katharina Landfester, *Macromolecular Rapid Communications*, **2018**, 40, 1800577.

[5] Minghan Hu, Stefan Peil, Yaowen Xing, Diana Döhler, Lucas Caire da Silva, Wolfgang H. Binder, Michael Kappl, Markus B. Bannwarth, *Materials Horizons*, **2018**, 1, 51-58.

Physical characterization of virus-like particles carrying B cell epitopes for surface glycoprotein of SARS-CoV-2 virus

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We use atomic force microscopy (AFM) to investigate the nanomechanical properties of virus-like particles (VLPs) assembled from *Acinetobacter* phage protein AP205 (forming a scaffold) conjugated with B cell epitopes for surface glycoprotein of SARS-CoV-2 virus. The scaffold is found to have a stiffness and diameter equal to about 100 pN/nm and 20 nm respectively from direct force measurements in PeakForce Tapping mode with peak forces below 400 pN (Fig. 1a-c). Small angle X-ray scattering reveals an undeformed diameter of 26.2 nm and protein shell thickness of 3.0 nm which together with the stiffness give an estimation for the elastic modulus equal to 65 MPa in agreement with other virus capsids [1]. Addition of B cell epitope amino acids (up to about 25% in weight as compared to the molecular weight of AP205) to the surface of scaffold is found to increase the diameter by about 5 nm but this leads to only a slight increase in the stiffness. When the epitope is repeated one more time on the surface of the scaffold, the diameter is found to increase by an additional 5 nm, and in this case, a rise in the stiffness by about two times is observed. Furthermore, some particles were found to be dumbbell-like showing that the assembly from peptide-conjugated AP205 may deviate from a spherical particle if the peptide is long. Preliminary in vivo investigations were performed in mice and the results showed variations among these particles in antibody response. We aim to find the relations between physical properties including size, shape, stiffness and modulus and immunogenicity leading to optimization of the former properties in order to increase the immune response induced by these VLPs.

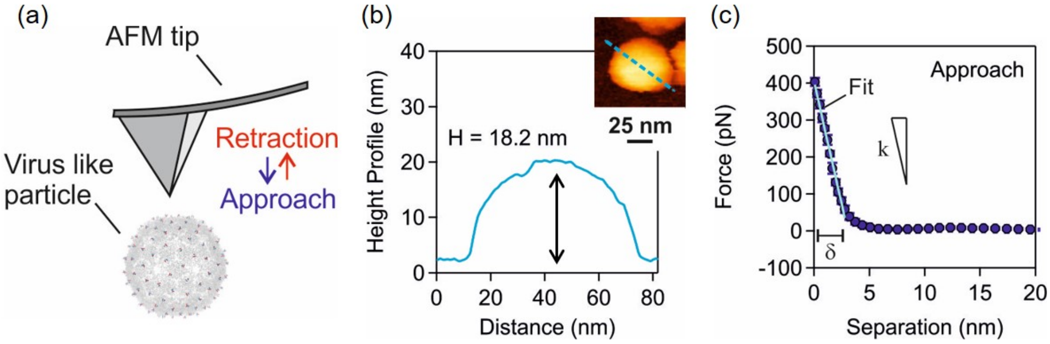

Figure 1: Schematic of atomic force microscopy investigations of virus like particles (a) leading to the evaluation of height profile from imaging (b) and stiffness from direct measurements of force-indentation (F - δ) curves (c) at single particle level.

[1] Andreas Fery, Richard Weinkamer, *Polymer*, **2007**, 48, 7221–7235.

Non-Classical Reaction Behavior of Complex Molecular Systems Based on Coupled Assembly Processes

T. Schnitzer[1], M. F. Mabesoone[1], S. A. Jansen[1], G. Vantomme[1], B. Meijer[1]*

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Complex molecular systems are key for device miniaturization, development of energy materials and efforts to mimic biological processes.[1-3] Self-assembly, the power of molecules to autonomously form defined aggregates, is a key player in the emergence of complexity in molecular systems. Yet, the construction of such systems is not easy. Inspired by total synthesis in organic chemistry, a paradigm shift from one-step assembly to multi-step non-covalent synthesis was proposed: Complex molecular systems are not obtained in a single non-covalent assembly step, but rather in a combination of covalent and non-covalent reaction steps.[4] This raises the question how to perform covalent organic reactions in combination with supramolecular structures. This is challenging because supramolecular structures are often assembled by weak forces, in continuous dynamic exchange and are highly sensitive to environmental changes.[1-5] Thus, supramolecular substrates are difficult targets for common organic syntheses. Alike small details that drive the unrepeatable crystallization of a desired polymorph or a sudden drop in reactivity of a catalyst from a different source, recently also supramolecular chemistry reached a level of complexity in which underappreciated subtleties can have an unexpected major impact on a system.

Here, we study the reaction behavior of a system in which the *in-situ* formation of discotic 1,3,5-benzenetricarboxamide (BTA) monomers is linked to an intertwined non-covalent reaction network including self-assembly into helical BTA polymers. This system shows an unexpected phase-separation behavior in which a complex interplay of reactant/product concentrations, site-products and solvent purity determines the system composition. These insights allow us to offer a guide on how to design the synthesis of new materials in a covalent/non-covalent fashion. We suspect that the non-classical reaction behavior observed in our simple model system might also play a role in biological reaction networks, providing an additional – yet underappreciated – level of complexity in reaction networks of living systems.

[1] J. F. Lutz, J. M. Lehn, E. W. Meijer, K. Matyjaszewski, *Nature Reviews Materials* **2016**, *1*, 16024.

[2] T. Aida, E. W. Meijer, S. I. Stupp, *Science* **2012**, *335*, 6070.

[3] T. Aida, E. W. Meijer, *Isr. J. Chem.* **2020**, *60*, 33.

[4] G. Vantomme, E. W. Meijer, *Science* **2019**, *363*, 6434.

[5] T. Schnitzer, G. Vantomme, *ACS Cent. Sci.* **2020**, *6*, 2060.

[6] T. Schnitzer, M. F. J. Mabesoone, S. A. H. Jansen, G. Vantomme, E. W. Meijer, *manuscript submitted*.

Conjugated Microporous Polymers Using a Copper-Catalyzed [4+2] Cyclobenzannulation Reaction: Promising Materials for Iodine and Dye Adsorption

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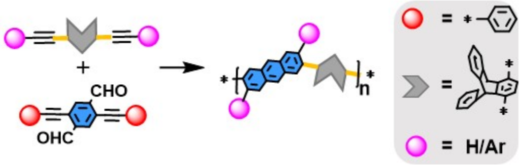
[1]Gulf University for Science and Technology, Kuwait, [2]Functional Materials Group - CAMB, GUST, Kuwait

A design strategy is disclosed to synthesize conjugated microporous polymers (CMPs) using a versatile copper-catalyzed [4+2] cyclobenzannulation reaction, which employs a diphenylethynyl terephthalaldehyde derivative **3** with a series of triptycene-based diethynyl aryl building blocks **2a-e**. Investigation of the intrinsic microporosity properties of **CBP1-5** using nitrogen adsorption measurements, reveal Brunauer-Emmett-Teller (BET) surface areas up to 794 m^2g^{-1} and average pore volumes reaching 0.63 cm^3g^{-1}. Inspection of the adsorption properties of the graphitic-like polymers **CBP1–5** divulges their high iodine uptake with a maximum of 166 wt%. Moreover, the target polymers **CBP1–5** prove their efficiency as selective dye adsorbents by removing up to 100% methylene blue over methyl orange from aqueous solution.[1]



[1] N. Baig, S. Shetty, S. Al-Mousawi and B. Alameddine, *Polymer Chemistry*, **2021**, DOI: 10.1039/D1PY00193K.

PLA-lignin films for sustainable food packaging

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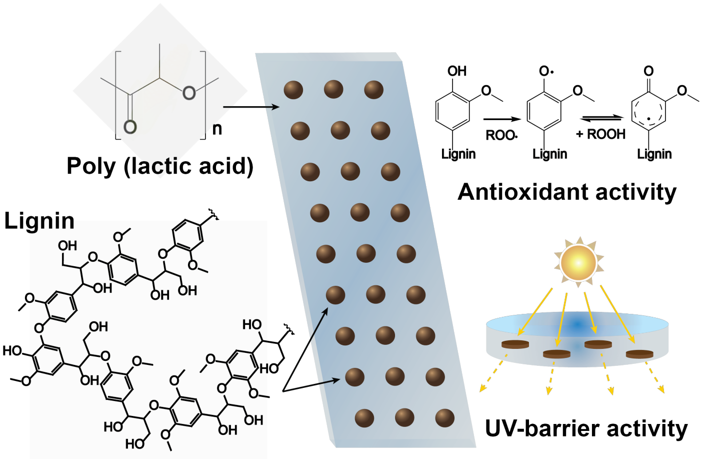
Lignin is one of the main constituents of the plant cell wall and represents the most abundant natural source of aromatics on our planet. Around 70 million tons of lignin is burned every year as a byproduct of the paper and pulp industry, hence significant attention has been given to a wide-scale use of this polymer for various applications.[1] The complex structure of lignin gives to this plant-derived polymer the potential to act as an antioxidant and inhibit radical oxidation reactions.[2] Lignin also possesses chromophoric groups, which can absorb UV-light.[3] Thanks to these properties, lignin is a promising material for the application in food packaging. It can protect food from auto-oxidation and UV-degradation processes, thus extending its shelf life.

In this research work, we incorporated lignin into another sustainable and biodegradable polymer, poly(lactic acid) (PLA). PLA is derived from starch and provides an excellent alternative to conventional petroleum-based plastics.[4] However, antioxidant and UV-barrier activities remain a challenge for PLA products, limiting their application in food packaging. By incorporating lignin into PLA films, we were able to overcome these limitations without significantly compromising the mechanical properties. In order to optimize the effects of lignin on the films features, lignin nanoparticles (LNPs) with high surface-to-volume ratio were prepared. Excellent dispersion of the LNPs was obtained by grafting some PLA chains from their surface, developing films with outstanding antioxidant and UV-barrier activity. These results pointed out the potential of such sustainable films for the application in food packaging.



[1] Brianna M. Upton, Andrea M. Kasko, *Chemical Reviews*, **2016**, 116, 2275-2306
[2] Sandra Domenek, Abderrahim Louaifi, Alain Guinault, Stéphanie Baumberger, *Journal of Polymers and the Environment*, **2013**, 21, 692-701
[3] Hasan Sadeghifar, Arthur Ragauskas, *Polymers*, **2020**, 12, 1134-1144
[4] Ray E. Drumright, Patrick R. Gruber, David E. Henton, *Advanced Materials*, **2000**, 12, 1841-1846

Understanding the role of monomer-monomer interactions in the formation of semi-crystalline surface patterns from trimeric DNA macromolecules

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Adsorption of colloidal particles from a bulk solution onto a perfectly planar substrate has been extensively exploited as a way to obtain ordered two-dimensional (2D) phases, called 2D colloidal crystals (2DCC). Even if these crystals have plenty of applications in the fields of biology, biomedicine and materials science, many questions still remain regarding the dynamics of their formation, such as how monomer-monomer interactions affect the assembly dynamics and the final assembled structure.

To gain insights on the fundamental assembly mechanisms, we engineered blunt-end trimeric DNA macromolecules that are able to form extensive semi-crystalline surface networks through pi-pi stacking of terminal bases upon adsorption on a mica surface. We are able to track the early stages of nucleation and growth of these trimeric DNA macromolecules through images obtained by high-speed atomic force microscopy (HS-AFM) to derive the fundamental mechanisms behind the nucleation, growth and error-correction kinetics in 2DCCs.

Using the unique programmability provided by DNA-nanotechnology, we show we can tune the monomer-monomer interactions by modifying the end-group affinity and the flexibility of the particles and relate the molecular monomer design to changes in network formation. We then combined our observations with Monte Carlo simulations of trimeric patchy particles to further estimate the range of physical energies involved in the experiments. Our findings contribute to the understanding of the fundamental mechanisms behind the formation of 2DCC and provide insights on the design of molecular building blocks in bottom-up nanotechnology.

pH Responsive Microgels as Reversible “*on demand*” Cation Carriers

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Stimuli responsive microgels are small polymeric materials which are well known for their outstanding potential in drug delivery applications.(1) Microgels, however, do not only serve as cargo carriers for small drugs, but can store and release other substances, such as proteins, low molecular weight polymers and ions. Cations, in particular, can be bonded and released upon chemical changes in the external environment of the microgels with trivial pH changes. (2) There is a multitude of biochemical and enzymatic reactions in the cell that are activated or involve cations such as Ca^{2+} or Mg^{2+}, such as actin polymerization within the cytoskeleton formation. When it comes to studying such biochemical processes which require cell environment conditions, spatial separation between reactants can be the bottleneck issue for the feasibility of the experiment. Employing microgels specifically designed to protect and "*on demand*" release cations in the systems addresses this need of compartmentalization to study biochemical processes.

Herein we present a thermo, pH, and ion responsive microgel system that can reversibly bind divalent earth alkali and transition metal cations over multiple cycles. (3) The microgels are composed of vinylcaprolactam, dimethylitaconate and itaconic acid, which acts as the reversible binding site for the cations. The gels were synthesized *via* dispersion polymerization and their chemical composition, structure and morphology were fully characterized. We studied their responsiveness towards temperature, pH and ion concentration with dynamic and static light scattering. To prove their capability of spatially separating ions from the external environment, we determined their ion loading capability and the cation release upon pH changes with ion chromatography. We were able to show that these gels can reversibly bind earth alkali cations over multiple cycles and possess a selectivity towards the binding of certain cations, with a preferential binding for Fe^{3+}. Such functional microgels can thus be employed in synthetic biology systems in which the system design requires a higher degree of spatial separation complexity, including switchable systems and “*on demand*” triggered uptake and release, which these gels are capable of supplying.

[1] Plamper, F. A., & Richtering, W. , *Accounts of chemical research*, **2017** *50*(2), 131-140.
[2] Chimisso, V., Fodor, C., & Meier, W., **2019** *Langmuir*, *35*(41), 13413-13420.
[3] Chimisso, V., Conti, S., Kong, P., Fodor, C., & Meier, W. P. **2020** *Soft Matter*, *17*(3), 715-723.

Mechano-pigments for high dynamic range mechano-sensing in polymeric materials

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Polymers are ubiquitous in the modern world, composing materials as diverse as deformable elastomers in car tires, soft hydrogels for tissue mimics and strong, tough ballistic glass. Understanding their ability to bear an applied mechanical strain or stress is essential to engineering these materials. The recent development of optically mechano-sensing polymeric materials has been driven by this fundamental and technological necessity.[1–3] However, the force sensitivity of existing mechano-sensing systems remains restricted, activating at just one, usually high, critical stress threshold.

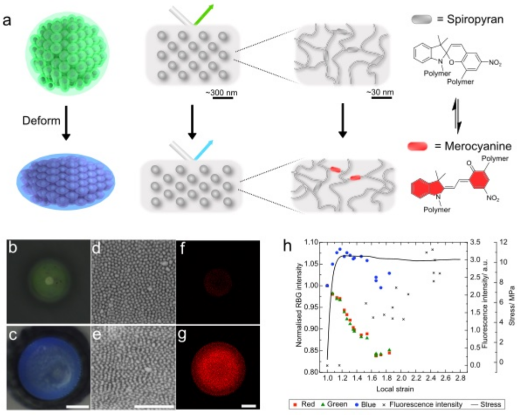

Figure 1: Mechano-pigments with microstructural and molecular mechanochromism: a) schematic; reflectance images of b) uncompressed and c) compressed sensors (scale-bar 50 µm); d), e) FIB-SEM images of interior colloidal arrangement for sensors in b) and c) (scale-bar 2 µm); fluorescence images of f) uncompressed and g) compressed sensors (scale-bar 50 µm); h) photonic and fluorescence response of sensors to tension in LLDPE.

This contribution presents broadly applicable, high dynamic range mechano-sensors, or “mechano-pigments”, capable of reporting on a wide range of deformations. The sensors are spherical, photonic assemblies of silica colloids, embedded in a soft, polymeric matrix cross-linked by a molecular mechano-sensor, spiropyran. The photonic array changes color at smaller deformations, and the spiropyran transforms to fluorescent merocyanine at larger deformations. Compression of single pigments revealed that the onset and extent of molecular mechano-activation is dependent upon the volume fraction of silica colloids in the structure. The mechano-pigments were also readily dispersed in different polymeric matrices, and used to investigate necking in linear low-density polyethylene.

[1] J. M. Clough, C. Weder, S. Schrettl, *Macromol. Rapid Commun.* **2021**, 42, 1.
[2] R. Göstl, J. M. Clough, R. P. Sijbesma, in *Mechanochemistry Mater.*, The Royal Society Of Chemistry, **2018**, pp. 53–75.
[3] J. M. Clough, J. van der Gucht, T. E. Kodger, J. Sprakel, *Adv. Funct. Mater.* **2020**, 30, 2002716.

Solvent-free synthesis of stretchable electrodes for application in "green" stacked dielectric elastomer actuators

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Stretchable, soft electronics have opened up a new range of possible applications expanding beyond the limitations of previously rigid electronic circuits.[1] Changing from rigid electronics to flexible electronics leads to a new class of deformable devices such as bendable displays, artificial skin, artificial muscles, wearable devices or soft robots. Besides their varying set-ups, most of these devices rely on flexible and stretchable electrodes. One application where conductive soft materials are subject to especially harsh conditions are dielectric elastomer actuators (DEA).[2,3] In short, DEA transform electrical energy into kinetic energy by applying charges on two electrodes that are sandwich around a dielectric elastomer.[3] For these applications electrodes, need to fulfill many challenging tasks leading to special electrical, mechanical and processing requirements that go beyond most standard requirements for flexible electrodes.[4] Here we introduce the synthesis of a highly conductive, soft, stretchable, and flexible electrode material using anionic polymerization of cyclosiloxane monomers in presence of graphene. The synthesis approach allows the material properties to be tuned specifically to the requirements of the soft device. Hence, the electrode can be used for many different applications. In this case, the electrode properties were selected for DEA application. Due to the solvent-free synthesis strategy, DEA stacks could be produced without the use of solvent by a green chemistry approach. Hence, to the best of our knowledge, this is the first "green" DEA stack manufactured not only using solvent free conductive and insulating inks, but also the synthesis of the respective inks starting from monomers, was solvent free.

[1] R. Ma, S.-Y. Chou, Y. Xie, Q. Pei, *Chem. Soc. Rev.,* **2019**, *48*, 1741-1786.
[2] S. Rosset, H. R. Shea, *Appl. Phys. A,* **2013**, *110*, 281-307.
[3] R. E. Pelrine, R. D. Kornbluh, J. P. Joseph, *Sens. Actuators A Phys.,* **1998**, *64*, 77-75.
[4] S. Rosset, C. de Saint-Aubin, A. Poulin, H. R. Shea, *Rev. Sci. Instrum.,* **2017**, *88*, 105002 (1-10).

One-pot Synthesis of Amphiphilic ABC Triblock Copolymer PEO-*b*-PEHOx-*b*-PEtOz and its Self-Assembly into Nanoscopic Asymmetric Polymersomes

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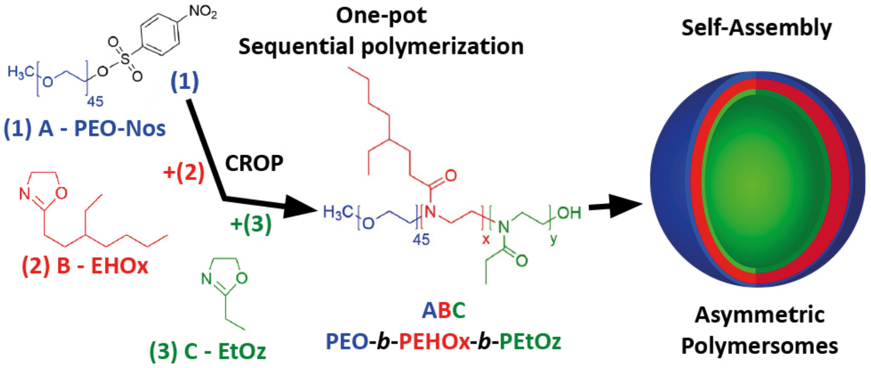
Based on our previously published PEO-*b*-PEHOx AB diblock copolymer with a peculiar self-assembly behaviour[1], a wide range of PEO-*b*-PEHOx-*b*-PEtOz ABC triblock co-polymers (ABC triblocks) was synthetized in one-pot using sequential cationic ring opening polymerization.[2] Following a detailed kinetic study and optimization of the polymerization conditions, an extensive library of well-defined PEO-*b*-PEHOx-*b*-PEtOz triblocks was synthetized and thoroughly characterized by NMR and GPC. We studied their self-assembly by film rehydration and solvent switch. The self-assemblies formed were comprehensively characterized by dynamic and static light scattering as well as TEM and Cryo-TEM, which shows our holistic approach. This allowed us to obtain a complete phase diagram of PEO-*b*-PEHOx-*b*-PEtOz comprising a vast array of different self-assembly structures. Micelles, worms, polymersomes and multi-compartment vesicles were obtained by fine-tuning the block-length ratio of all three blocks. Two independent methods, namely bicinchoninic assay (BCA) and 2D-^{1}H-NOESY NMR, allowed for a thorough and pin-pointed analysis of the surface composition of the polymersomes from the self-assembled asymmetric ABC triblocks. Our system was able to form both, asymmetric polymersomes and polymersomes with a mixed surface, again underlining the versatility of PEO-*b*-PEHOx-*b*-PEtOz triblocks. Coupled with the peptide-like nature of the membrane formed with PEHOx as an oxazoline, this preferred orientation opens up new opportunities toward the direct insertion of transmembrane proteins into asymmetric polymersomes.[3]



[1] Davy Daubian, Jens Gaitzsch, Wolfgang Meier. *Polymer Chemistry*, **2020**, 11, 1237-1248.
[2] Davy Daubian, Alexandra Fillion, Jens Gaitzsch, Wolfgang Meier. *Macromolecules*, **2020**, 53, 11040-11050.
[3] Evgeniia Konishcheva, Davy Daubian, Jens Gaitzsch, Wolfgang Meier. *Helvetica Chimica Acta***,** **2018,** 101 (2), e1700287-n/a.

Synthesis of polymeric particles with multiple lobes

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The formation of particles with multiple lobes has been the focus of several investigations because of their potential applications as colloidal molecules. Such particles can be used as a building block in the processes of self-assembly, or they can be used as carriers of different substances and functionalities, where each lobe can be different from the others in the same entity. In the production of multi-lobed particles, it is important to develop protocols that are reproducible and robust, with good yield, and where it is easy and simple to recover the particles at the end of the synthesis.

If one wants to form non-spherical particles, the surface tension force that drives a particle to adopt a spherical shape must be overcome. In this work, we show how this can be achieved by using a method based on multiple swelling and polymerization steps, starting from simple polystyrene colloids. By combining monomers, such as vinylbenzyl chloride and 3-(trimethoxysilyl)propyl methacrylate, to styrene, and sometimes by introducing a crosslinker, we have been able to induce a phase separation during some of the swelling-polymerization steps, which allowed us to create multi-lobed particles. Our method allows us to selectively functionalize some of the lobes independently thanks to the use of functional monomers. Examples of the self-assembly properties of these particles will be showcased.

Keywords: *multi-lobed particles, phase separation, emulsion polymerization, orthogonal functionalization.*

Supramolecular Assembly of Sugar Modified Disubstituted Pyrene Oligomer

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Nanoscale materials have been thoroughly studied in the past decade, as they exhibit interesting properties such as light-harvesting and nonclassical optoelectronic behavior and, therefore, find application in numerous fields. Previous work demonstrated the formation of 2D supramolecular polymers assembled from phosphodiester di-alkynyl-substituted pyrene trimers[1,2]. In this work, those building blocks have been functionalized with α-Mannose, enabling the possible decoration of the nanostructures with lectins. Spectroscopic measurements describing the aggregation process of the pyrene monomers will be presented.

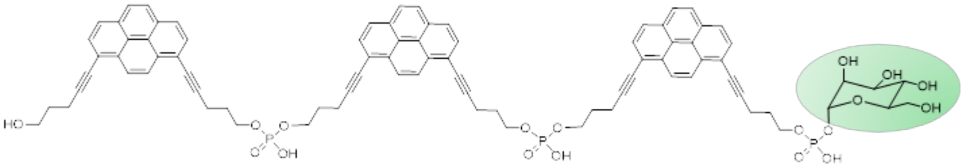

Figure 1: α-Mannose modified di-pentynyl-substituted pyrene trimer.

[1]: Mykhailo Vybornyi, Aleaxander V. Rudnev, Simon M. Langenegger, Thomas Wandlowski, Gion Calzaferri, Robert Häner, *Angew. Chem. Int. Ed.* **2013**, *52*, 11488–11493.

[2]: Mykhailo Vybornyi, Yuliia Vyborna, Robert Häner, *ChemistryOpen* **2017**, *6*, 488-491.

Covalent Triazine Frameworks Incorporating Charged Polypyrrole Channels for High-Performance Lithium-Sulfur Batteries

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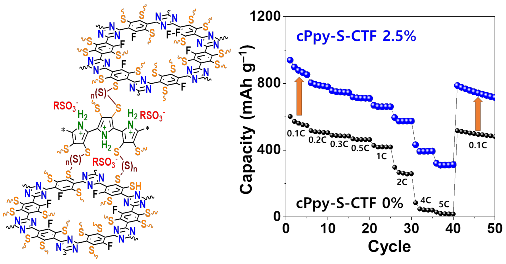
Covalent triazine frameworks (CTFs) have emerged as promising electrode materials for lithium-sulfur (Li-S) batteries owing to their pristine pyrdinic sites, conjugated backbone, and ability to stabilize remarkable sulfur contents. Following the first synthesis of sulfur-CTFs under catalyst and solvent-free reaction conditions[1], new synthetic strategies have been extensively investigated to improve CTFs properties for Li-S batteries applications. Further upgrading for CTFs was introduced to achieve extremely high sulfur contents CTFs via employing nucleophilic aromatic substitution reaction (SNAr) between perfluoroaryl units and elemental sulfur.[2] However, the previous (SNAr) approach possessed immense sulfur content up to 82%, it is challenging to endure high ionic and electronic conductivity with mitigation of Li-polysulfide (Li-PS) shuttling. These fatal problems limit their cycling performance at high active mass loadings. In an effort to tackle the previously mentioned problems, a new approach incorporates the integration of one-dimensional charged conducting polymers with a two-dimensional covalent triazine framework in the presence of elemental sulfur.[3] Noticeably, the addition of charged conducting polymers triggers a 3D nanochannel formation in the CTF framework with high-affinity anchoring sites towards Li-PS while achieving decent ionic and electronic conductivity. The resulting polymers showed significantly improved ionic, electronic conductivities, and high sulfur loadings. Because of these remarkable properties, we are able to obtain exceptional electrochemical performance at high mass loading of 3 mg sulfur per cm^2 with a specific capacity of 1275.2 mAh g^{-1} at 0.05C.



[1] S. N. Talapaneni, T. H. Hwang, S. H. Je, O. Buyukcakir, J. W. Choi, A. Coskun, *Angew. Chemie - Int. Ed.* **2016**, *55*, 3106–3111.
[2] S. H. Je, H. J. Kim, J. Kim, J. W. Choi, A. Coskun, *Adv. Funct. Mater.* **2017**, *27*, 1–9.
[3] J. Kim, A. Elabd, S-Y. Chung, A. Coskun, J. W. Choi. *Chem. Mater.* **2020,** 32, 10, 4185–4193

Controlled Enzyme (Co)Immobilization by Simple and Stable Adsorption of Polymer-Enzyme Conjugates within Porous Silica

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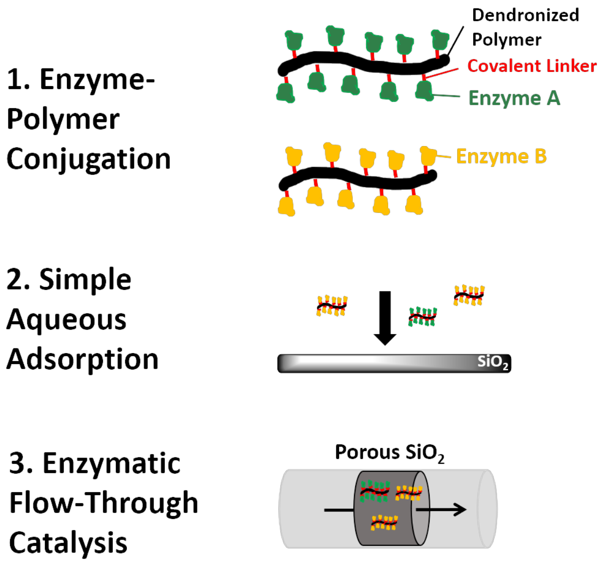
Through stable bis-aryl hydrazone bonds (covalent BAH linker), several enzyme molecules can be attached to polycationic, dendronized polymers (denpols) [1]. The obtained aqueous solutions of enzyme-denpol conjugates can be immobilized by stable non-covalent adsorption on silica surfaces [2]. Porous silicates were used successfully for obtaining enzymatic flow-through reactors [3, 4]. Once a long-time storable conjugate stock solution was prepared, simple exposure of the former to silica surfaces was enough to prepare diverse enzymatic flow-through reactors repeatedly. Since the chemical modification is done before surface exposure, silicate surfaces of choice can be covered later, using defined enzyme concentrations for incubation by arbitrary dilution of a conjugate stock. Exposing defined amounts of conjugates, the immobilized activity observed for the enzymes horseradish peroxidase (HRP) and bovine carbonic anhydrase (BCA) could be regulated, allowing for a controlled coimmobilization.



[1] Andrea Grotzky, Thomas Nauser, Huriye Erdogan, A. Dieter Schlüter, Peter Walde, *J. Am. Chem. Soc.,* **2012**, 134, 11392–11395.
[2] Andreas Küchler, Jozef Adamcik, Raffaele Mezzenga, A. Dieter Schlüter, Peter Walde,*RSC Adv.,* **2015**, 5, 44530–44544.
[3] Chengmin Hou, Nicolas Ghéczy, Daniel Messmer, Katarzyna Szymańska, Jozef Adamcik, Raffaele Mezzenga, Andrzej B. Jarzębski, Peter Walde, *ACS Omega,* **2019**, 4, 7795–7806.
[4] Nicolas Ghéczy, Kai Sasaki, Makoto Yoshimoto, Sajad Pour-Esmaeil, Martin Kröger, Pasquale Stano, Peter Walde, *RSC Adv.,* **2020**, 10, 18655–18676.

This project is financially supported by the Swiss National Science Foundation (200021_175440).

Easy synthesis of nano- and micro-sized light-responsive cargo carrier for organ-on-a-chip device

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Within cells, reaction compartments and cargo carriers such as organelles and lipid vesicles are shuttled on spatially defined paths as an integral part of the cell machinery. Polymersomes are ideally suited as cargo carriers and light-responsive polymersomes[1] that can be shuttled to defined places would be a versatile way of delivering cargo with spatio-temporal control. Herein, we present the simple synthesis of polyethylene glycol-*b*-poly(hexyl methacrylate) (PEG-*b*-PHMA) di-block copolymer containing a *o*-nitro benzyl (NBO) UV-light-sensitive moiety through reversible addition−fragmentation chain-transfer (RAFT) and its subsequent self-assembly into both nano- and micro-particles by solvent exchange or microfluidic.[2] The particles were analysed by light-scattering (LS) and confocal laser scanning microscopy (CLSM). The assemblies were loaded with different dyes and the disassembly subsequent to UV-light irradiation (λ = 365 nm) was monitored by fluorimetry and LS. These types of carriers could be employed in the precise delivery of different types of cargos (small molecules, enzymes, proteins, *etc.*) in organ-on-a-chip devices.[1]

[1] Cabane *et al., Soft Matter*, **2011**, 9167-9176

[2] Klán, P. *et al., Chem. Rev.*, **2012**, 119-191

[3] Nikolaev *et al., Nature* **2020**, 574-578

Cyclodextrine as a tool to follow the blue-to-red transition of polydiacetylenes

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Polydiacetylenes (PDA) are mechanochromic polymers, that show a colour change (e.g. blue to red) upon external stimuli such as heat, stress or changes in the chemical environment[1]. Using the addition of a chemical to trigger the blue-to-red transition of PDA has been widely studied[1-2], however, there are still open questions in the field. For instance, the exact mechanism of the blue-to-red transition is still not clear: is applying a trigger at a given location on a PDA film enough to trigger the phase transition similarly to the domino-effect? Or do different parts of the PDA film need to be separately triggered by e.g. the addition of a chemical in order for the transition to take place in the different regions?

In order to study this hypothesis, we are going to use alpha-cyclodextrin. Cyclodextrins are cyclic oligosaccharides, having the structure of a macrocyclic ring of glucose subunits. While beta-cyclodextrins don't interact with PDAs[3], alpha-cyclodextrins are supposed to form an inclusion complex with the headgroups of the PDA molecule[3-4], thus disrupting the H-bonds between adjacent headgroups and leading to the blue-to-red colour change of PDA. While the red phase of PDA is highly fluorescent, the blue phase is not[5], thus the colour-transition of PDA can be easily followed by the fluorescence of the red phase. In order to colocalise the colour-change of PDA and the interaction of the cyclodextrine with the PDA headgroups, the alpha-cyclodextrine molecules are going to be labelled with a dye.

We believe that the colocalization of the colour change and the chemical interaction of PDA would present a significant contribution to the understanding of the phase transition of PDAs and aid the development of thin-film based polydiacetylene sensors.

[1] R. D. Ortuso, U. Cataldi and K. Sugihara, *Soft Matter* **2017**, 13, 1728-1736.
[2] a) J. Nuck and K. Sugihara, *Macromolecules* **2020**, 53, 6469-6475; b) S. Lee and J. M. Kim, *Macromolecules* **2007**, 40, 9201-9204.
[3] J. M. Kim, J. S. Lee, J. S. Lee, S. Y. Woo and D. J. Ahn, *Macromolecular Chemistry and Physics* **2005**, 206, 2299-2306.
[4] J. T. Cho, S. M. Woo, D. J. Ahn, K. D. Ahn, H. Lee and J. M. Kim, *Chemistry Letters* **2003**, 32, 282-283.
[5] a) R. W. Carpick, D. Y. Sasaki and A. R. Burns, *Langmuir* **2000**, 16, 1270-1278; b) R. Lecuiller, J. Berrehar, C. Lapersonne-Meyer, M. Schott and J. D. Ganiere, *Chemical Physics Letters* **1999**, 314, 255-260.

Plasticization of a rigid metallosupramolecular polymer network

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Metallosupramolecular polymers (MSPs) are obtained through the assembly of ligand-functionalized (macro)monomers with suitable metal ions.[1] The metal-ligand complexes are dynamic in nature and the polymers can be reversibly (dis-)assembled upon exposure to external stimuli such as light or heat, enabling, for example, healing of damaged samples.[2,3] The relevant dynamic processes in MSPs are primarily governed by the metal ion, counter ion, or ligand, and the mechanical properties are also influenced by aspects like the macromonomer backbone and the microstructure.[4,5] Frequently, polymers with low glass transition temperatures (T_g) are used, and the resulting MSPs display relatively poor mechanical properties. We now report that the assembly of trifunctional, low-molecular-weight building blocks with methylbenzimidazolyl pyridine ligands can lead to the formation of a semicrystalline MSP network. Addition of zinc triflimide triggers the complex formation and furnishes an MSP with a T_g around 140 °C and a melting transition at 220 °C. The stiff material becomes dynamic and can be readily disassembled by heat or light. We explored the influence of plasticization, which has barely been investigated for supramolecular polymers,[6] and observed that the T_g can be lowered by up to 65 °C, improving the MSPs' toughness and processability. In addition to appreciable mechanical properties, the material displays healing behavior upon exposure to suitable stimuli such as heat or light.

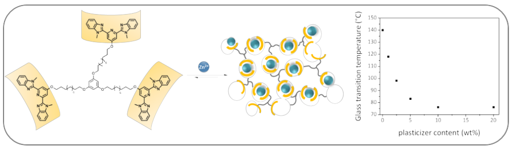

Figure 1: *a)* Structure of the monomeric building block and the metallosupramolecular polymer upon the assembly with $Zn(NTf_2)_2$. *b)* Plot showing the change in the glass transition temperature upon addition of an increasing fraction of a plasticizer.

[1] Andreas Winter, Ulrich S. Schubert, *Chemical Society Reviews* **2016**, *45*, 5311–5357.
[2] Mark Burnworth, Liming Tang, Justin R. Kumpfer, Andrew J. Duncan, Frederick L. Beyer, Gina L. Fiore, Stuart J. Rowan, Chris. Weder, *Nature* **2011**, *472*, 334–337.
[3] Laura N. Neumann, Emad Oveisi, Albrecht Petzold, Robert W. Style, Thomas Thurn-Albrecht, Chris Weder, Stephen Schrettl, *Science Advances* **2021**, *7*, eabe4154.
[4] Laura N. Neumann, Ilja Gunkel, Amber Barron, Emad Oveisi, Albrecht Petzold, Thomas Thurn-Albrecht, Stephen Schrettl, Chris Weder, *Macromolecules* **2020**, 53, 13, 5068–5084.
[5] Wayne C. Yount, David M. Loveless, Stephen L. Craig, *Angewandte Chemie International Edition* **2005**, *44*, 2746–2748.
[6] Philippe Cordier, François. Tournilhac, Corinne Soulié-Ziakovic, Ludwik Leibler, *Nature* **2008**, *451*, 977–980.

Highly porous nanofiber sponge immobilized MOF for efficient CO_2 capture

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The steady increase in the earth's average temperature has been associated with a costant growth of anthropogenic CO_2 emissions. One method of effectively reducing the concentration of CO_2 in the air is direct air capture (DAC) [1]. For DAC, several materials with good capacities have been published in recent years, including the metallic organic framework (MOF) mmen-Mg_2(dobpdc), where mmen= N,N′-dimethylethylenediamine and dobpdc = 4,4′-dioxido-3,3′-biphenyldicarboxylate [1,2]. In this work, an innovative method has been developed to immobilise mmen-Mg_2(dobpdc) and other MOFs on ultralight and highly porous sponge produced from short electrospun nanofibers of polyacrylonitrile and polyamide 6 using solid templating [3]. The mmen-Mg_2(dobpdc) was immobilised by direct synthesis on polyamide 6 nanofibres with 83 % MOF loading and a final material apparent density of 32.66 mg/ml. Using a custom-made heat exchanger-mass spectrometer, breakthrough and temperature swing adsorption (TSA) experiments were carried out identifying adsorption and desorption temperatures at 15 °C and 75 °C. The composite material has a capacity of 0.12 mmol CO_2/g, using a 50 % CO_2 mixture in argon at 1 bar and a flow rate of 5 ml/min. For the TSA experiments, it was possible to reduce the adsorption and desorption cycles to 4 min. Having short TSA adsorption and desorption cycles and a good capacity are crucial factors to reduce the space and energy used for CO_2 separation and to make DAC economically attractive and sustainable.

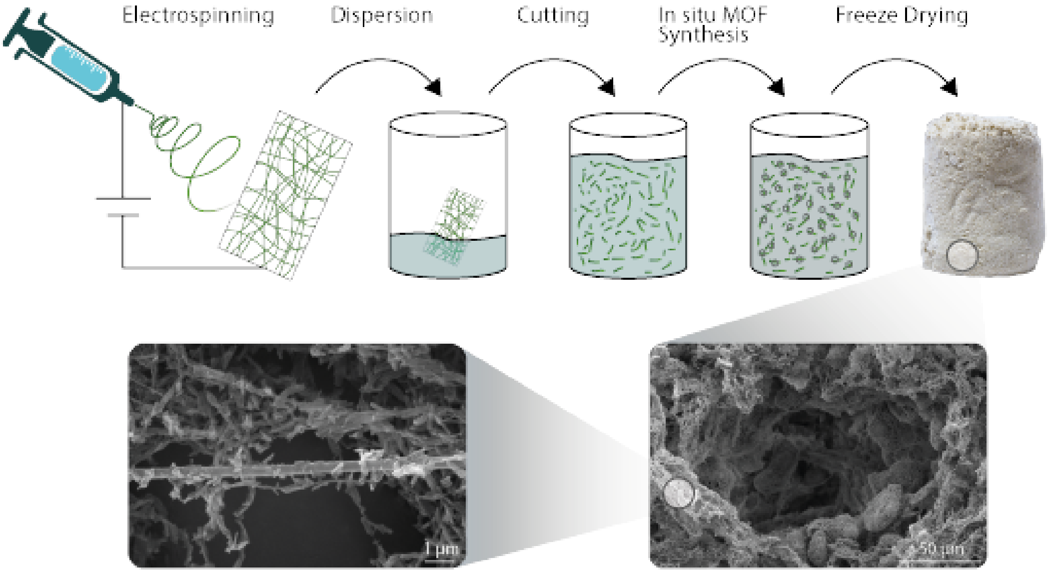

Figure 1: Preparation of nanofibers sponge immobilized MOF. Nanofibers are produced by electrospinning then dispersed and cutted in a solvent. MOFs are synthetized in situ directly on the fibers. The solvent is removed by freeze drying, leaving a highly porous sponge behind.

[1] Eloy S. Sanz-Pérez et al., *Chem. Rev.* **2016**, *116* (19), 11840–11876.
[2] Fabian Deuber et al., *Chemistry Select,* **2016**, *1* (18), 5595–5598.
[3] Thomas M McDonald et al., *J. Am. Chem. Soc.* **2012**, *134* (16), 7056–7065.

Exploiting phase transitions in polymer bilayer actuators

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Mechanically morphing and adaptive polymers with the ability to change their density, shape, stiffness, porosity or hardness in response to a specific stimulus are the basis of many soft, sometimes bio-inspired robotic systems that can execute a variety of elaborate tasks such as gripping or locomotion. Heating is a frequently used stimulus that can be applied through radiation, oscillating magnetic fields, or Joule heating. Recently we reported a novel type of temperature responsive bilayer bending actuator with an integrated Joule heater, which relies on the dissimilar thermal expansion of the two polymer layers for actuation.[1] To maximize the effect, the discontinuous volumetric change associated with a first-order phase transition in one of the components was exploited, which allows for a large dimensional change and within a narrow temperature range (25-65 °C). This was achieved with a segmented polyurethane elastomer as a phase-changing material featuring a crystallizable polyester-based soft segment, which is responsible for the large discontinuous thermal expansion, and a hard segment with hydrogen bonding sites acting as physical cross-links to prevent flow above the melt transition temperature. By replacing the polyester soft segment of the previously reported system with a crystallizable polyether, it was possible to improve the thermal expansion across the melt transition by an order of magnitude. The higher degree of crystallization and sharper thermal transitions of this new polyether-based polyurethane are responsible for larger bilayer deflection and faster recovery. These bilayer bending actuators were fabricated by joining the large-thermal-expansion polyurethane material with a polyimide film. Additionally a thin Joule heating electrode, patterned via photolithography, was sandwiched between the two polymer layers to enable electro-thermal actuation control. To predict the deflection of bilayer bending actuators a finite element model was created. With this modelling approach the mechanical properties, geometrical factors and thermal transport issues can be taken into account to optimize the actuation performance and subsequently enable the implementation of such actuators into complex soft robotic systems. Furthermore, such a modelling approach is expected to expedite the identification of material property requirements to facilitate the material selection or allow a synthesis-on-demand approach for specific applications.

Picture series of melt-processed PEG-PU (275 µm) and polyimide (125 µm) bilayer bending actuator with an integrated copper (200 nm) Joule heater between the two layers. The anisotropic thermal contraction across the bilayer is responsible for the bent state in ambient condition. The bilayer bending actuator quickly flattens when powered (~4 W) and returns into its bent state when power is turned off.

[1] Muff, L. F.; Weder, C. Exploiting Phase Transitions in Polymer Bilayer Actuators. *Adv. Intell. Syst.* **2020**, 2 (12), 2000177

Synthesis of Covalent Chitosan-Based Derivatives for Gene Delivery

L. Nicolle[1], C. M. Journot[1], P. Robin[1], J. Casper[2], P. Detampel[2], M. Williman[3], H. Grisch-Chan[3], B. Thöny[3], S. Gerber-Lemaire[1]*, J. Huwyler[2]*

[1]Group for Functionalized Biomaterials, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, [2]Division of Pharmaceutical Technology, Department of Pharmaceutical Sciences, University of Basel, Basel, Switzerland, [3] Division of Metabolism and Children's Research Center, University Children's Hospital Zürich, Zürich, Switzerland

There is an increasing interest in cationic polymers as important constituents of non-viral gene delivery vectors. Among them, chitosan (CS) is a promising polymeric backbone due to its biocompatibility, biodegradability and its versatility towards functionalization. This project aims to develop a CS-based gene delivery vehicle for liver-targeted diseases. In order to ensure optimal biological applications, the CS backbone was first depolymerized through a microwave-assisted controlled degradation method, leading to water-soluble chains (dCS; 6–9 kDa).[1] Low molecular weight linear polyethylenimine (LPEI; 2.5 kDa) was then covalently grafted on the dCS backbone and the resulting conjugates were analyzed for their physico-chemical properties, before being assessed *in vitro* and *in vivo* for gene delivery applications.[2] We identified a lead dCS-LPEI derivative which showed a 10-fold higher transfection signal in wild-type mice when compared to the commercially available non-viral delivery vector *in vivo*-jetPEI. This promising non-viral gene delivery system is now further investigated for additional covalent derivatization with heterobifunctional polyethylene glycol chains (PEG; 2 kDa and 0.4 kDa), cell-penetrating peptides (CPP), fluorophores and hepatocyte-targeting ligands (Figure 1). We expect to improve the copolymer's biocompatibility by taking advantage of the shielding effect of PEG. Then, the transfection efficiency shall be increased thanks to the addition of a CPP and a targeting ligand. Finally, the cross reactive PEG chains will provide further stabilization of the polymeric vehicle *via* cross-linking between the different chain ends. Fluorescent labelling was also implemented to allow more in-depth study of the DNA delivery mechanism occuring both *in vitro* and *in vivo* with such system. We herein disclose the results on the functionalization of dCS-LPEI system, including physico-chemical characterization, *in vitro* evaluation and *in vivo* studies.

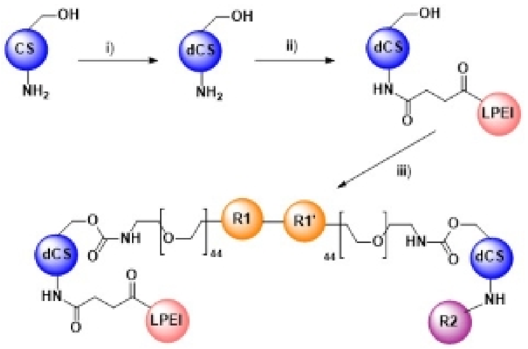

Figure 1: Synthetic pathway toward multi-functional polymeric gene delivery vehicle. i) CS depolymerization *via* microwave-assisted depolymerization method. ii) Grafting of LPEI on dCS using a succinyl linker. iii) Derivatization of the initial dCS-LPEI system with heterobifunctional PEG, CPP, fluorophore and hepatocyte-targeting ligand. R1, R1' = maleimide, thiol, and acrylate functionalities. R2 = CPP, fluorophore or targeting ligand.

[1] Céline M. A. Journot, Laura Nicolle, Yann Lavanchy, Sandrine Gerber-Lemaire, *Polymers*, **2020**, 12, 1274.

[2] Laura Nicolle, Jens Casper, Melanie Willimann, Céline M. A. Journot, Pascal Detampel, Tomaž Einfalt, Hiu-Man Grisch-Chan, Beat Thöny, Sandrine Gerber-Lemaire, Jörg Huwyler, *Int. J. Mol. Sci.*, **2021**, 22, 3828.

Electrospun chitosan nanofiber sponge for filtration of microplastics

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Ultralight and compressible nanofiber sponges are an emerging field of research, which also includes nanofibers made from biopolymers. Here, we present the development of a biocompatible and ultralight chitosan-glutaraldehyde nanofiber sponge filter derived from marine biomass, i.e. chitin. Nanofiber sponges have previously been used in aerosol filtration [1] and water/oil separation [2,3]. However, their potential in clearing particle suspensions has not yet been explored, such as for microplastics.

Pure chitosan nanofibers were produced by surface-free electrospinning of chitosan/PEO solution, subsequent extracting of PEO, homogenizing and freeze-drying, which resulted in pure chitosan nanofiber sponges. They were crosslinked in glutaraldehyde vapor for increased pH stability. The resulting chitosan-glutaraldehyde nanofiber sponges had an apparent density of 5.77 mg cm^{-3} and a porosity of 99.59 %. The hierarchical and open cellular pore structure was ideal for particle adsorption. A hydrostatic filtration reduced the turbidity of a microplastics suspension by 99.5 % NTU. Because of its compressibility, an external actuated nanofiber sponge can remove particles from suspension, similar to the feed mechanism of oysters. Compared to static filters, the active movement increases the mass transport through the pores [4]. With an oyster-inspired setup, actuation/relaxation cycles could significantly reduce the turbidity of particle suspensions. In conclusion, we have demonstrated that chitosan-glutaraldehyde nanofiber sponges can be employed as filters for environmental harmful particles such as microplastics.

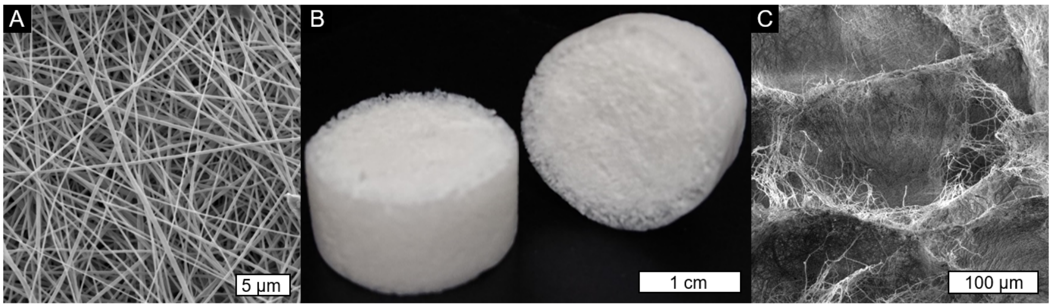

Figure 1. (A) Chitosan/PEO nanofibers with diameter of 309 ± 56 nm; (B) chitosan nanofiber sponges with their hierarchical open pore architecture shown in a cross section image (C).

[1] Fabian Deuber, Sara Mousavi, Lukas Federer, Marco Hofer, Christian Adlhart, *ACS Appl. Mater. Interfaces*, **2018**, 10 (10), 9069-9076.
[2] Yang Si, Jianyong Yu, Xiaomin Tang, Jianlong Ge, Bin Ding, *Nat. Commun.*, **2014**, 5 (1), 5802.
[3] Gaigai Duan, Shaohua Jiang, Valérie Jérôme, Joachim H. Wendorff, Amir Fathi, Jaqueline Uhm, Volker Altstädt, Markus Herling, Josef Breu, Ruth Freitag, Seema Agarwal, Andreas Greiner, *Adv. Funct. Mater.*, **2015**, 25.
[4] Sara Mousavi, Fabian Deuber, Sergio Petrozzi, Lukas Federer, Majid Aliabadi, Farhad Shahraki, Christian Adlhart, *Colloids Surf. A Physicochem. Eng. Asp.*, **2018**, 547, 117-125.

Multifunctional silica-based sensors for real-time viral screening

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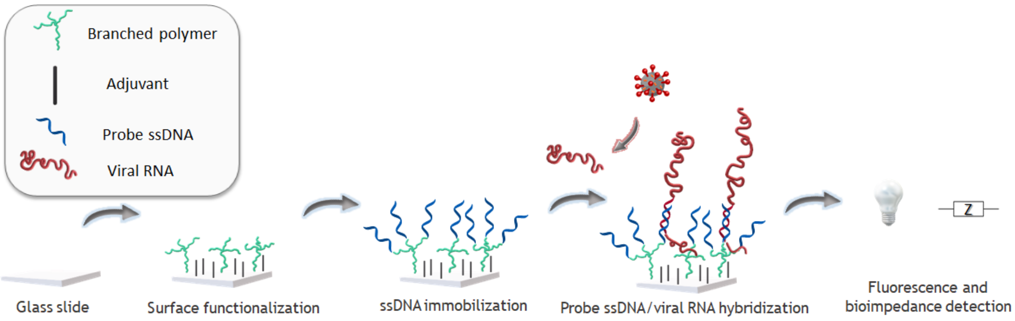
[1]Group for Functionalized Biomaterials, Institute o, [2]Group for Functionalized Biomaterials, Institute of Chemical Sciences and Engineering, [3]Department of Biomedical Sciences, University of Lausanne, [4]Institute of Oncology Research, Faculty of Biomedical Sciences, [5]Department of Innovative Technologies, Institute of Systems and Applied Electronics

The emergence of the coronavirus disease in 2019 (COVID-19) highlighted the need for rapid, accurate and massive virus detection techniques to control the widespread of infectious diseases. Epidemic-causing mosquito-borne viruses such as Dengue, Zika or Chinkungunya, are under tight surveillance by sanitary organizations, as may be next to emerge on the global stage[1]. In Europe, although those viruses circulation is up to now limited, concerns have been raised about the recent emergence of Tiger mosquitos[2]. Monitoring potential arboviruses in the mosquitoes' established populations is of great interest for European health organizations to stay one step ahead.



We suggest an approach to address the limitations of current detection procedures using a low-cost and highly responsive biosensor, which would remove the need for biomedical personnel and advanced laboratory infrastructures. The biological samples could be taken from humans or any viral hosts and be processed to detect a variety of viruses.

Most viral detection techniques require the immobilization of biomolecules on a sensor surface. Silica-based materials are ideal sensor plateform for viruses due to their inexpensiveness, ease of functionalization and good temperature and mechanical stability[3]. We herein disclose a panel of surface conjugation strategies for the immobilization of single-strand DNA (ssDNA) probes on silica-based slides. Depending on the surface coating, both covalent immobilition or adsorption through electrostatic interactions will be studied. The resulting sensing platforms will be assessed for SARS-COV-2 and Zika detection. Fluorescence and bioimpedance measurements were chosen for the detection of the hybrization events between the viral RNA strands from the biological samples and the immobilized ssDNA strands (Figure 1). The orientation and density of the ssDNA probes at the surface of the sensor are known to play a major role on the efficacy of hybridization events[4]. Therefore, variation of size, branching degree, density and functionality of the polymers as well as adjuvants will be investigated for optimal sensor sensitivity.

[1]Kading, Rebekah C., Brault, Aaron C., Beckham, J. David., *Infectious Diseases and Tropical Medicine*, **2020** 5(3), 142.
[2] Ryan, Sadie J., *PLOS Neglected Tropical Diseases*, **2019,** 13(3), e0007213.
[3] Wittmann, C., Bier, F. F., *Springer*., **2005**
[4] Campàs, M., Katakis, I., *Trends in Analytical Chemistry*, **2004**, 23(1), 49-62.

Stabilization of nanoparticle emulsion based ion selective optodes through zwitterionic surfactants

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Emulsion based optodes continue to be an attractive option for ion sensing due to their ease of fabrication, high sensitivity and convenient optical readout. These sensors work by maintaining electroneutrality in a hydrophobic particle core and exchanging an analyte of interest either with a solvatochromic dye or hydrogen ion bound to a chromoionophore transducer [1]. Due to the hydrophobic nature of the particle core, surfactants are generally employed to impart stability and avoid aggregation. Despite the importance of the surfactant for stabilisation, exploration of effect on sensor response is extremely limited although previous work on electrodes suggests that non-ionic surfactants such as F127, commonly utilised for particle stabilisation, can negatively impact sensor selectivity [2].

This becomes especially important for an emerging class of optodes which utilise a solvatochromic dye with lipophilic tail to avoid concentration dependant effects. In this type of sensor the solvatochromic transducer localises to the surface rather than partitioning completely into the aqueous phase like earlier solvatochromic sensors. We found the surfactant chosen can significantly alter the signal of the solvatochromic transducer and cause competition for space at the particle/fluid interface, Fig.1.

In this presentation we will discuss our latest findings regarding zwitterionic alternatives to F127 and other non-ionic surfactants and their effects on emulsion-based optode sensor response including selectivity, sensitivity and stability.

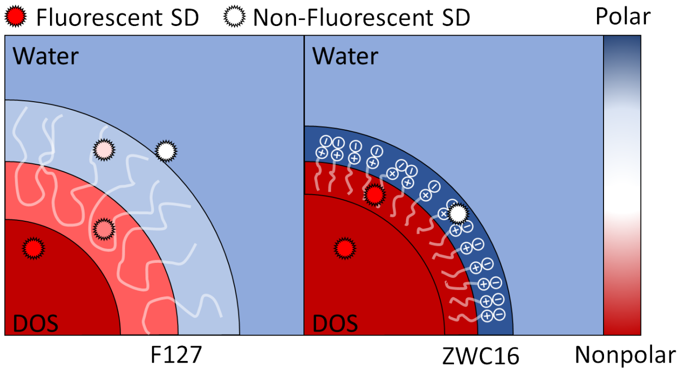

Figure 1: F127 can alter solvatochromic signal in the particle prior to ion exchange where as a zwitterionic surfactant has less intitial influence but greater surface competition.

[1] X. Xie, E. Bakker, Anal. Bioanal. Chem., **2015**, *407(14)*, 3899-3910.
[2] E. Malinowska, M.E. Meyerhoff, Anal. Chem., **2015**, *70(8)*, 1477-1488.

In situ polymerization in a microfluidic chip

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Hydrogels are versatile materials used in various applications due to their unique mechanical and chemical properties. Forming hydrogels inside microfluidic chips allows to explore fundamental phenomena and implement novel applications thanks to the physics of liquids at the microscale and the small volumes required. However, forming hydrogels in specific locations of microfluidic devices remains challenging and the most common methods employ photopolymerization, which involves toxic initiators and bulky optical equipment [1]. In this work, we introduce a novel approach to form hydrogels with a well-defined geometry in capillary-driven microfluidic chips by interfacial polymerization.

A PEG-based hydrogel was formed through a thiol-maleimide reaction [2]. Precursor 1 (4-armed PEG maleimide, 4PM) and precursor 2 (PEG-dithiol, PDT) are introduced sequentially on chip with the liquid interface between both solutions being pinned by specific microfluidic structures. PDT diffuses quickly through 4PM and a hydrogel forms only in the area originally occupied by precursor 1 (Fig. 1).

Using this method, we polymerized rectangular-shaped PEG-based hydrogels inside a sealed microfluidic chip in less than 3 minutes, using only 200 nL of precursor solutions. We could control the mesh size of the hydrogel by varying the chemical composition and the concentration of the precursor solutions and we characterized the resulting hydrogels by measuring the diffusivity of molecules with different molecular weights across it. By choosing a suitable hydrogel mesh size, large molecules such as antibodies, can be trapped inside the hydrogel, while small analytes are able to diffuse through it.

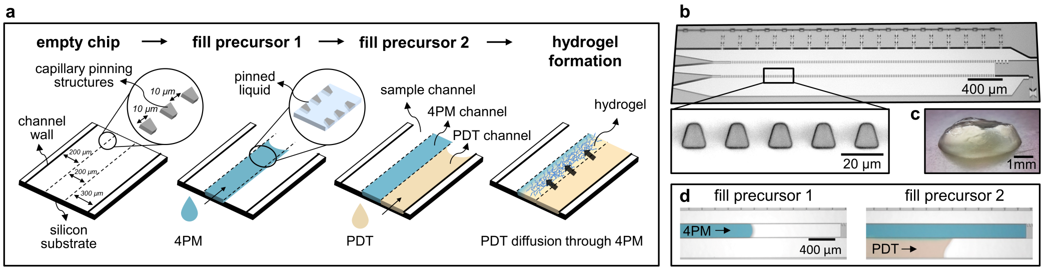

Figure 1. Formation of a hydrogel in situ by interfacial polymerization inside a microfluidic chip. (a) The hydrogel precursors (4PM and PDT) are introduced sequentially into parallel microchannels (b), which are delimited by capillary pinning structures and walls. (c) PEG-hydrogel formed on a glass slide using a thiol-maleimide reaction. (d) Optical micrographs showing the filling of 4PM in the middle channel with pinning of the liquid preventing its excursion to the adjacent channels, followed by filling of PDT. A blue dye was added to the 4PM solution for better visualization.

[1] Xuanqi Zhang, Lingjun Li, Chunxiong Luo, *Lab on a Chip*, **2016**, 16, 1757
[2] Lauren Jansen, et al., *Acta Biomaterialia*, **2018**, 70, 120-128

Effect of Polymerization Components on Oxygen-Tolerant Photo-ATRP

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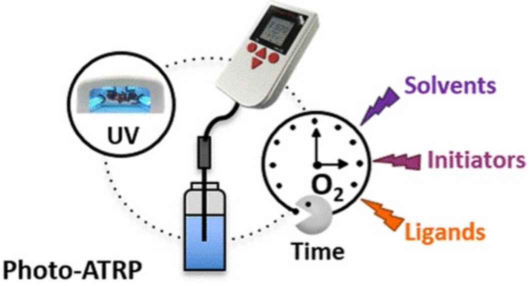
Photo-ATRP has recently emerged as a powerful technique that allows for oxygen-tolerant polymerizations and the preparation of polymers with low dispersity and high end-group fidelity. However, the effect of various photo-ATRP components on oxygen consumption and polymerization remains elusive. Herein, we employ an in situ oxygen probe and UV–vis spectroscopy to elucidate the effects of ligand, initiator, monomer, and solvent on oxygen consumption. We found that the choice of photo-ATRP components significantly impacts the rate at which the oxygen is consumed and can subsequently affect both the polymerization time and the dispersity of the resulting polymer. Importantly, we discovered that using the inexpensive ligand TREN results in the fastest oxygen consumption and shortest polymerization time, even though no appreciable reduction of $CuBr_2$ is observed. This work[1] provides insight into oxygen consumption in photo-ATRP and serves as a guideline to the judicious selection of photo-ATRP components for the preparation of well-defined polymers.



[1] Manon Rolland, Richard Whitfield, Daniel Messmer, Kostantinos Parkatzidis, Nghia Phuoc Truong, Athina Anastasaki*.* *ACS Macro Lett.* **2019**, 8, 1546-1551.

AIE-Active DNA Conjugates Self-Assemble into DNA-Addressable Vesicles

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In contrast to many polyaromatic hydrocarbons, aggregation-induced emission (AIE) type chromophores become highly fluorescent upon aggregation. Implementations of this AIE effect range from sensing applications to optoelectronic systems. Self-assembly of AIE-active DNA conjugates result in functional supramolecular constructs that are appealing for example in the field of DNA nanotechnology. In this work, we present findings of supramolecular aggregates assembled from AIE-active tetraphenylethylene (TPE) DNA conjugates. As evidenced by cryo-electron microscopy (cryo-EM), these TPE-DNA conjugates self-assemble into two distinct vesicular architectures. The divergent addressability of the DNA in the two different vesicular constructs is demonstrated by DNA intercalation experiments using ethidium bromide (EthBr).

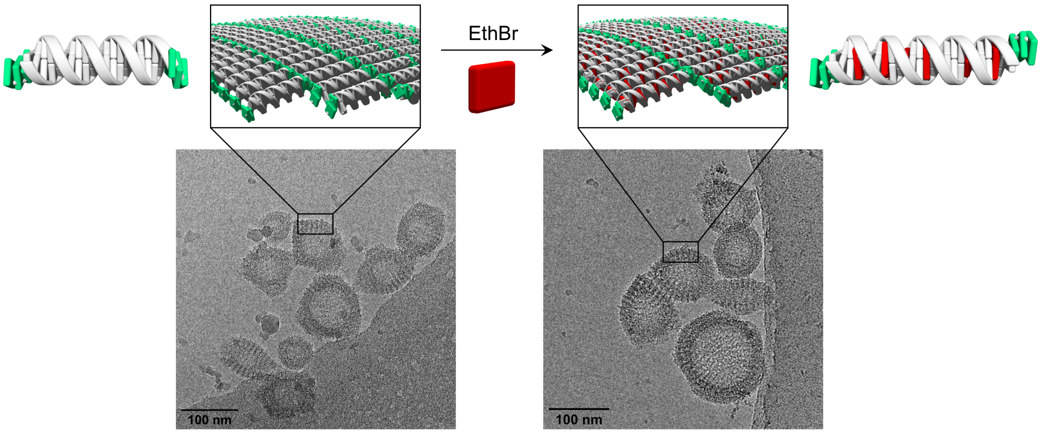

Figure. Illustration of the TPE-DNA duplex and EthBr intercalation into DNA-constructed vesicles. TPE is represented in green, DNA in gray, and EthBr in red.

[1] Simon Rothenbühler, Ioan Iacovache, Simon M. Langenegger, Benoît Zuber, Robert Häner, *Nanoscale*, **2020**, 12, 21118–21123.

[2] Caroline D. Bösch, Jovana Jevric, Nutcha Bürki, Markus Probst, Simon M. Langenegger, Robert Häner, *Bioconjugate Chem.*, **2018**, 29, 1505–1509.

[3] Ju Mei, Nelson L. C. Leung, Ryan T. K. Kwok, Jacky W. Y. Lam, Ben Zhong Tang, *Chem. Rev.*, **2015**, 115, 11718–11940.

Fluorinated Iron(II) Clathrochelate Units in Metalorganic Based Copolymers: Improved Porosity, Iodine Uptake, and Dye Adsorption Properties

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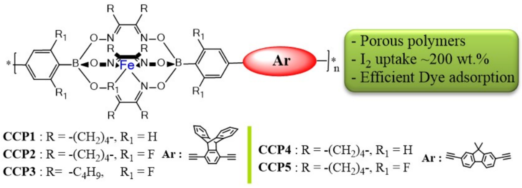
We report the synthesis of metalorganic copolymers made from the palladium catalyzed Sonogashira cross-coupling reaction between various iron(II) clathrochelate building blocks with diethynyl- triptycene and fluorene derivatives. The target copolymers **CCP1-5** were isolated in excellent yield and characterized by various instrumental analysis techniques. Interestingly, investigation of the copolymers’ porosity properties disclose BET surface areas up to 337 m^2g^{-1} for the target compounds bearing fluorinated iron(II) clathrochelate units **CCP2,5**. Moreover, the fluorinated copolymers display an outstanding uptake capacity of iodine with a maximum adsorption of 200 wt.%. The target metalorganic copolymers **CCP1-5** reveal very good adsorption of organic dyes, namely, methyl blue and methylene blue, from aqueous media.[1]



[1] S. Shetty, N. Baig, A. Hassan, S. Al-Mousawi, N. Das and B. Alameddine, *RSC Advances*, **2021**, Accepted

Molten Salt Templated Synthesis of Covalent Isocyanurate Frameworks with Tunable Morphology and High CO_2 Uptake Capacity

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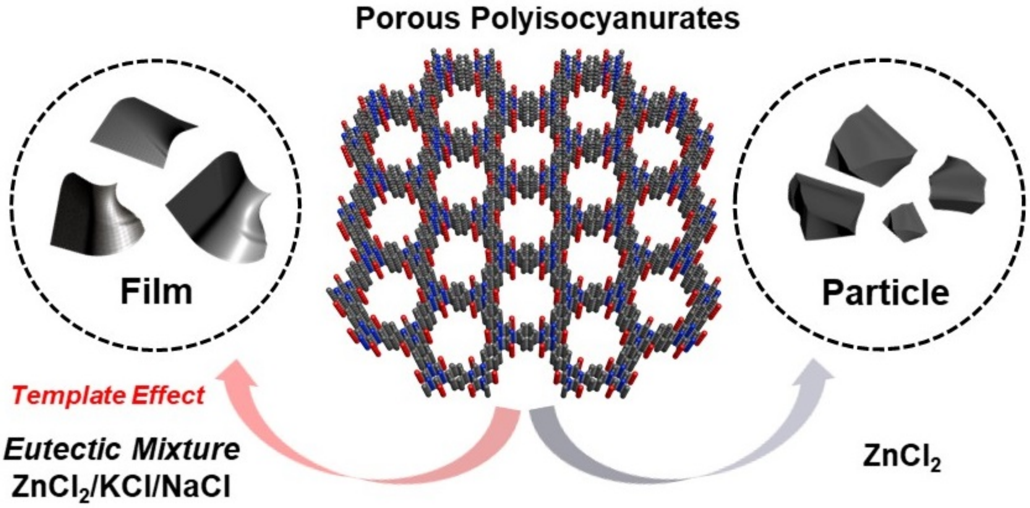
Covalent Triazine Frameworks (CTFs) have been investigated in recent years due to their synthetic modularity, tunable porosity and high heteroatom content and have already found applications in CO_2 capture and separation, energy storage, heterogeneous catalyst and environmental remediation. CTFs are generally synthesized under ionothermal reaction conditions using $ZnCl_2$ through the trimerization of aromatic nitriles. Notably, the soft templating effect of $ZnCl_2$ plays a crucial role in the formation of a highly microporous, semicrystalline polymer network at temperatures below 400°C. However, higher reaction temperatures (>400 °C) lead to a significant mesopore formation and depletion of a nitrogen content due to its partial carbonization and other side reactions. Accordingly, we reasoned by replacing nitrile moieties in the monomers with isocyanates and using eutectic salt mixture ($ZnCl_2$/KCl/NaCl and lowest m.p. = 200 °C) could strengtehen the ion-dipole interactions between the monomer and the molten salt, thus introducing a templating effect. The resulting polymer called Covalent Isocyanurate Frameworks (CICFs) showed highly promising textural properties and high affinity towards CO_2. [1] In this presentation, the impact of the molten salt templation on the morphology, textural properties and gas uptake properties of porous organic polymers will be discussed.



[1] Kyung Seob Song, Siddulu Naidu Talapaneni, Timur Ashirov, and Ali Coskun, *ACS Appl. Mater. Interfaces* **2021**, DOI: 10.1021/acsami.1c06326

Supramolecular Assembly of Pyrene-DNA Conjugates into Vesicles

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Over the last two decades, supramolecular polymers have been successfully used for the assembly of organized molecular arrays. Complementary DNA strands create a defined arrangement upon hybridizing and the obtained DNA framework can be exploited for the introduction of modifications at spatially controlled places of the supramolecular assemblies. In previous work, assemblies containing DNA were decorated with sticky ends containing polyaromatic hydrocarbons (PAH). Our group observed light-harvesting properties in supramolecular vesicles assembled from phenanthrene-DNA conjugates.[1] In addition, aggregation-induced emission (AIE) type chromophores were introduced as sticky ends forming AIE-active supramolecular assemblies using *E*-tetraphenylethylenes instead of phenanthrene.[2] In this work, 2,7-pyrene (Figure 1A), 1,6-pyrene, and 1,8-pyrene was investigated as stick end modification to DNA. AFM studies of 2,7-pyrene reveal the self-assembly of the conjugates into spherical objects (Figure 1B). Similar results were obtained for DNA-conjugates of the 1,6-pyrene and 1,8-pyrene isomers. In addition to AFM studies, fluorescence and UV-vis spectroscopy will be presented and discussed.

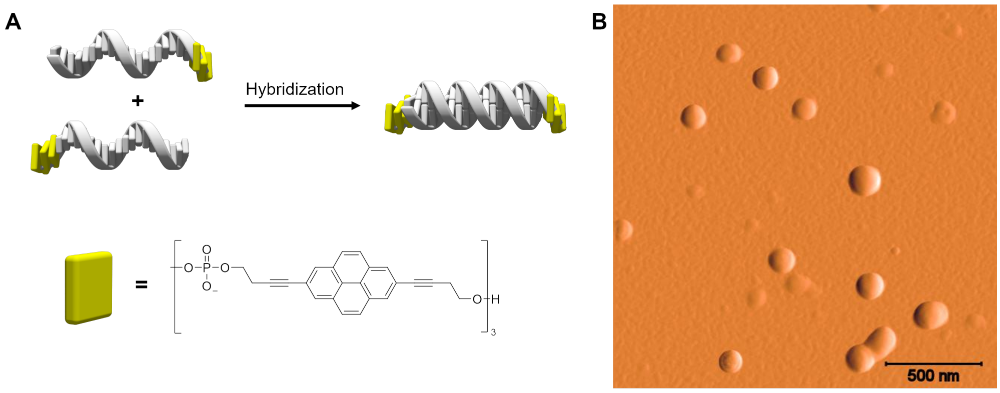

Figure 1 (A) Sequence of 2,7-Pyrene-DNA conjugates. (B) AFM image of the self-assembled vesicles.

[1] C. D. Bösch, J. Jevric, N. Bürki, M. Probst, S. M. Langenegger, R. Häner,*Bioconjugate Chem.*, **2018**, 29, 1505–1509.
[2] S. Rothenbühler, I. Iacovache, S. M. Langenegger, B. Zuber, R. Häner, *Nanoscale*, **2020**, 41, 21118-21123.

Shining light on surface-initiated organocatalyzed atom transfer radical polymerization

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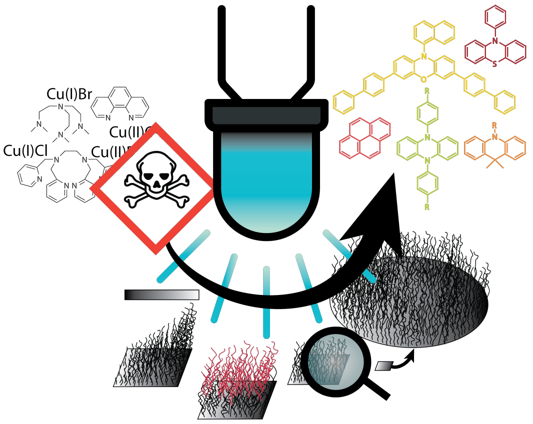
Surface-initiated organocatalyzed atom transfer radical polymerization (SI O-ATRP) provides a greener alternative to conventional ATRP by substituting organic dyes for copper salts.[1] Consequently, this method yields polymer brushes free from metal contaminants, which are highly desirable in semiconductor and medical sectors. The organic dyes used in SI O-ATRP are photoactivated, which further allows for facile generation of surface patterns, complex polymer brush architectures, and molecular weight gradients. However, research on SI O-ATRP has focused mainly on small substrates (1 cm^2), and brush films on larger substrates (20 cm^2 silicon wafers) as well as block copolymer brushes are limited to thicknesses <50 nm.[2,3] We investigated side reactions in SI O-ATRP allowing us to carefully adapt reaction parameters and expand the available range of dry film thickness to >200 nm on a 20 cm^2 silicon wafer. Furthermore, we were able to grow hydrophilic, hydrophobic, as well as diblock copolymer brushes using a very small (ppm) amount of a photocatalyst. Linear polymerization growth profiles and up to five reinitiation cycles from the same substrate reveal the controlled nature of our SI O-ATRP protocol. The photocontrolled nature of the reaction further allowed us to prepare thickness gradients and patterns, from which we gained interesting new insights into the growth and characteristics of block copolymer brush films. We are convinced that our findings and the simplicity of this technique will widen the interest of the polymer brush community in SI O-ATRP.



[1] Emre H. Discekici, Athina Anastasaki, Javier Read de Alaniz, & Craig J. Hawker, *Macromolecules,* **2018**, 51, 7421-7434.
[2] Benjaporn Narupai, Dr. Zachariah A. Page, Dr. Nicolas J. Treat, Alaina J. McGrath, Dr. Christian W. Pester, Emre H. Discekici, ... & Craig J. Hawker, *Angewandte Chemie International Edition,* **2018**, 57, 13433-13438.
[3] Emre H. Discekici, Christian W. Pester, Nicolas J. Treat, Jimmy Lawrence, Kaila M. Mattson, Benjaporn Narupai, ... & Craig J.Hawker, *ACS Macro Letters,* **2016**, 5, 258-262.

The Role of Hydrodynamic Interactions on the Aggregation Kinetics of Sedimenting Colloidal Particles

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The aggregation kinetics of sedimenting colloidal particles under fully destabilized conditions has been investigated using the recent PSE algorithm (proposed by Fiore et al.[1]) for the Rotne–Prager-Yamakawa (RPY) approximation of long-range Hydrodynamic Interactions (HI), over a wide range of particle volume fractions (Φ) and Peclet numbers (Pe). Fast Lubrication Dynamics[2,3] (FLD) and simple Brownian Dynamics (BD) methods for large-scale simulations have also been employed to provide a quantitative comparison of the different methods on the resulting aggregation dynamics. It has been observed that, at low particle volume fractions, long-range hydrodynamic interactions lead to faster and more pronounced aggregation rates, manifesting themself with an explosive-like cluster growth after a given time. On the contrary, simulations employing only short-range hydrodynamic interactions (such as FLD) and BD, which neglect completely hydrodynamic interactions, are completely incapable of predicting this very rapid kinetics, because sedimentation simply leads to all clusters to move vertically with identical velocity. However, dissipative lubrication forces play a key role at high concentrations and in the early stages of the aggregation process, when aggregation mostly occurs between primary particles and diffusion is the predominant mechanism governing aggregation. From simulations employing the RPY approximation of HI, an increase in the particle volume fraction leads to a substantial increase in the rate at which the dimensionless number of clusters decreases over time. Additionally, at specific conditions, the curves show an inflection point, followed by a very rapid cluster consumption, which coincides with the time at which a gel point is formed. Similar results were observed as the Peclet number, which characterizes the strength of sedimentation to that of diffusion, increases. Time evolution of the average cluster size and radius of gyration show that sedimentation has a strong accelerating effect on the clustering kinetics and a significant influence on the structure of the formed clusters. It was also observed that as Pe increases, the anisotropy of the resulting clusters decreases, suggesting that denser clusters with spherical-like morphology are formed. This is mainly due to the high convective motions generated during sedimentation at high Pe, leaving clusters exposed to the flow field with the possibility to rearrange and reorient. However, the effect induced by Pe becomes negligible at high particle volume fractions ($\Phi=0.2$) when particles are in close proximity and concentration instead of sedimentation is the predominant mechanism controlling the process. Moreover, for dense dispersions of particles ($\Phi\geq0.05$), lubrication is of crucial importance for assessing the role of tangential inter-particle interactions on the cluster microstructure. In the majority of cases investigated in this study, long-range hydrodynamic effects have been of crucial importance for the understanding of the aggregation dynamics of settling clusters, revealing important features of the complex interplay between sedimentation, colloidal interactions, and hydrodynamics.

[1] Fiore, A. M.; Usabiaga, F. B.; Donev, A.; Swan, J. W. Rapid Sampling of Stochastic Displacements in Brownian Dynamics Simulations. The Journal of Chemical Physics **2017**, 146 (12), 124116.
[2] Bybee, M. D. Hydrodynamic Simulations of Colloidal Gels: Microstructure, Dynamics, and Rheology. PhD Thesis, University of Illinois at Urbana-Champaign, **2009**.
[3] Kumar, A. Kumar, A. Microscale Dynamics in Suspensions of Non-Spherical Particles. Ph.D. Thesis, University of Illinois, Champaign County, IL, USA. **2010**.

Tailoring polymer dispersity by (PET)-RAFT polymerization: a versatile approach

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Unlike natural biopolymers, such as DNA and proteins, synthetic polymers have a distribution of different molecular weight species. This distribution is measured by a dispersity value and has a significant influence on polymer properties. It is therefore highly beneficial to develop strategies to systematically tune the dispersity, but to date, current methods have limitations in monomer scope, block co-polymer accessibility, and attainable dispersity range.[1] Here, we report a straightforward and versatile batch method based on reversible addition-fragmentation chain transfer (RAFT) polymerization to tailor the molecular weight distributions for a wide range of monomer classes, including acrylates, acrylamides, methacrylates, and styrene. In addition, our methodology is compatible with more challenging monomers, such as methacrylic acid, methyl vinyl ketone, and vinyl acetate. Control over dispersity is achieved by mixing two RAFT agents with sufficiently different chain-transfer activities in various ratios, affording polymers with monomodal molecular weight distributions.[2] Moreover, the present approach can be applied also in photo-induced electron/energy RAFT (PET-RAFT) polymerization. Benefits of the approach include the use of visible light irradiation, ppm concentrations of a photo-redox catalyst, and the possibility to manipulate dispersity in the absence of external deoxygenation methodologies, which significantly simplify the process.[3]

[1] Kostas Parkatzidis, Hyun Suk Wang, Nghia Truong Phuoc, Athina Anastasaki, *Chem*, **2020**, 6, 1575-1588.
[2] Richard Whitfield, Kostas Parkatzidis, Nghia Truong Phuoc, Tanja Junkers, Athina Anastasaki, *Chem* **2020**, 6, 1340–1352.
[3] Kostas Parkatzidis, Nghia Truong Phuoc, Maria Nefeli Antonopoulou, Richard Whitfield, Dominik Konkolewicz, Athina Anastasaki, *Polym. Chem.*, **2020**, 11, 4968-4972.

Self-healable dielectric elastomer actuators operated at low electric fields

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Dielectric elastomer actuators (DEAs) are a class of electromechanical transducers characterized by an outstanding shape flexibility and elasticity, which have great potential to find applications in soft robotic devices or artificial muscles in the near future.[1] Increasing the dielectric permittivity of the dielectric elastomer allows reducing the driving voltage needed for actuation and increasing the generated force.[2]

We report a nitrile group-modified polar polysiloxane elastomer with a permittivity of up to 18.2 at 10 kHz. The material is obtained by in situ polymerisation and cross-linking by anionic ring-opening polymerization of 1,3,5,7-tetramethyl-1,3,5,7-tetra(3-cyanopropyl)cyclotetrasiloxane (D_4^{CN}), octamethylcyclotetrasiloxane (D_4), and a specially designed co-monomer (tris-D_4) that functions as cross-linker. The initiator tetrabutylphosphonium hydroxide remains active in the product and the equilibrium between network and monomers can be shifted as a function of temperature. The material reversibly softens upon heating and undergoes self-healing. The mechanical properties can be tuned easily by variation of the cross-linker concentration. We prepared elastomer thin films by melt pressing and incorporated the films in DEAs, which show a lateral strain of 3.6% at an electric field of 5.2 V/µm. After a dielectric breakdown, the actuator is able to self-heal and recover the initial actuation in the next cycle.

[1] Ron Pelrine, Roy Kornbluh, Qibing Pei, Jose Joseph, *Science*, **2000**, 287, 836–839.
[2] Dorina M. Opris, *Advanced Materials*, **2018**, 30, 1703678.

Chiral nano- and microscopic vesicles composed of fully amorphous isotactic block copolymers

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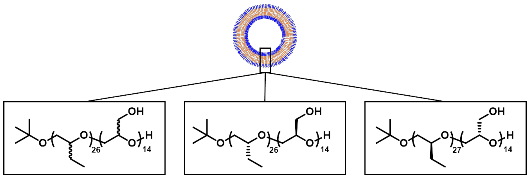
The introduction of chirality into nanoscopic self-assemblies by using isotactic block copolymers (BCPs) is an emerging field of interest.[1, 2] As a result of the isotacticity, those BCPs typically exhibit crystalline behaviour, limiting their potential use in advanced applications involving membrane proteins or sensitive cargo.[3] In this talk, an alternative isotactic, yet non-crystalline BCP on polyether basis is introduced that is able to overcome those limitations. A set of three highly similar BCPs composed of atactic or isotactic poly(butylene oxide)-*block*-poly(glycidol) (PBO-*b*-PG) was synthesised.[4] The three BCPs, differing solely in their tacticity (*R*/*S*, *R* and *S*), were thoroughly characterised in bulk and solution. Their self-assembly into polymersomes (referred to as small unilamellar vesicles, SUVs) was analysed. In addition microscopic giant unilamellar vesicles (GUVs) were prepared *via* a microfluidics based approach. The potential of PBO-*b*-PG for biomedical applications was proven by the reconstitution of the Outer membrane porin F (OmpF) in the membrane of GUVs composed of the atactic BCP. We conclude that self-assemblies composed of amorphous PBO-*b*-PG are a promising alternative for advanced biomedical applications to commonly used crystalline polymers such as PLLA.



(*R*/*S*)-BCP
(*R*/*S*)-PBO$_{26}$-*b*-(*R*/*S*)-PG$_{14}$

(*R*)-BCP
(*R*)-PBO$_{26}$-*b*-(*R*)-PG$_{14}$

(*S*)-BCP
(*S*)-PBO$_{27}$-*b*-(*S*)-PG$_{14}$

[1] M. Vleugels, M. de Zwart, J. Magana, B. Lamers, I. Voets, E. Meijer, K. Petkau-Milroy, A. Palmans, *Polymer Chemistry*, **2020**, 11, 7170-7177.

[2] K. Petkau-Milroy, A. Ianiro, M. Ahn, J. Magana, M. Vleugels, B. Lamers, R. Tuinier, I. Voets, A. Palmans, E. Meijer, *ACS Macro Letters*, **2020**, 9, 38-42.

[3] M. Garni, S. Thamboo, C. Schoenenberger, C. Palivan,*Biochimica et Biophysica Acta 1859*, **2017**, 619-638.

[4] R. Wehr, J. Gaitzsch, D. Daubian, C. Fodor, W. Meier, *RSC Advances*, **2020**, 10, 22701-22711.

Drug loaded hollow mesoporous silica nanoparticles–DNA self-assembly for responsive antimicrobial coatings

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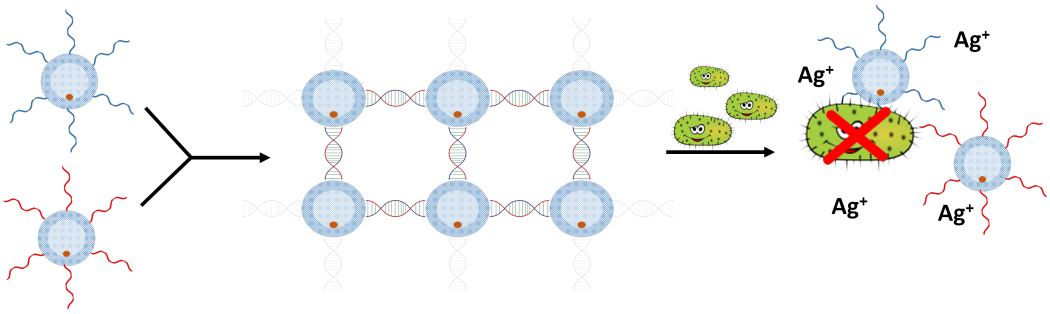
Implants are biomaterials that are used in medicine to replace missing body parts, deliver medications or support body functions. With the average life expectancy increasing on one hand, and implant technology becoming more advanced on the other hand, the number of implants used per year is steadily growing. However, they are subjected to failure particularly due to device-associated infections. Bacterial adhesion on medical implant surfaces may lead to biofilm formation. This matrix will protect bacteria against antibiotics by limiting their penetration. Thus, biofilms are almost impossible to eradicate with antibiotics, leading to the necessity to remove and replace the implant.[1]

To prevent bacterial adhesion on implants, their surface should be coated with an antimicrobial compound with a control of the release over time by using for example nanocapsules loaded with antimicrobial molecules or structures such as nanorattles with an antimicrobial as core which were developed in our group previously for silver.[2, 3]

Currently, we are working on the self-assembly of DNA-decorated hollow mesoporous silica nanoparticles (HMSN) loaded with an antimicrobial compound (such as silver nanoparticles). They are expected to release their cargo upon recognition of bacterial DNA as perfect matching sequences and, in this way, kill the bacteria. (Scheme 1)



Scheme 1: Schematic representation of drugs release from an antimicrobial compound loaded DNA-decorated HMSN self-assembly and bacteria's killing trigger by bacteria specific DNA recognition

[1] Carla Renata Arciola, Davide Campoccia, Lucio Montanaro, *Nature Reviews Microbiology,* **2018**, 16, 397–409.
[2] Magdalena Priebe, Katharina M. Fromm, *Chemistry – A European Journal*, **2014**, *20*, 3854-3874.
[3] Sarah-Luise Abram, Jacinthe Gagnon, Magdalena Priebe, Nelly Hérault, Katharina M. Fromm, *Chimia,* **2018**, 72, 249-252.