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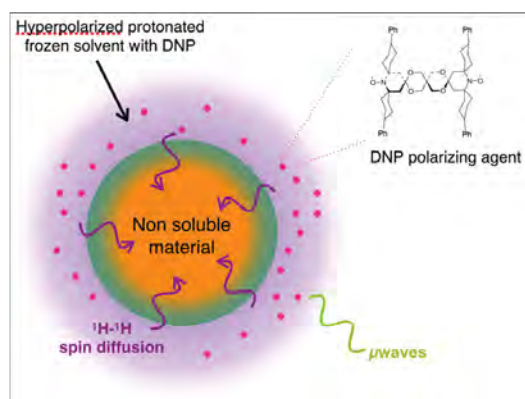
Relayed Dynamic Nuclear Polarization to Image the Morphology of Complex Materials

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Dynamic Nuclear Polarization (DNP) is an emerging efficient approach to hyperpolarize sample in solid-state MAS NMR. Previously, we have established how the propagation of nuclear DNP hyperpolarization can be used to determine the morphology in complex materials.¹This is achieved by impregnating a material with a solution containing a DNP polarizing agent. Upon microwave irradiation ¹H nuclei of the frozen solvent are rapidly hyperpolarized to generate a source of hyperpolarization; this hyperpolarization then gradually propagates, through spontaneous ¹H -¹H spin diffusion, into adjacent particles (as illustrated in Figure 1).¹⁻³Polarization build-up of resonances as function of time inside the target materials depends on their size and location with respect to the source (typically a frozen solvent doped with stable organic radical).

Using this approach, we show here that R-DNP can be used to determine a series of complex structures and morphologies, including core-shell structures of organic and inorganic nanoparticles as well as lignocellulosic and functionalized cellulose samples with industrial relevance. In these cases, the complex nature of the materials means they are not amenable to other approaches.



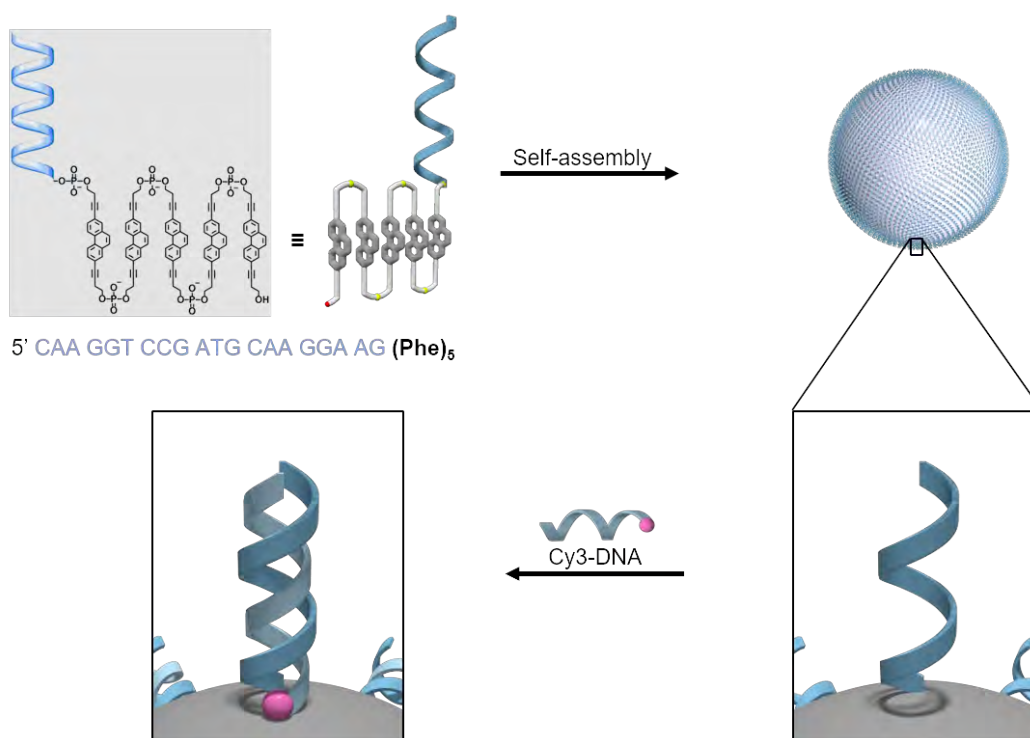
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Supramolecular Self-Assembly and Functionalization of DNA-Modified VesiclesN. Bürki¹, S. M. Langenegger¹, R. Häner^{1*}¹Department of Chemistry and Biochemistry, University of Bern

In previous work, we showed that phenanthrene oligomers conjugated to DNA assemble into vesicles.[1] The here presented DNA-phenanthrene conjugates were also found to assemble into vesicular objects. The DNA-modified vesicles were investigated by hybridization with a DNA single strand with fluorescence acceptor dyes. By excitation of the DNA-phenanthrene conjugates, energy transfer from the phenanthrene to the fluorescence dye was observed. The vesicles were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), UV-vis and fluorescence spectroscopy. In this poster, we will present and discuss the morphology of the supramolecular assemblies as well as the effects of energy transfer.



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Pt⁽⁰⁾-containing metallosupramolecular polymers as precursors for nanoparticle composites

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Composites of metallic nanoparticles (NP) and polymers can offer a combination of the functional characteristics of the former and the structural and mechanical properties of the latter and promise to be useful for a wide range of applications.¹ However, the preparation of such materials is usually tedious, and typically requires first synthesizing the NPs in a liquid-phase synthesis, stabilization of these NPs by a surfactant, purification, before they can be embedded in polymeric matrices.² This approach also makes it difficult to incorporate the NPs in a spatially controlled manner in the polymer.

Building on a previously reported synthetic approach in which bis(η^2 -alkyne)platinum(0) complexes were created to cross-link poly(*p*-phenylene ethynylene)s,³ we investigated the use of metallosupramolecular polymers (MSPs) based on zero-valent Pt complexes as precursors for the in-situ preparation of metallic NPs within a polymer matrix. Diphenylacetylene-functionalized telechelic poly(tetrahydrofuran) was prepared and used to create MSPs upon chain extension through the formation of bis(η^2 -alkyne)platinum(0) complexes. Heating the MSPs above a threshold temperature leads to an irreversible dissociation of the metal-ligand complexes, Pt⁰-atoms are released, and the nucleation and growth of crystalline Pt-NPs is observed. The particles are homogeneously distributed in the polymeric matrix and the process completely avoids the typically required harsh reduction step.⁴ Moreover, irradiation with UV light can be used to trigger the NP formation in a spatially resolved manner. The use of macromonomers of different molecular weight allows one to control the Pt content, and influences the resulting NPs, the properties of the composites, as well as their catalytic activity.

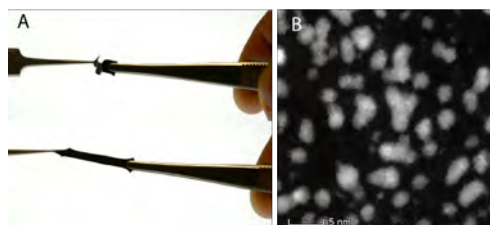


Figure 1: (A) Photographs documenting that elastic nanocomposites containing platinum nanoparticles are obtained upon heating the metallosupramolecular polymers studied here to 200 °C. (B) Dark field transmission electron microscopy image showing the Pt nanoparticles formed in the process.

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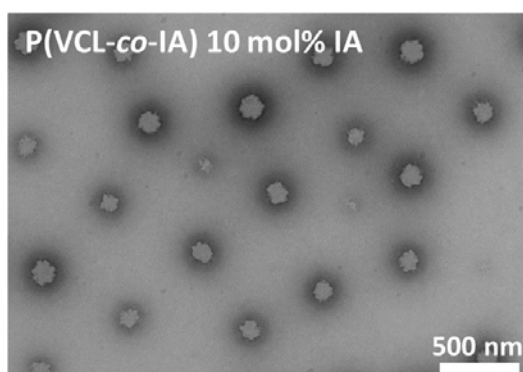
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Alkali Ion Responsive Microgel Systems

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Stimuli responsive microgels have been under strong focus for their promising use as sensors, filters, in several biomedical applications and drug delivery systems. Due to their peculiar soft and porous structure, extensive research has been done on their ability to uptake and selectively release drugs and proteins.[1] However, smaller interest has been shown for their responsiveness towards alkali ions, despite their fundamental role in biological processes such as muscle contraction.[2]



Anionic ion responsive vinyl caprolactam (VCL) based microgels have been prepared and their behaviour towards alkali ions has been investigated in aqueous media. The gels are designed to be biocompatible and responsive to multiple stimuli, such as temperature, pH and metal ion concentrations.[3] The gels have been synthesized by precipitation polymerisation and their structure, chemical composition and morphology were characterised. Their responsiveness towards temperature and pH has also been studied via dynamic light scattering (DLS), behaving in accordance to the literature. Their responsiveness towards alkali ions has also been investigated via DLS, and the quantification of ion uptake has been measured *via* ion chromatography. Moreover, we present herein the dynamics of binding, which might play a determining role for future applications in synthetic biology.

[1] Felix Plamper, Walter Richtering, *Accounts of chemical research*, **2017**, 50(2), 131-140.

[2] Gary Eichenbaum, Patrick Kiser, Dipak Shah, William Meuer, Patrick Needham, Sidney Simon, *Macromolecules*, **2000**, 33(11), 4087-4093.

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Copolymers of phenylene methylene units and its derivatives: Photoluminescent, Corrosion-Protective Coating Materials

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In this study copolymers on the basis of poly(phenylene methylene) (PPM, Figure 1 a) are explored as protective coating for the high strength aluminum alloy AA2024, widely employed in aerospace applications. PPM is a hydrocarbon polymer which consists of an alternating sequence of phenylene and methylene units obtained, e.g., by catalytic polymerization of benzyl chloride. PPM unexpectedly exhibits photoluminescence, due to the rare phenomenon of homoconjugation which is a consequence of overlapping of p-orbitals of adjacent electronically separated phenylene rings through space (Figure 1 b) [1]. In addition, PPM possesses high thermal stability [1] (onset of decomposition 450 °C - 470 °C) that overcomes the thermal stability of common organic materials, and shows hydrophobicity [2]. Copolymers were synthesized by copolymerization of benzyl chloride and substituted benzyl chloride (octyloxy, heptyl, methoxy, hydroxy), in different ratios of 1%, 5% and 10% mol/mol with the goal to impede crack formation of PPM homopolymer which prevents the use of neat PPM as a protective coating [2]. For this purpose, first the compatibility between the hydrophilic surface of the aluminum alloy and the hydrophobic PPM was improved by application of a layer of polybenzylsiloxanes (thickness 1mm). Subsequently the substrates were covered with PPM copolymer films prepared by hot pressing. The mechanical stability, the homogeneity of the films, the elastic modulus and the glass transition temperature of the films or copolymers, respectively, were investigated. The corrosion protection properties of the organic barrier layers were tested by electrochemical measurements (anodic polarization, potentiodynamic analyses...) and the results were then compared with other organic coatings (including PPM itself. Self-healing properties, which were found for films of PPM itself, are also addressed in this study.

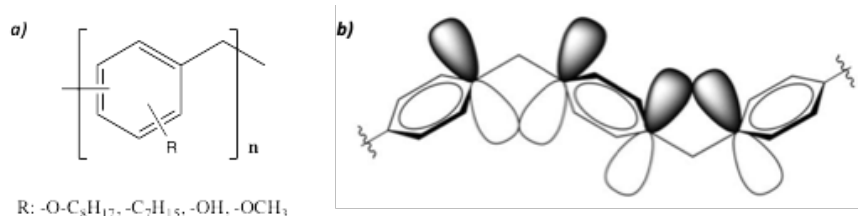


Figure 1 (a) Chemical structure of poly(phenylene methylene) (PPM); (b) Schematic representation of homoconjugation in PPM as a result of overlapping p-orbitals of phenylene rings which are separated by a methylene group.

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Programmable and Dynamic Assembly of Mobile MicromachinesA. F. Demiroers¹¹Complex Materials, ETH Zurich

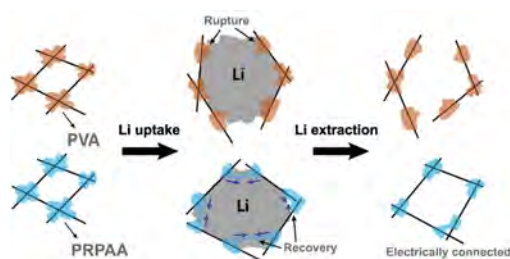
Machines and robots at all scales rely on organization of multiple components to achieve advanced locomotion and functions. In the microworld, micromachines comprising diverse parts can carry out sensing, manipulation and other tasks, or be integrated into more complex systems, enabling life-inspired hierarchical assemblies. To this end, field-directed and self-propelled colloidal assembly have been used to build mobile and reconfigurable colloidal walkers, swimmers and spinners. However, integrating heterogeneous components into a micromachine with specified structure, function and dynamics remains a significant challenge. Here, we show mobile micromachines that spontaneously self-assemble into desired configurations through pre programmed physical interactions between structural and motor sub-units. The assembly is driven by dielectrophoretic interactions, encoded in the three-dimensional shape of individual parts. Micromachines assembled from magnetic and self-propelled motor parts exhibit reconfigurable locomotion modes and additional rotational degrees of freedom not available to conventional monolithic microrobots.

Highly Elastic Polyrotaxane Binders for Mechanically Stable Lithium Hosts in Lithium Metal Batteries

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¹University of Fribourg

Lithium metal anodes have gained increasing attention, as they offer attractive properties in terms of specific capacity and operating voltage. The theoretical specific capacity reaches up to 2060 mAh mL⁻¹ or 3860 mAh g⁻¹, and the thermodynamic redox potential is as low as -3.04 V vs standard hydrogen electrode (SHE). Nevertheless, the inherent drawbacks of the Li metal anodes such as continuous electrolyte decomposition and dendrite growth over cycling still pose formidable challenges, rendering the given technology to linger at a research stage.^[1-3] Among the reported strategies to tackle limitations of Li metal anodes, the integration of a three-dimensional (3D) conductive network acting as a host for Li storage has been proved to offer reliable operation with Li metal anodes. One of the mechanisms in alleviating the Li dendrite growth by 3D conductive networks is the reduction of effective current density. For a given electrode area, the 3D network lowers the effective areal current density, a critical parameter in determining the magnitude of dendrite growth in correlation with Sand's time.^[4] Another mechanism is to guide Li deposition into the pores of a 3D network by implementing nucleation seeds^[5] or functionalization of the carbon surface.^[6] One of the promising candidates of 3D conductive Lithium hosts are carbon nanotubes (CNTs) because of their capability of percolating a conductive network. However, CNT networks are prone to rupture easily due to large tensile stress generated during lithium uptake-release cycles. Herein, we present CNT networks integrated with a highly elastic binder, called PRPAA, via supramolecular interactions, in which the unique ring-sliding motion of flexible polyrotaxane containing binder endowed extraordinary stretchability and elasticity to the entire binder network. In comparison to a control sample with the inelastic binder (PVA), the CNT network with PRPAA binder can endure large stress during repeated lithium uptake-release cycles, thereby enhancing the mechanical integrity of the corresponding electrode over battery cycling. As a result, the PRPAA-incorporated CNT network exhibited substantially improved cyclability in lithium-copper asymmetric cells and full-cells paired with olivine-LiFePO₄, indicating that high elasticity enabled by mechanically interlocked molecules such as polyrotaxanes can be a useful concept in advancing lithium metal batteries.^[7] Figure 1: Graphical presentation of CNT network configuration during lithiation and delithiation: *f*CNT-PVA network vs *f*CNT-PRPAA network.



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Spatiotemporal Imaging of Water in Operating Voltage-gated Ion Channels Reveals the Slow Motion of Interfacial Ions

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Ion channels are responsible for numerous physiological functions and rely on a complex molecular interfacial architecture that heavily relies on water. Although ion channel structure has been studied, the molecular mechanism of operational ion channels and in particular the role of water in it has not been achieved. Here, we perform spatiotemporal second harmonic imaging and capacitance measurements of operational voltage-gated alamethicin ion channels in a freestanding lipid membrane surrounded by aqueous solution on either side and having the same physiologically relevant salt concentration. The image contrast of the opening and closing of ion channels which is controlled by an external bias is due to changes in the orientational distribution of water molecules induced by electric field gradients. Only a fraction of 10^{-4} of the transported ions arrives at the hydrated membrane interface, leading to interfacial electrostatic changes on the time scale of a second. Our study shows that ion transport along the membrane, which is thought to be involved in the propagation of action potential, is taking place over seconds. This observation suggests a more complex mechanism for the propagation of action potentials.

Biodegradable and pH-Responsive Nanoparticles from Radical Ring-Opening Polymerization

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Amphiphilic block-copolymers are ideal for self-assembly into nanoparticles and have shown a very high potential for drug delivery as well as for nanoreactors.^[1] While the majority of self-assembly studies are performed with non-degradable polymers, aliphatic polyesters are also feasible candidates for the formation of polymeric nanoparticles and they are biodegradable. We therefore work on radical ring-opening polymerisation (RROP) from cyclic ketene acetals (CKAs) to create such nanoparticles.

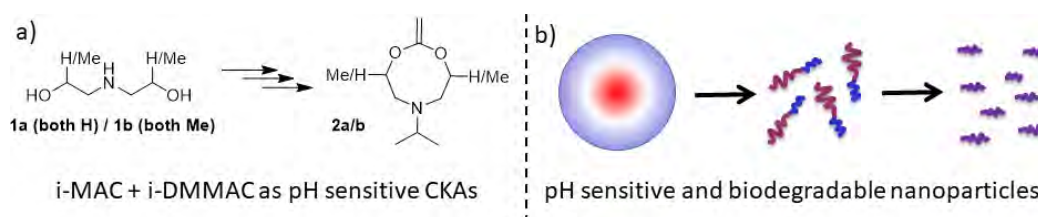


Figure 1: a) The diols **1** containing an amine are transformed into the pH sensitive CKAs **2** by ring closure and functional group transformations. b) The nanoparticles from the resulting polyesters can then disassemble upon acidification (protonation of the amines) or adding esterase, triggering biodegradation.

In order to enhance the scope toward pH-triggered responsiveness, an N-functionalized group was introduced into each monomer. RROP combines the advantages of radical polymerization in being able to incorporate stimuli responsive groups and ring-opening polymerization (ROP) to enable biodegradability^[2]. Although homopolymerization of the N-functionalized CKAs monomers by RROP was a challenging task, co-polymerization with PEG-based end groups was accordingly efficient. The resulted amphiphilic diblock copolymers introduced to form nanoparticles by self-assembly. The abilities toward biodegradation and pH-responsiveness were proven by dynamic light scattering (DLS). Based on the observed results, the nanoparticles were responsive upon pH-triggers and enzymatic degradation.

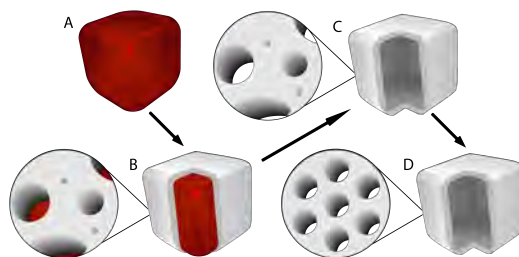
We are certain that these results mark a great improvement for RROP and Nanoparticles in general.

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Hollow silica cubes with customisable porosityS. H. Gallagher¹, O. Trussardi¹, D. Brühwiler^{1*}¹Zurich University of Applied Sciences (ZHAW), Switzerland.

Mesoporous silica particles contain advantageous properties, such as large specific surface areas, defined pore structures and versatile surface chemistry.^{1,2} The internal volume of the particles can be maximised by using a template to prepare hollow silica particles. However, the common synthesis procedure yields a macroporous silica shell with a low surface area. We present a method to prepare hollow cubic particles with a well-defined mesoporous silica shell and a surface area of up to 650 m²g⁻¹. A cubic morphology was chosen as it is seldom represented in the literature but offers attractive packing properties.



Scheme 1. Procedure for the synthesis of hollow mesoporous silica cubes (HMSC). Hematite cubes (A) are first coated with a silica layer (B). A macroporous silica shell remains after extraction of the hematite core (C). Defined mesopores are subsequently introduced by pseudomorphic transformation (D).

Information regarding porosity was elucidated through argon and krypton sorption measurements. Customisability was achieved by tuning the pore diameter through selection of the structure directing agent (SDA). Varying the conditions of the pseudomorphic transformation (PT) changed the relative amount of defined mesopores in the silica shells. Complete transformation increased the specific surface area by a factor of 76, whilst the internal void volume and cubic morphology were retained. The hollow mesoporous silica cubes could be conveniently arranged into a dense monolayer.

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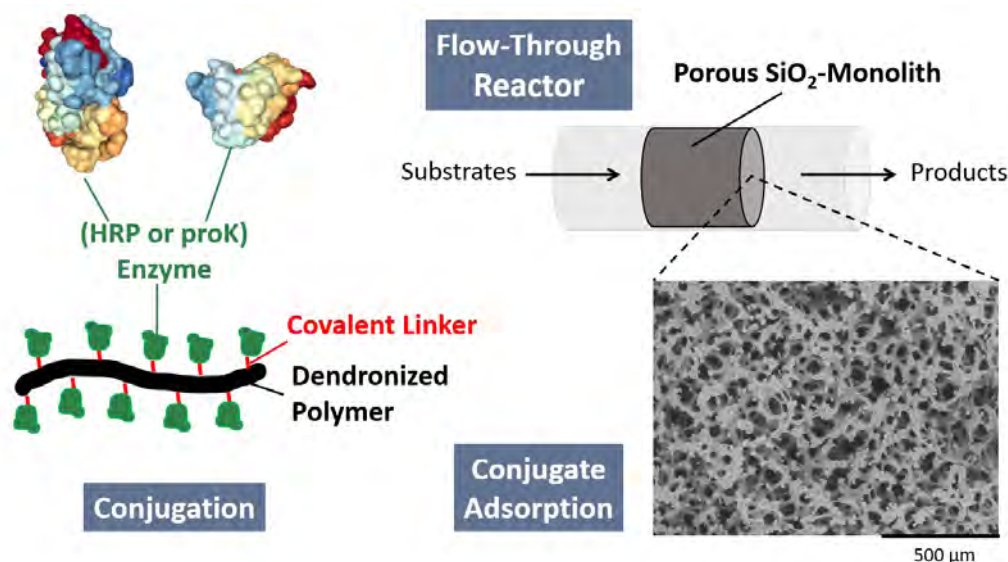
[2] D. Brühwiler, *Nanoscale*, **2010**, 2, 887–892.

Stable Immobilization of Enzyme-Polymer Conjugates in a Porous Silica Monolith

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Through stable bis-aryl hydrazone bonds (BAH), a large number of enzyme molecules can be attached covalently to polycationic, dendronized polymers (denpols) [1]. The obtained water soluble enzyme-denpol conjugates can be immobilized under mild aqueous conditions and under retention of enzymatic activity by stable non-covalent adsorption on flat silica surfaces [2,3]. Using conjugates made from horseradish peroxidase (HRP) or proteinase K (proK) and a second-generation denpol, successful enzyme immobilization was recently demonstrated in a macro- and mesoporous silica monolith [4]. These monoliths containing immobilized HRP were used as flow-through reactors for the quantitative determination of hydrogen peroxide [4].



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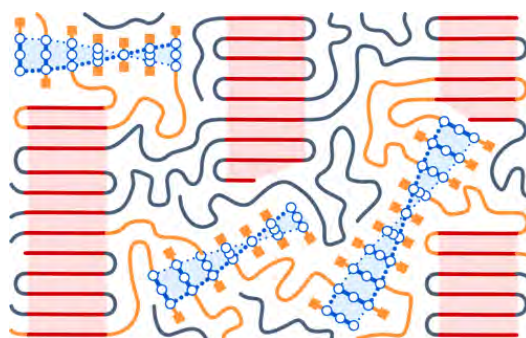
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Supramolecular Thermoplastic Materials Based on Polyethylene

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Much interest has been shown in supramolecular network formation in soft hydrogen-bonded polymers due to their ability to form reversible physical crosslinks, giving rise to thermoplastic elastomers with sharp softening transitions. The applicability of self-assembly concepts in semicrystalline polymers such as polyethylene (PE), on the other hand, is limited because the macroscopic bulk properties are largely dominated by the crystallinity of the polymer matrix. The introduction of hydrogen bonding units, however, into these materials may be beneficial for avenues such as self-healing, enhanced processing, and recyclability.



Here, we show how the supramolecular structure formation in high-density polyethylene (HDPE), the most abundant polymer used today, can be established in order to obtain novel thermoplastic materials. To this end, we modify the end groups of HDPE with short oligopeptides that form beta-sheet tapes or nanofibrils in the bulk material. As revealed by our detailed rheological, IR spectroscopic, and calorimetric studies, the self-assembled and serve as physical cross-links for the PE matrix. As a result, the material behaved as a thermoplastic elastomer above the crystallization temperature and showed a plateau modulus $G' \approx 10^6$ MPa, while the room temperature tensile properties were not conversely affected by the presence of the supramolecular structures. Moreover, the latter even served as a stabilizing agent for HDPE at elevated temperatures. Our bioinspired approach of the supramolecular modification of PE demonstrates that the thermomechanical characteristics of semicrystalline polymers in general, and polyethylene in particular, can be tailored for improved processing and a broadened scope of applications.

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Reinforced Supramolecular Polymer Networks - From Conceptual Design Towards Materials Standardization

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Supramolecular networks obtained from polymers with self-assembling end groups result in thermoplastic elastomers with well-defined and tailorable thermal transitions.^[1] However, current examples exclusively rely on low or moderate molecular weight polymer segments, since end group self-assembly becomes progressively inefficient at increasing polymer molecular weight. This severely limits the resulting materials' tensile properties, particularly at large strains, as these properties largely depend on polymer entanglement.

Here, we present how the supramolecular modification of different high molecular weight polymers can be employed to obtain a wide variety of elastomeric or thermoplastic materials with often extraordinary thermomechanical property profiles. To this end, we made use of oligopeptide end groups that are self-complementary and ditopic in nature and therefore self-assemble into well-defined, one-dimensionally extended nanostructures.^[2] This particular feature renders them capable to co-assemble with a corresponding low molecular weight additive, independently of the chosen polymer molecular weight (Figure 1). As revealed by our detailed thermomechanical analysis, complemented by spectroscopic, scattering, and imaging techniques, such supramolecular nanostructures provide an effective structural reinforcement of entangled polymers at additive concentrations as low as 5 wt%, which leads to a robust polymer network that remains thermodynamically stable up to the dissociation temperature.

We demonstrate that this approach constitutes a universal pathway to new supramolecular elastomers and thermoplastic materials with unusual combinations of high softening temperatures, strain at break, yield strength, ductility, toughness, and processing options. The tailorability of these parameters may hence pave the way towards the standardization of plastic materials based on a reduced amount of used base polymers in order to foster the transition to a circular and more sustainable economy.

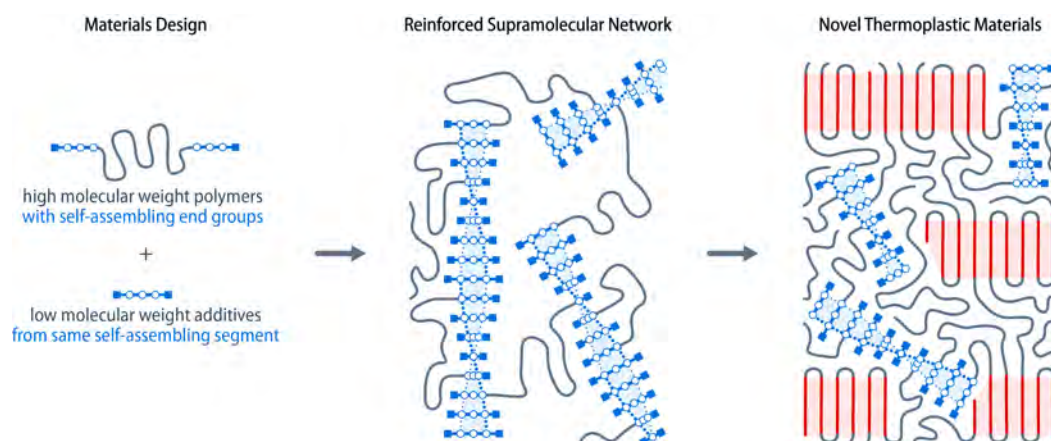


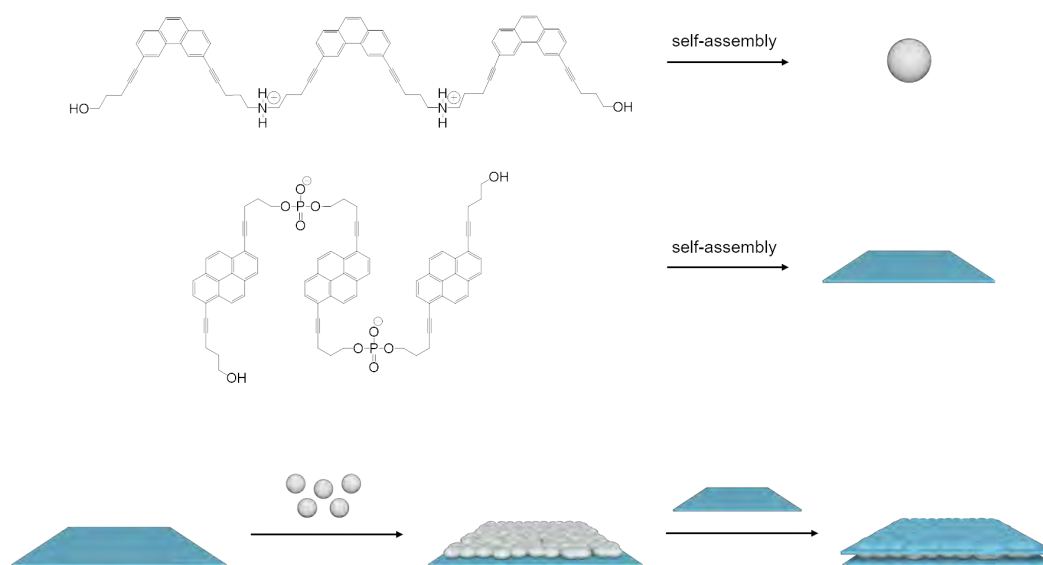
Figure 1. Co-assembly of molecularly uniform polymer end groups and matching additives leads to reinforced nanostructures, which gives rise to novel supramolecular elastomers and thermoplastics.

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Layer-by-Layer Self-Assembly of Cationic and Anionic Supramolecular PolymersJ. Jevric¹, S. M. Langenegger¹, R. Häner^{1*}¹Department of Chemistry and Biochemistry, University of Bern

The self-assembly of several amine-linked supramolecular polymers with a positively charged backbone in aqueous medium is studied. Previously, it was shown that 1,6-disubstituted phosphodiester-linked pyrene trimers – possessing a negatively charged backbone – assemble into sheets. Due to electrostatic interactions of the cationic and anionic species, alternated layering of the self-assembled structures is possible. The supramolecular polymers are usually preformed in their specific environment, in order to avoid problems because of different ambient conditions. Therefore, the layering on a mica substrate is done in a stepwise procedure. The structures formed by layer-by-layer self-assembly are analyzed by microscopy (AFM, TEM).



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

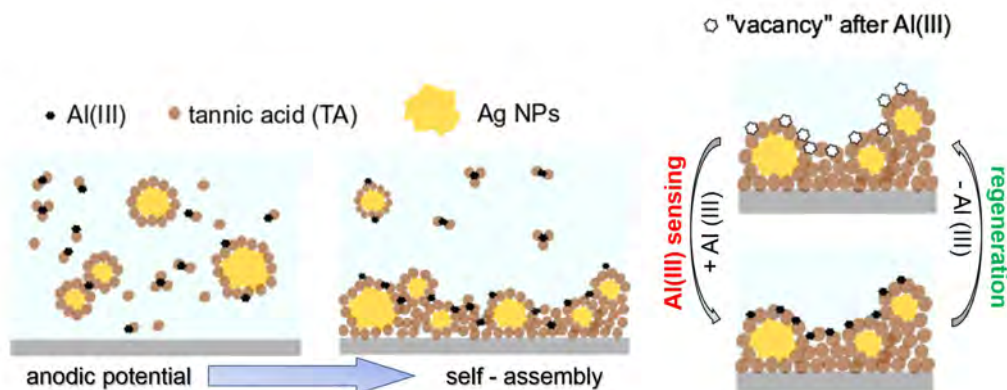
[2] Mykhailo Vybornyi, Alexander V. Rudnev, Simon M. Langenegger, Thomas Wandlowski, Gion Calzaferri, Robert Häner, *Angew. Chem. Int. Ed.* **2013**, 52, 11488-11493.

Electro-triggered self-assembly and in-situ nanoparticle sensitization of supramolecular metal-polyphenolic nanofilms designed for voltammetric sensing of aluminum in blood serum

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Nanomaterial-doped supramolecular metal-polyphenolic thin sensor films represent a unique class of composite materials. Their properties and sensitivity can be easily modified via controlled self-assembly of their molecular components. In this work we present a novel ionically-imprinted thin sensor film based on tannic acid, TA, and silver nanoparticles, Ag NPs, which was tailor-designed for voltammetric tracing of aluminum ions (III), Al^{3+} , in biological fluid. In the first stage, Ag NPs were obtained via direct reduction of Ag^+ by TA resulting in tannic acid-capped silver nanoclusters of size ranging between 2 and 10 nm, as observed by dynamic light scattering and transmission electron microscopy. Next, the TA molecules adsorbed on these nanoclusters were subjected to complexation with Al^{3+} before the application of anodic potential of 0.7 V, to self-assemble the $(\text{TA@AgNPs})_x \text{Al}$ species on the surface of the electrode. The potential applied was sufficient enough to cause cross-linking between the molecules of TA and thus, to improve the chemical robustness of the film, i.e. to avoid its destruction under physiological conditions. The Al^{3+} ions imprinted on the surface of the film, were then chemically removed from the film, as monitored by cyclic voltammetry and X-ray photoelectron spectroscopy, creating vacancies ready to bind the Al^{3+} present in the analyzed fluid. The obtained film was employed for sensing of Al^{3+} present in the blood serum. A correlation between the current value of TA/Al^{3+} CV peak and the concentration of Al^{3+} in the range corresponding to aluminum levels for a healthy individual, from 0 to 6 $\mu\text{g/L}$, was obtained.



Linking kinetics to viscoelasticity in dynamic covalent hydrogels by 2D ^1H NMRB. Marco-Dufort¹, M. W. Tibbitt^{1*}¹Department of Mechanical and Process Engineering, ETH Zürich

Dynamic covalent networks enable the formation of responsive, mouldable, and self-healing materials, as the bonds in the network can break and reform in response to external stimuli. The macroscale properties of these networks depend on the specific chemistry of the cross-link binding pairs as well as the network topology [1]. In this work, we related the viscoelastic properties of dynamic covalent networks, as measured by dynamic mechanical analysis, to the microscopic behaviour of the reversible junctions, through kinetic studies using 2D ^1H NMR exchange spectroscopy (EXSY). Boronic ester-based hydrogels (**Figure 1a**) were used as model dynamic covalent networks, as their viscoelastic properties can be tuned over several orders of magnitude by tailoring the chemistry of the acid-diol binding pair or by changing network pH [2].

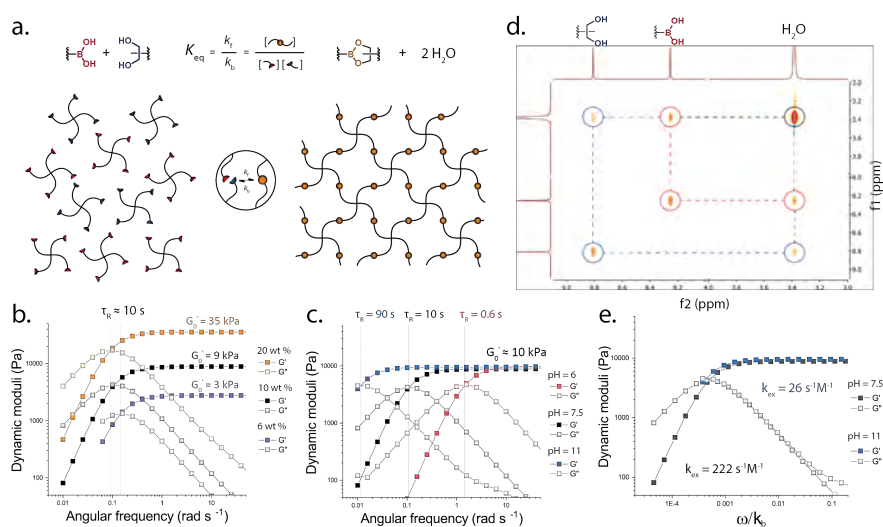


Figure 1 a) Reversible network formation for a typical boronic ester-based hydrogel. Frequency sweeps showing plateau modulus G_0' and relaxation time τ_r are shown for gels formed at **b)** different weight percentages and **c)** varying pH. **d)** A representative 2D ^1H NMR spectrum shows how forward and backward reaction rates k_f and k_b between exchanging boronic acids and diols are obtained in EXSY from the relative intensities of the cross-peaks to the diagonal at different mixing times (0s, 0.3s, and 1.0s). **e)** Frequency sweeps for gels at different pH scale with the reaction rates obtained from EXSY.

Oscillatory shear rheometry revealed that tuning network density controlled the plateau modulus G_0' but did not influence the relaxation time τ_r (**Figure 1b**). In contrast, varying the pH changed τ_r but did not affect G_0' (**Figure 1c**). To relate junction kinetics to material properties, the reaction rates for binding and unbinding of the boronic ester cross-links were obtained using 2D ^1H NMR EXSY (**Figure 1d**) [3]. This method was used to calculate the reaction rates for selected boronic acids and diols at different pH. **Figure 1e** shows how the frequency sweeps for gels at different pH scale with the reaction rates obtained from EXSY. This work, which links dynamics of the junction chemistry in a reversible network to its bulk behaviour, is being used to develop physical models that relate binding pair thermodynamics and kinetics to macroscale properties in order to enable the rational design of hydrogel systems.

[1] B. Marco-Dufort, M. W. Tibbitt, *Materials Today Chemistry*, **2019**, 12, 16–33.[2] V. Yesilyurt, D. Anderson, *Adv. Mater.*, **2015**, 28, 86–91.[3] J. Lu, D. Zhu, *J. Chem. Soc., Dalton Trans.*, **1998**, 0, 2267–2273.

Squaraine-containing phosphodiester-linked polymers: variety of compounds for various applications

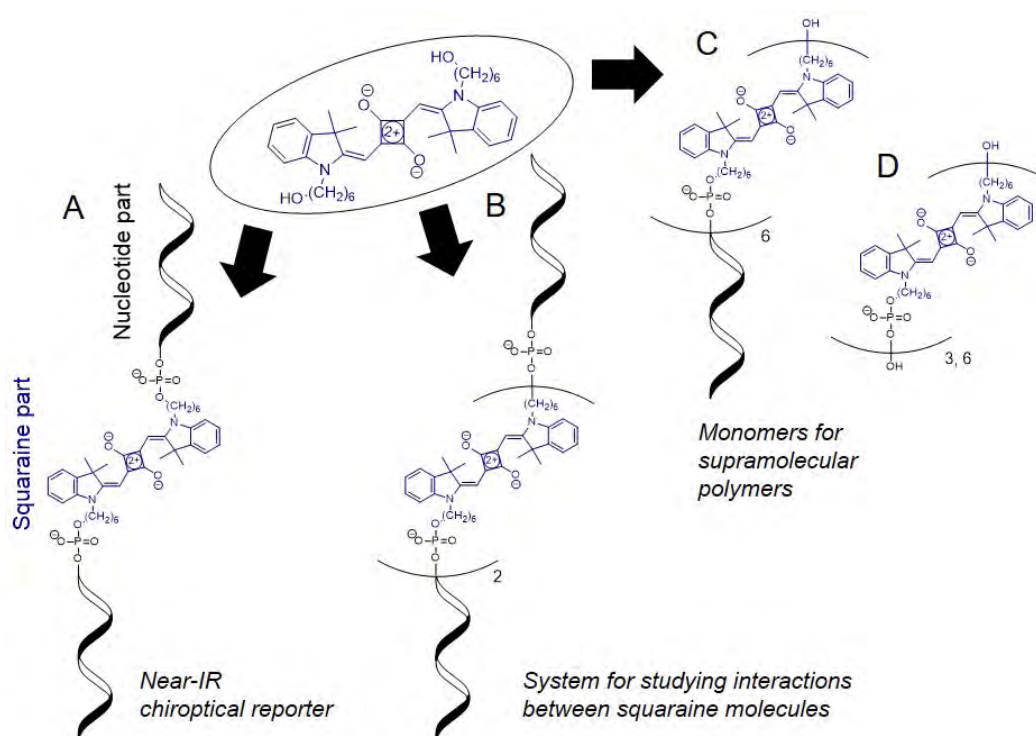
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The methods developed for preparation of synthetic DNA open broad perspectives for synthesis of new materials with unique properties. Thus, not only natural nucleotides can be involved in the synthesis but also artificial molecules which properties will determine the properties of the synthesized oligomer.

Squaraines or squaraine dyes belong to chromophores which absorb and emit light in the long-wavelength (near-IR) region of the visible spectrum. They exhibit a molar absorptivity of up to 260 000 M⁻¹cm⁻¹ and strong dependence of the fluorescence characteristics on environmental. Furthermore, they tend to form well-ordered aggregates in organic and aqueous solutions.

In this work, we present an overview of the squaraine-containing phosphodiester-linked polymers which we have synthesized by a solid phase phosphoramidite approach and figure out the fields of their application.



We found that the squaraine-containing phosphodiester-linked oligomers can be potentially used like near-IR chiroptical reporters (type A) [1, 2]. Type B oligomers are a promising system for studying interactions between squaraine molecules. Oligomers C and D form long-wavelength supramolecular polymers in aqueous solutions.

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Ultralight graphene carbon nanofiber aerogels for combined gas and particle filtrationN. A. Moeschlin¹, C. Adlhart^{1*}¹Institute of Chemistry and Biotechnology, Zurich University of Applied Sciences ZHAW

Particle or aerosol filtration is the major application of nanofiber mats (NFM). Such NFMs are typically obtained from electro-spun nanofibers [1]. Removal of volatile organic gases using NFMs, is relatively new, but the high specific surface area, the porous structure of NFMs provide a promising and versatile platform for gas adsorption [2].

Here, we synthesized a 3D ultralight composite from nanofibers and graphene, also known as nanofiber sponge or nanofiber aerogel (NFA) with the purpose of combining gas and particle filtration within the same material. The NFAs were prepared from electro-spun polyacrylonitrile (PAN) nanofibers through drying and subsequent peroxidation (average diameter of 340 nm), followed by cutting (average length of 39 μm), dispersing them in deionized water and mixing the dispersion with a graphene oxide suspension. Freezing the suspension at $-18\text{ }^{\circ}\text{C}$, followed by freeze-drying and final treatment at $800\text{ }^{\circ}\text{C}$ resulted in a graphene carbon NFA as already described by Huang *et al.* [3]. The NFA showed ultralow densities of $3.9 \pm 0.3\text{ mg cm}^{-3}$, a high porosity up to 99.98%, a permeability of $430 \cdot 10^{-4}\text{ mm}^2$, a specific surface area of $61\text{ m}^2\text{ g}^{-1}$ and a Young's modulus of up to 19.68 kPa. The reversible CO_2 adsorption capacity at $25\text{ }^{\circ}\text{C}$ was 36 mg g^{-1} , while N_2 and O_2 did not adsorb. Currently we are evaluating the particle adsorption capacity of the NFAs which may reach up to 99.998% [1] - to exploit the potential of combined gas and particle filter.

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Synthesis of Chitosan-Based Nanomaterials for Condensation of DNA in Gene Therapy of Liver Diseases

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¹ISIC, Ecole Polytechnique Fédérale de Lausanne, ²Pharmaceutical Sciences, University of Basel, ³Paediatrics, University Children's Hospital Zürich, ⁴Institute of Chemical Sciences and Engineering, EPFL Lausanne

Gene therapy can make profit of viral and non-viral vectors to deliver RNA or plasmid DNA (pDNA).¹ Whereas the former offers better transfection efficiencies, non-viral vectors provide safer profiles with no or low immunogenicity and ease of production and administration to the patient.² These biocompatible delivery systems are based on biodegradable polymers such as chitosan (CS) or polyethylene glycol (PEG). We herein describe the development of a pDNA polymeric-based nanocarrier for gene therapy of liver diseases. This delivery system is first composed of a CS backbone conjugated to branched polyethyleneimine (BPEI) chains allowing condensation of pDNA. A second CS-based component include grafted PEG derivatives presenting cross-reactive end functionalities. Combination of these CS derivatives with variation on the nature of the covalent grafting linkage and on the crosslinking strategy showed significant impact on solubility in acidic buffer, packing properties and also transfection efficiency. The chemical composition of the multifunctional polymers obtained was determined by 1D and 2D NMR spectroscopy. The first results of *in vitro* and *in vivo* evaluation are also disclosed.

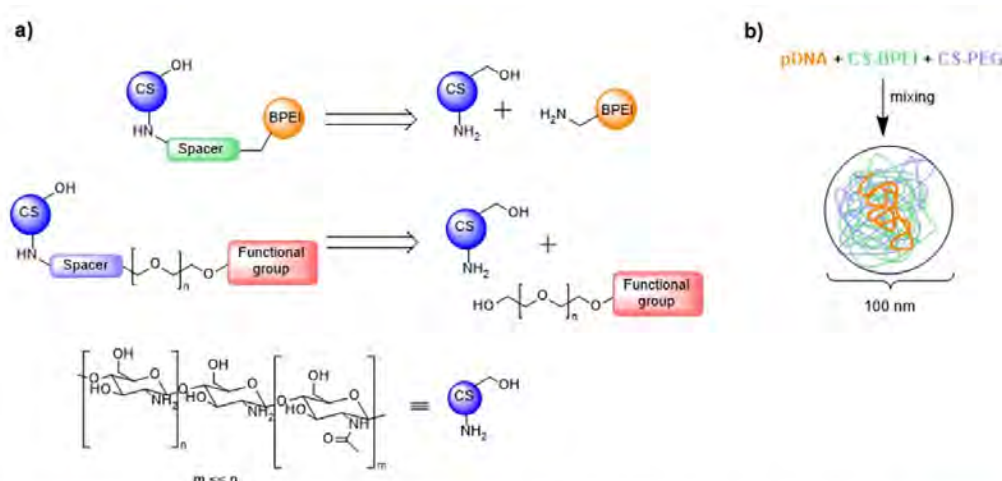


Fig. 1. a) Retrosynthesis of CS-based hybrid polymers. b) Three-component polymeric-based nanocarrier for pDNA delivery.

[1] Guimiao Lin, Li Li, Nishtha Panwar, Jie Wang, Swee Chuan Tjin, Xiaomei Wang, Ken-Tye Yong, *Coordination Chemistry Review*, **2018**, 374, 133-152

[2] Dongni Wu, Yongnu Zhang, Xiaoting Xu, Ting Guo, Deming Xie, Rong Zhu, Shengfeng Chen, Seeram Ramakrishna, Liumin He, *Acta Biomaterialia.*, **2018**, 72, 266-277

Complex Chemical Dynamics for Time-Domain Control of Self-Assembly and Supramolecular Gelation

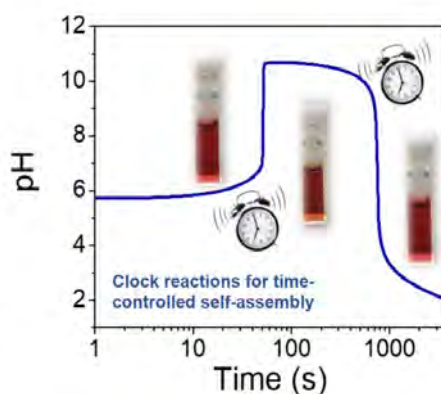
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¹Laboratory for Soft and Living Materials, Department of Materials, ETH Zurich

The ability to control self-assembly of polymers and colloids in the time domain will open new exciting perspectives for materials science, especially for the development of active, out-of-equilibrium biomimetic materials (1). Complex chemical dynamics such as those displayed by clock reactions, systems in which product formation occurs abruptly after a tailorable induction time, are fundamental tools to achieve this goal.

Here we provide an account of the results accomplished in our Laboratory by coupling different chemical clocks as *in situ* sources of stimuli (pH, redox) with molecular and macromolecular building blocks to obtain particles and gels.

We show how the formaldehyde-sulfite reaction allows the pH-driven, time-controlled precipitation of chitosan, a biopolymer with broad technological applications (2). We prove that transient, pH-mediated supramolecular self-assembly of perylenediimide dyes can be achieved with unprecedented temporal control (Figure 1). In addition, we demonstrate how supramolecular gel formation can be controlled by means of clock reactions.



[1] Elena Toth-Szeles, Judit Horvath, Gabor Hollo, Roszsa Szucs, Hideyuki Nakanishi, Istvan Lagzi, *Mol. Syst. Des. Eng.* **2017**, 2, 274-282.

[2] Guido Panzarasa, Alina Osyova, Alba Sicher, Arie Bruinink, Eric R. Dufresne, *Soft Matter* **2018**, 14, 6415-6418

[1] Elena Toth-Szeles, Judit Horvath, Gabor Hollo, Roszsa Szucs, Hideyuki Nakanishi, Istvan Lagzi, *Mol. Syst. Des. Eng.* **2017**, 2, 274-282

[2] Guido Panzarasa, Alina Osyova, Alba Sicher, Arie Bruinink, Eric R. Dufresne, *Soft Matter* **2018**, 14, 6415-6418

Role and influence of carbohydrates on supramolecular self-assemblyG. Picca¹, R. Häner¹, S. M. Langenegger¹¹Department of Chemistry and Biochemistry, University of Basel

Supramolecular polymers are arrays in which the single units are held together through non-covalent bonds. They represent promising candidates for a wide range of applications, such as drug delivery, gene transfection, protein delivery, bio-imaging and diagnostics, tissue engineering, and biomimetic chemistry.[\[1\]](#)

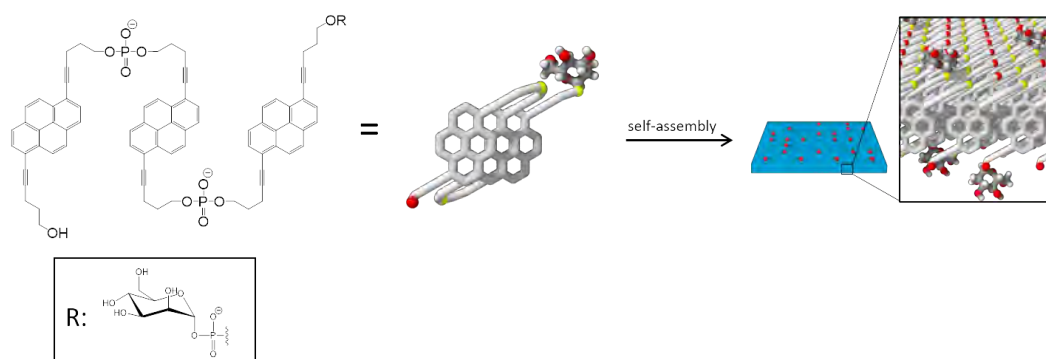


Figure 1: Illustration of the self-assembly of a phosphodiester-linked pyrene trimer modified with an α -D-mannose unit into 2D supramolecular polymers.

As we demonstrated in our research group, a trimer derived from pyrene (Figure 1) self-assembles into a nanosheet structures.[\[2\]](#) Here, we study the influence of a D-mannose attached to one of the two ends of the pyrene-trimer. The purpose of this project is to follow the process of self-assembly in the presence of a carbohydrate and in particular if the sugars are placed on both or on one side of the supramolecular structure. Spectroscopic measurements and imaging results will be shown.

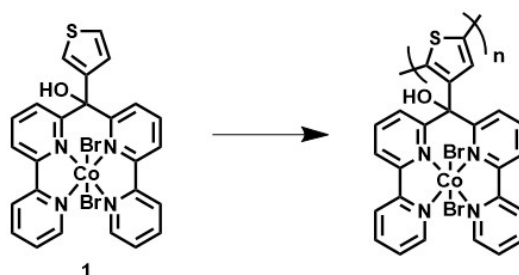
[1] Dong R., Zhou Y., Huang X., Zhu X., Lu Y., Shen J, *Adv. Mater.* 2015, 27, 498-52

[2] Vybornyi M., Rudnev A. V., Langenegger S. M., Wandlowski T., Calzaferri G., Häner R., *Angew. Chem. Int. Ed.* 2013, 52, 11488 -11493

Water Reduction Catalyst Embedded in a Semi-Conducting PolymerF. Rahn¹, B. Probst¹, R. Alberto^{1*}¹University of Zurich, Department of Chemistry, Winterthurerstrasse 190, 8057 Zürich

Homogeneous photocatalytic water reduction is investigated by our group with polypyridyl-based cobalt containing water reduction catalysts (WRC) and rhenium- or ruthenium-based photosensitisers (PS).[1] As for a whole water splitting system the oxidation and reduction have to be separated, different approaches to immobilise water reduction catalysts and photosensitisers are currently followed. One approach is the preparation of a photocathode consisting of polymerised PS and polymerised WRC on a conductive support. We present here the progress with one WRC monomer.

A thiophene was added to the basic structure of selected and highly active polypyridyl ligands. With this thiophene, a polymerisable unit was introduced to the ligand that can form a semi-conducting polymer. After complexation to cobalt, the monomeric WRC **1** was obtained. Polymerisation of thiophene and its derivatives with Fe(III) in presence of different doping anions has been described.[2] This method was successfully applied to **1** and resulted in a water soluble, catalytically active polymer. It is possible to precipitate this poly-cation with the poly-anion polystyrene sulfonate from the aqueous solution. Alternatively, electropolymerisation allows a direct grafting onto an electrode. Direct electropolymerisation on glassy carbon (GC) was not achieved. However, when a small amount of 2,5-di-(2-thienyl)-pyrrole was first polymerised on GC, subsequent electropolymerisation of **1** onto this modified electrode was successful.



[1] Stephan Schnidrig, Cyril Bachmann, Peter Müller, Nicola Weder, Bernhard Spingler, Evelyne Joliat-Wick, Mathias Mosberger, Johannes Windisch, Roger Alberto, Benjamin Probst, *ChemSusChem*, **2017**, 10, 4570-4580.

[2] Zhaoyan Guo, Yucong Qiao, Huan Liu, Chunmei Ding, Ying Zhu, Meixiang Wan, Lei Jiang, *Journal of Materials Chemistry*, **2012**, 22, 17153-17158.

Label-free and charge-sensitive second-harmonic imaging of giant vesicle hydrationD. Roesel¹, M. Eremchev¹, S. Roke^{1*}¹Laboratory for fundamental BioPhotonics (LBP), École polytechnique fédérale de Lausanne (EPFL)

A biological membrane forms a dynamic and complex barrier between compartments of the living cell and its environment. However, its *in vivo* studies are difficult because it consists of a high variety of lipids and proteins and is continuously reorganized by the cell. Therefore, membrane model systems with precisely controlled composition are used to investigate fundamental interactions of membrane components under well-defined conditions. Giant unilamellar vesicles (GUVs) are a powerful model system of the cell membrane due to their comparable size and membrane curvature. The majority of studies carried out on GUVs utilize fluorescence microscopy in combination with fluorescent markers. However, these methods of membrane imaging typically neglect molecular level details. As a consequence, there is virtually no knowledge on the role of membrane hydration, even though it is clear that without water lipid bilayer membranes cannot exist. A recent improvement in imaging throughput has resulted in the construction of a second harmonic imaging device that can non-resonantly and dynamically image interfacial water molecules [1,2]. This microscope was subsequently used to image the hydration of macroscopic free-floating membranes in aqueous solutions [3]. Here, we envision to extend our approach to SH image the interfacial hydration of GUVs. By varying the ionic strength of the adjacent solutions and lipid composition of the vesicles, we show that the nonresonant SH response of water molecules aligned by charge–dipole interactions with charged lipids can also be used as a label-free probe of membrane structure of GUVs.

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AIE-Active Supramolecular Assemblies of TPE-DNA Conjugates

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Opposite to many chromophores that suffer from aggregation-caused quenching (ACQ), aggregation-induced emission (AIE) type chromophores exhibit intense fluorescence and efficient energy transfer in molecular assemblies. That is why aggregation-induced emitters have gained much attention in the fields of optoelectronic devices and the creation of artificial light-harvesting systems among others.^[1] Previous work demonstrated light-harvesting in supramolecular vesicles assembled from phenanthrene-DNA conjugates.^[2] In this work, the phenanthrenes have been replaced by either *E*-tetraphenylethylenes (TPEs) (Figure 1A) or *Z*-TPEs and resulted in the formation of AIE-active supramolecular assemblies. As evidenced by AFM, duplex **1** self-assembles in aqueous medium into spherical objects (Figure 1B). Similar results are also obtained for *Z*-TPE-modified DNA conjugates. Spectroscopic data as well as physicochemical properties of the supramolecular arrays will be presented and discussed on this poster.

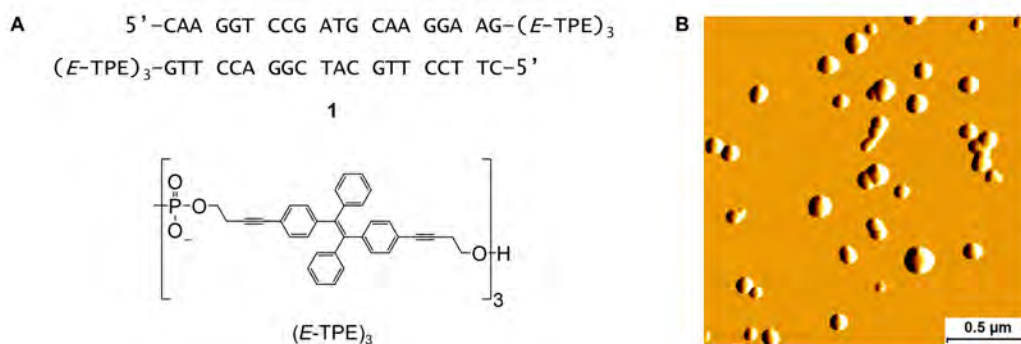


Figure 1. (A) Sequences of *E*-TPE-DNA conjugates. (B) AFM deflection scan of the self-assemblies.

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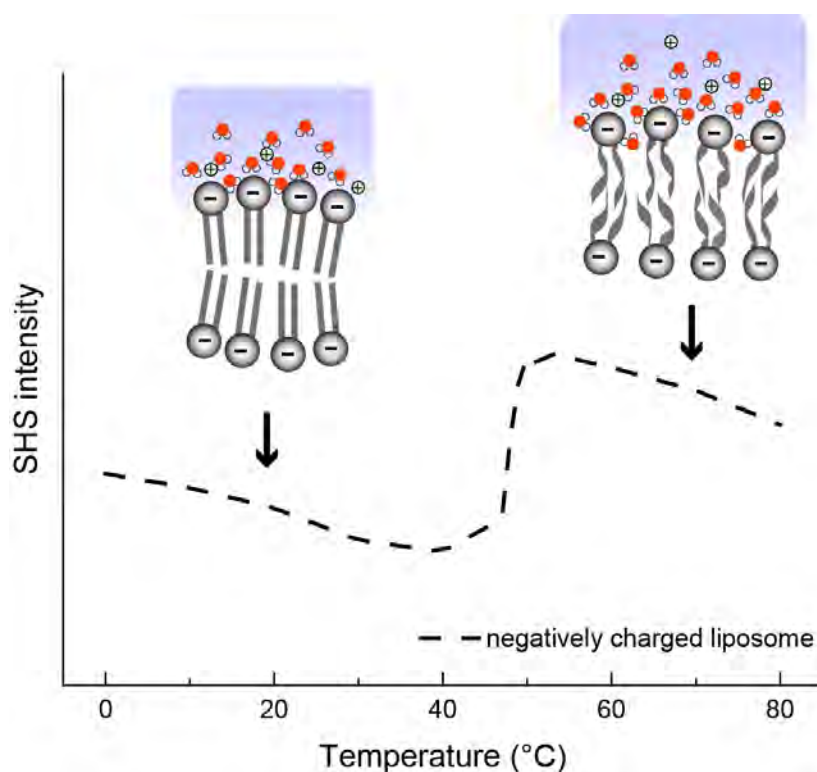
[2] Caroline D. Bösch, Jovana Jevric, Nutcha Bürki, Markus Probst, Simon M. Langenegger, Robert Häner, *Bioconjugate Chem.*, **2018**, 29, 1505–1509.

Lipid membrane phase transitions involve structural redistribution of interfacial water

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Morphological transitions of lipid membranes are thought to depend primarily on the chain length diversity of its components. However, the role of different lipid head groups, their counter ions and hydrating water molecules in the close proximity of the membrane on the gel-to-liquid phase transition of lipid is mostly unknown. We employed second harmonic (SH) scattering measurements to probe asymmetric distribution of water molecules between the lipid leaflets. Measurements on the same acyl chain length and single lipid component liposomes consisting of 1,2-dimyristoyl-*sn*-glycero-3-phosphate (sodium salt) (DMPA), 1,2-dimyristoyl-*sn*-glycero-3-phospho-L-serine (sodium salt) (DMPS), 1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-*rac*-glycerol) (sodium salt) (DMPG) and 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) showed a significant lipid hydration alteration as a function of temperature. More specifically, we observed a > 20% increase in the second harmonic intensity at the phase transition temperature for liposomes made of charged lipids. Zwitterionic DMPC lipids on the other hand, display only smaller (~ 8%) changes. This data implied that an increasing number of water molecules anisotropically oriented towards surface normal above the phase transition and the charge state of the lipids play key role on the gel-to-liquid phase transition. The increase in SH intensity, which reflects an increase in the amount of interfacial ordered water molecules is explained as a consequence of the change in lipid density (all lipids) and a consequential increase in charge-dipole interactions (charged lipids). Our data demonstrate that lipid phase transitions not only lead to structural changes in the bilayer itself but also in the adjacent aqueous phase.



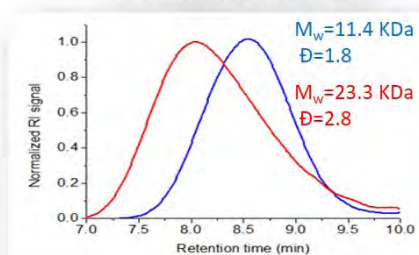
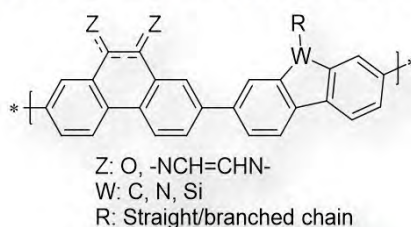
Conjugated Co-Polymers Derived from Phenanthrene-9,10-dione- and Dibenzo[*f,h*]quinoxaline

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Donor-Acceptor (D-A) conjugated polymers bearing phenanthrene-9,10-dione and dibenzo[*f,h*]quinoxaline as the acceptor units were synthesized via an optimized Suzuki cross-coupling reaction. Each of the abovementioned acceptors was reacted with three different donor co-monomers, namely, fluorene, carbazole and silafluorene derivatives bearing long alkyl chains. The resulting co-polymers display excellent solubility in common organic solvents with high chemical stability, allowing for the determination of their structural, thermal, and optical properties by various analytical techniques.

Total 6 examples yield 83-100 %



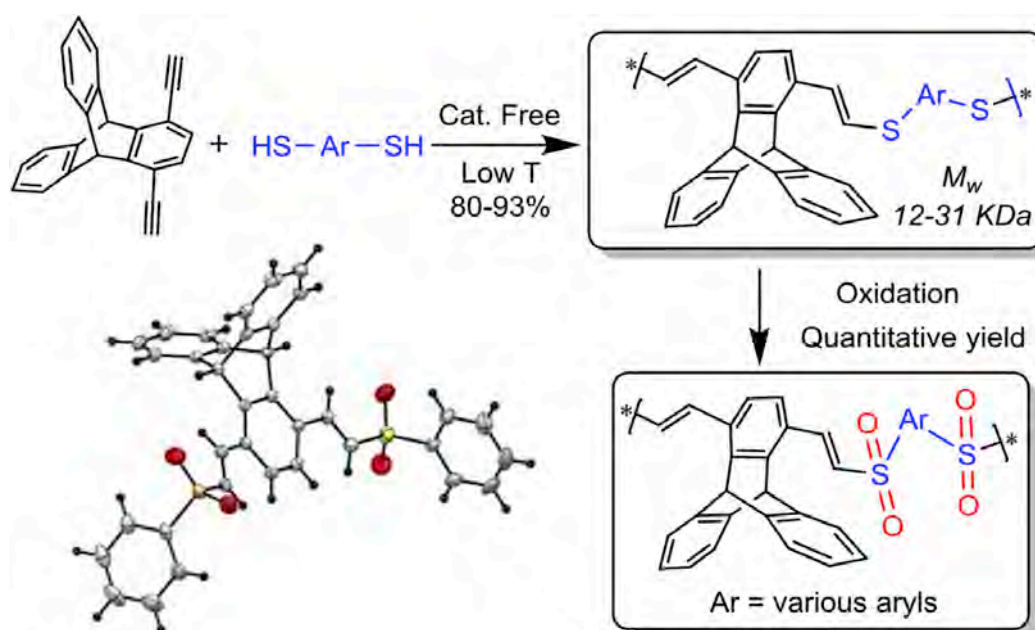
[1] Baig, N.; Shetty, S.; Al-Mousawi, S.; Al-Sagheer, F.; Alameddine, B. *Materials Today Chemistry* **2018**, *10*, 213-220.

Triptycene-Containing Poly(vinylene sulfone) Derivatives From a Metal-Free Thiol-Yne Click Polymerization Followed by a Mild Oxidation Reaction

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Triptycene-derived vinyl sulfide polymers **4a-d** were synthesized from a versatile catalyst-free thiol-yne click reaction using 1,4-diethynyl triptycene **1** with various aryl dithiol building blocks **3a-d**. The resulting triptycene-bearing poly(vinylene sulfide)s **4a-d** display excellent solubility and chemical stability allowing for their structural, thermal, and photophysical characterization by various instrumental analysis techniques. The thioether groups in polymers **4a-d** were selectively oxidized into their respective sulfone derivatives via mild reaction conditions affording the corresponding triptycene-based poly(vinylene sulfone)s **5a-d** in quantitative yield.¹



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Multicomponent alginate-based hydrogels presenting tunable properties for allo- and xenogeneic cell transplantation

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¹Institute of Chemical Sciences and Engineering, Group for Functionalized Biomaterials, ²University Hospital of Geneva, Surgical Research Unit

Over the last two decades, cell-based therapy has emerged as a highly promising approach to replace damaged or dysfunctional cells in the context of metabolic and degenerative disorders, and end-stage organ failure.[1] In particular, the transplantation of human pancreatic islets in type-1 diabetic patients who do not achieve glucose regulation despite exogenous insulin supply restored optimal glycemic control in 60% recipients, together with improved quality of life.[2] However, the development of cell-based therapies is limited by the shortage of human donor materials, the variable quality of human donor cells suitable for transplantation and the need for permanent immunosuppressive medication which has detrimental effects for both grafted cells and the recipients. Immunoprotection of effector cells into 3D semi-permeable hydrogels holds the potential to overcome these shortcomings by maintaining cell functionality without the need for immunosuppression and by paving the way to the transplantation of xenogeneic cells which would give access to standardized cell sources.

Our work is focusing on the assembly of multicomponent cross-linked alginate-based hybrid hydrogels presenting tunable mechanical properties and optimal environment for the long-term functionality of encapsulated endocrine cells. This is achieved by covalent functionalization of alginate with cross-reactive poly(ethylene glycol) (PEG) derivatives and anti-inflammatory drugs. Microspheres are formed by concomitant ionic gelation in the presence of divalent cations and spontaneous covalent crosslinking between complementary PEG chains. The resulting dual ionic-covalent hydrogel microspheres displayed enhanced elasticity and stability against ion exchange in comparison with conventional alginate hydrogels.[3] In addition, sustainable release of anti-inflammatory drugs (i.e. ketoprofen) from the hydrogel matrix resulted in a significant decrease of pericapsular fibrotic overgrowth in the context of the transplantation of microencapsulated insulin producing cells.[4] Detailed results of *in vitro* investigations using human and xenogeneic cells as well as the outcome of cell transplantation in mice model will be presented.



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Mechanically Responsive Polymers Based on Dye Interactions

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Mechanochemical transduction schemes, which translate a mechanical stimulus into a chemical event, are omnipresent in Nature and can serve as a blueprint for the design of artificial materials that display useful mechanoresponsive properties.^[1] Polymers with embedded rotaxanes comprised of interlocked fluorophore and quencher moieties were found to display a reversibly switchable fluorescence in response to bulk mechanical deformation,^[2] but their synthesis is very complex. Examples of "loopy" mechanoresponsive motifs based on excimer forming dyes or dye pairs capable of a Förster resonance energy transfer (FRET) have shown promising fluorescence color changes and are synthetically less demanding.^[3]

Inspired by these concepts, a weakly associated donor-acceptor pair was linked by a covalent loop structure and incorporated as mechanophore into polymers, based on the expectation that external stimulation by mechanical force would separate the dye complex and trigger a defined fluorescence response (Figure 1). A π -extended benzothiadiazole was chosen as donor and covalently linked with an oligo ethylene glycol linker to a naphthalene bisimide acceptor to obtain the desired loop motif. The optical characterization of the loop structure by solution-phase fluorescence and UV-vis spectroscopy suggests that fluorescence quenching occurs in polar environments, in which the donor and acceptor stack to each other, whereas nonpolar solvents cause disassembly. The new motif was then incorporated into polyurethanes to establish its utility as a mechanophore in bulk materials.

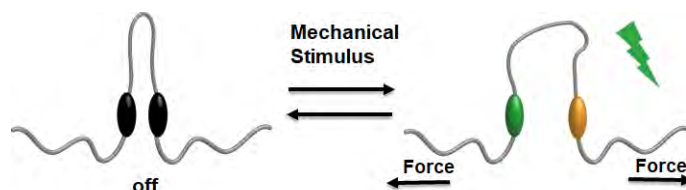


Figure 1 : Concept of novel loop mechanophores based on non-covalent donor-acceptor dye interactions.

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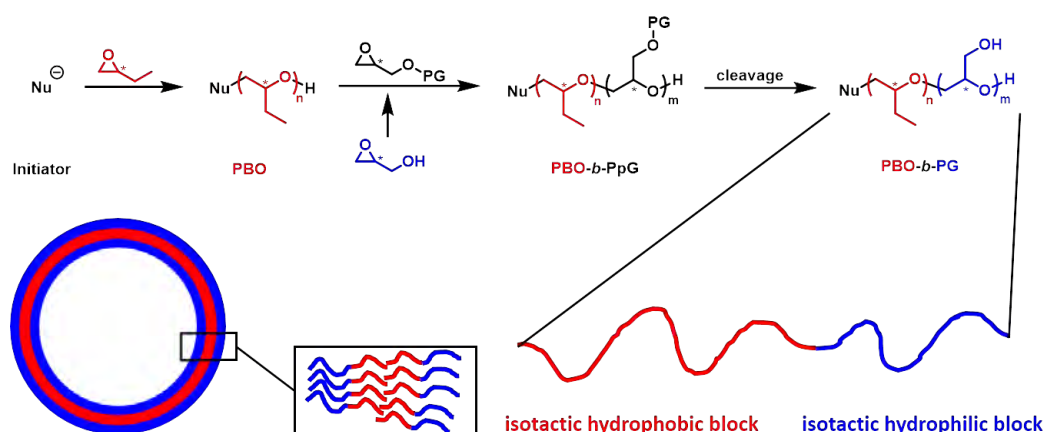
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Chiral Nanoparticles: The Effect of Tacticity in Amphiphilic AB Diblock Copolymers

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Chirality is a key factor in biological processes as many specific functions strongly depend on chiral recognition.^[1] Examples are enzymatic reactions or the selective impact of enantiopure pharmaceuticals. The self-assembly of amphiphilic block copolymers into nanoparticles in aqueous media has been studied in depth.^[2] However, the effect of tacticity in the polymers has been neglected so far. It is well known that isotactic polymers differ in their bulk properties from atactic ones, regarding crystallinity, glass transition or melting temperatures.^[3] In consequence, interaction of nanoparticles from chiral polymers with enantiopure compounds holds an enormous potential to considerably widen the applications of aqueous self-assemblies.



The diblock copolymer poly(butylene oxide)-*block*-poly(glycidol) (PBO-*b*-PG) was synthesized in two sequential microwave-based anionic ring-opening polymerizations, starting from the monomers butylene oxide and a protected glycidol derivative. Cleavage of the protective group led to the final PBO-*b*-PG diblock copolymer. By using enantiopure monomers the tacticity of each block could be adjusted accordingly. Self-assembly in water or PBS buffer via film rehydration or solvent exchange led to the formation of chiral micelles, worms or vesicles, establishing this new class of chiral nanostructures. Analysing their chiral interaction with enantiopure compounds will be relevant in many biological or biomedical processes.

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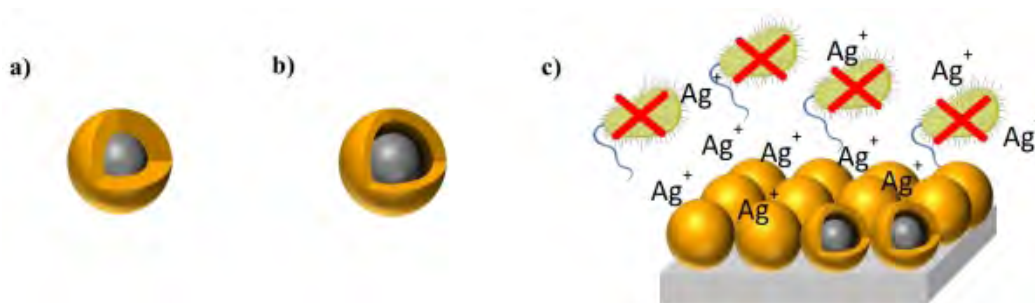
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Ag@SiO₂ nanorattles for antimicrobial coatingsP. Yep¹, S. Abram¹, K. M. Fromm^{1*}¹University of Fribourg, Department of Chemistry

Nanorattles or yolk-shell nanoparticles are similar to core-shell nanoparticles but with a void between the core and the shell (Scheme 1). This kind of structure has many applications in different fields such as catalysis, batteries or drug delivery depending on the chemical composition of the core/shell and the void/pore size. [1]

Our group has developed Ag@SiO₂ nanorattles as an antimicrobial agent. [2] The antimicrobial properties of silver are well-known for centuries and gain back interest due to its multimodal antibacterial activities. [3] In addition, the presence of the silica shell around the silver nanoparticles helps to avoid aggregation, controls the release of Ag⁺ and enlarges the possibilities of functionalization with different functional groups. Finally, these nanorattles will be deposited on a surface to act as an antimicrobial coating.



Scheme 1 : a) Ag@SiO₂ core-shell, b) Ag@SiO₂ nanorattles, C) Ag@SiO₂ nanorattles as an antimicrobial coating

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Dissolution Inhibition Effect of Diazonaphthoquinone Photoactive Compounds on Positive Tone Photosensitive Polyimides—A Computational StudyF. Zheng¹, Q. Lu¹¹Tongji University

Positive tone photosensitive polyimides (*p*-PSPIs) composed of poly(amic acid) (PAA) and a diazonaphthoquinone photoactive compound (DNQ PAC) have been greatly contributed to the progress of microelectronics. However the relationships among PAC molecular structures, hydrogen bonding interactions and dissolution inhibition for *p*-PSPIs have not been well understood. In this study, multiscale molecular modeling was utilized to evaluate such relationships. Density functional theory (DFT) calculations were used to predict the polarity of various DNQ PAC models and their corresponding indenylidene ketene (IK) compounds. Molecular dynamics (MD) simulations were performed to mimic the interactions between DNQ PAC and PAA polymer chains by calculating parameters such as the energy of mixing (ΔE_{mix}) and Flory-Huggins parameter (c_{AB}). The computational results showed that c_{AB} values of PACs containing mono functional phenols significantly differed before and after UV exposure. Their corresponding suppositional *p*-PSPI films were found to form a “skin layer” by covering high concentration of PAC on the surface of the film. Experimental dissolution behavior measurements of selected *p*-PSPI films strongly supported the computational observations. Succinctly, this work demonstrated the applicability of atomistic molecular simulations for the evaluation of dissolution inhibition effect of DNQ PACs and to understand the possible dissolution inhibition mechanisms of *p*-PSPIs.

Tip-enhanced Raman spectroscopy for structural analysis of two-dimensional covalent monolayers synthesized on water and on Au (111)L. Zheng¹, M. Servalli², A. D. Schlüter², R. Zenobi^{1*}¹Department of Chemistry and Applied Biosciences, ETH Zurich, ²Department of Materials, Institute of Polymer Chemistry, ETH Zurich

Two-dimensional (2D) polymers, which are one atom- or one monomer unit-thin, long-range periodically structured, covalent networks, have attracted intense attention due to their potential applications in electronics and sensing.¹ When it comes to monolayer analysis, one is faced with the extremely small quantities of material available and the intrinsic softness and flexibility 2D polymers can exhibit, a characteristic due to their high density of nano-pores. Therefore, many routine analytical techniques such as XRD and conventional NMR spectroscopy are not applicable. Fortunately, there are some new techniques that are sensitive enough to analyze monolayers, such as tip-enhanced Raman spectroscopy (TERS).

TERS is about to become an important method for structural analysis of 2D polymers: our group has reported several innovative works on the characterization of 2D polymers using TERS.²⁻⁴ TERS offers the opportunity to monitor the polymerization progress at an air/water interface, which is important for studying the kinetics and determining when the polymerization reaction is complete. TERS is not limited to studying 2D polymers after transfer from the air/water interface, but also allows to compare one and the same reaction performed on a metal surface.

Here we report on the air/water interfacial behavior of a macrocyclic anthraphane monomer and the structural analysis of the covalent sheet obtained when irradiating the spread monolayer at $\lambda = 385$ nm to trigger anthracene dimerization reaction. For this, different analytical techniques were employed, including *in-situ* Brewster angle microscopy (BAM), SEM (after transfer onto holey copper grids), AFM (after transfer onto SiO₂-coated Si wafers) and finally TERS (after transfer onto Au substrates). TERS mapping (with Ag-tips) was also used to monitor and quantify the conversion of the polymerization after different irradiation times. Finally, a monolayer of monomer was transferred onto a Au (111) surface *prior* to polymerization, followed by irradiation at 385 nm. The conversion number of the polymerization on this metal surface was compared to that of the polymerization at the air/water interface.

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The evolution of polymer chemistry in the preservation of monuments

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Conservation science was born around the 1970s when, with the increasing of the pollution in the atmosphere, evident signs of deterioration were observed on the surface of the monuments in relation to the action of acid rains. Currently, around 60 forms of material degradation are defined due to the interaction of water and air (polluted and not) on monumental surfaces [1]. Considering in Europe the presence about 3,500,000 monuments, the preventive conservation of monumental surface is an important goal both of cultural and economic nature.

Since the 1970s, a close interaction was established between conservation scientists and producers of coatings. A coating should allow at the masonry to breathe, without altering the appearance and showing a high compatibility and reversibility. Many studies identified two categories of coatings as protectives and consolidants: silica-based polymers and acrylic-based polymers [2].

The family of siloxane resins can be distinguished in resins polymerizing in situ and polymerized resins to be applied directly by brush or spray. Among the most famous products, ethyl silicate is certainly applied as a consolidant on various materials.

Acrylic-based polymers are generally MMA/EMA copolymers. Surely the most applied product is Paraloid (Rhom & Haas) for its reversibility and transparency characteristics.

The technical-scientific evolution helped a deeper knowledge of the nature of ancient materials and their decay, increasing the knowledge of their chemical interaction and compatibility with coatings, identifying strengths and weaknesses of their nature and function.

Lately, the diffusion of new nanostructured polymers has led towards a new interest in these new materials, whose properties seem to match well with the conservative needs. However, it is still necessary a full understanding of their characteristics and their behavior in the time.

Some experiments have shown a full applicability of cleaning systems on painted surfaces based on hydrogels, while the application of polymeric composite and hybrid systems are still under study (Fig. 1), especially to increase the self-cleaning, anti-microbial and hydrophobic behavior [3].

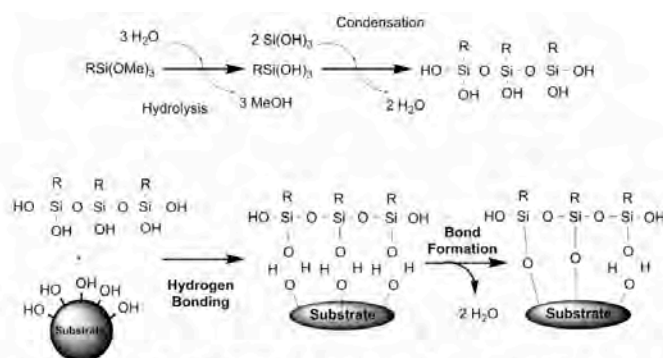


Fig. 1 - Reaction mechanism of the hydrolytic deposition of an organosilane on a silica substrate. [4]

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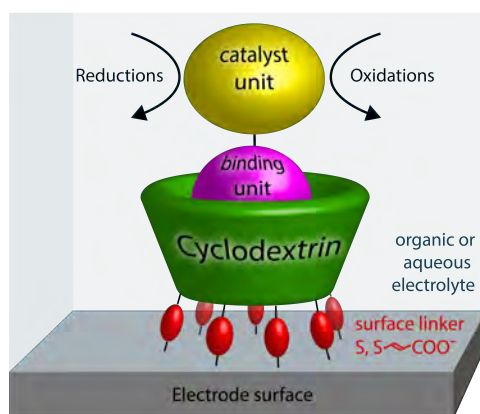
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Host-guest interactions on electrode surfaces for immobilization of molecular catalystsL. Severy¹, J. Szczerbinski², M. Iannuzzi¹, G. Tocci¹, R. Zenobi², D. Tilley^{1*}¹Department of Chemistry, University of Zurich, ²Department of Chemistry and Applied Biosciences

Connecting molecules to (photo-)electrode surfaces is one of the main challenges for molecular approaches in catalytic transformations driven by renewable resources such as sunlight. Classical grafting strategies include anchoring groups to bind the molecules onto the substrates, functionalization onto carbon-based materials as well as polymer scaffolds to fix catalysts close to the electrode surface [1]. However, many of these grafting methods suffer from drawbacks such as unstable binding to the surface, complicated synthesis and purification of ligands and decrease of activity due to necessary modifications of the catalysts [2].

We propose a new approach that relies on host-guest complex formation, a highly specific form of non-binding interactions, using modified cyclodextrin molecules as surface-bound host domains. We demonstrate the simple preparation of molecularly functionalized electrodes, facile catalyst adaptation to carry a guest domain and that electrocatalysis with these systems can be performed efficiently in water or organic solvent. Using spectroscopic and surface sensitive characterization methods as well as computational simulations, we show that the catalyst molecules are attached to the surface via their guest-substituent as a host-guest complex with the cyclodextrin. Electrochemical measurements demonstrate that electron transfer to the guest metal center leads to catalysis in both organic and aqueous electrolyte systems. This makes host-guest interactions a very attractive method for attaching molecular catalysts onto both metal and metal-oxide electrode supports.



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Carbon Nanomaterial Formation at the Liquid-Liquid Interface

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The liquid-liquid interface is a high-energy interface that can be stabilized using interfacially active molecules. The surfactants self-assemble at the oil-water interface, exposing their polar head group to water and apolar tail group to the oil phase, allowing the use of the liquid-liquid interface as template for two-dimensional assembly. Here we report the in-situ formation of 2D carbon nanomaterial at the liquid-liquid interface, starting from reactive carbon-rich surfactants based on hexaynes, that undergo spontaneous two-dimensional interfacial polymerization. Our laboratory had previously used carbon-rich reactive surfactants to fabricate carbon nanosheets at the air-water interface.^[1] In the work presented here, we employ hexayne amphiphiles with a phosphonic acid head group that readily self-assemble at the oil-water interface and spontaneously react to form a cross-linked carbon-rich membrane. This membrane can be further crosslinked by UV irradiation, forming a thin 2D carbon nanomaterial at the interface. In contrast to molecular surfactants, the resulting nanomaterial present distinctive properties of a Pickering emulsion, such as buckling upon a change in the interfacial area. The chemical structure of the formed 2D nanomaterial is investigated in depth through various spectroscopic techniques. Furthermore, the transition from molecular surfactant stabilization to a colloidal stabilization of the interface can be followed by drop tensiometry as well as interfacial rheology and allows to gain fundamental insights into the interfacial stabilization process.

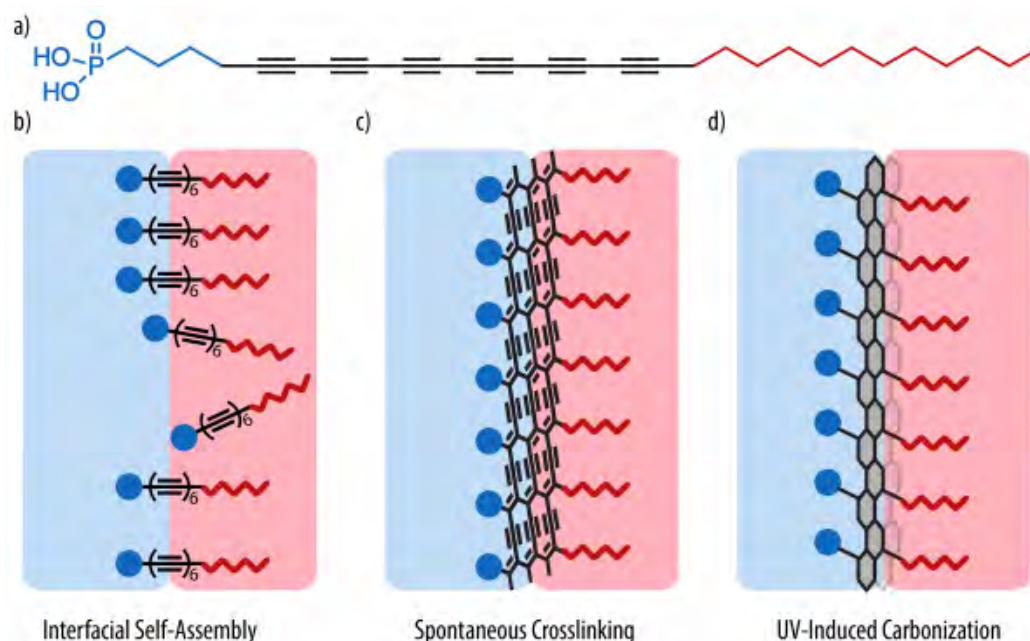


Figure 1. 2D carbon nanomaterial formation a) molecular structure of the surfactant b) self-assembly at the oil-water interface c) spontaneous crosslinking inducing the formation of a polydiacetylene-like membrane d) carbonization through UV-irradiation into a carbon membrane

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The interplay of channel geometry and molecular features determine diffusion in lipidic cubic phases

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The transport behavior of inverse bicontinuous cubic phases is experimentally investigated as the combined outcome of solute molecular structure and geometrical details of the confining symmetry. Molecular diffusion is discussed in relation to curvature, bottlenecks and interfacial properties of each cubic phase. Point-like molecules show faster diffusion across the double diamond ($Pn3m$) symmetry, while unfolded macromolecules display better performance inside the double primitive ($Im3m$) cubic phase. The former observation is in agreement with previous simulation work, whereas the latter indicates that dedicated theory needs to be developed for diffusing polymers. Further, the effect of electrostatic interactions is assessed by a study of diffusion of nanoparticles, and is rationalized via a combination of simulations and theoretical considerations as the result of a competition between water mobility and geometrical features of the channel.



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Performance at Interfaces - from hair to ceramic tilesD. Kuppert¹¹Clariant, Frankfurt, Germany - dirkroland.kuppert@clariant.com

Chemistry and materials are at the heart of the specialty chemicals industry. Customer focus and innovation are the keys to success in that industry. By working closely with customers, we translate unmet market needs into leading-edge technologies and performance product solutions to add value to our customers and to reduce our impact on the environment. To enable us to do that efficiently the leverage of international scientific expertise and knowledge with industry know-how is necessary.

Different kinds of interfaces and the interaction of molecules with those interfaces play a crucial role in the development of high-performance products. Even if understanding the interactions of chemical compounds at interfaces is challenging, it constitutes a highly valuable approach for the development of new and innovative solutions.

Practical examples will be presented how such an understanding of interaction at interfaces lead to the development of e.g. new polymers with optimized topologies and innovative bio-based surfactants with outstanding performance properties in different application areas. The applications will cover such diverse fields like e.g. hair conditioning agents, auxiliaries for cleaning polyester fabrics or hard surfaces like bathroom or kitchen tiles.

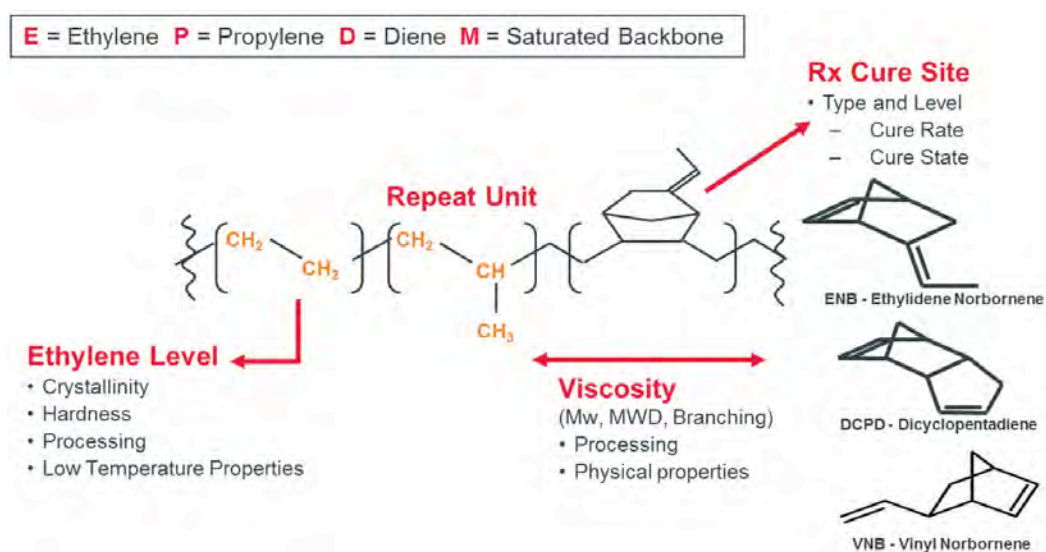
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EPDM Rubber Developments Enabled By Advanced Molecular Catalyst Technology

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Ethylene Propylene Diene (EPDM) hydrocarbon rubber is used in many applications due to its excellent weathering, chemical, and heat aging resistance properties. The major applications include automotive sealing and under the hood parts, construction membranes and gaskets, consumer parts, appliances gaskets, and wire and cable. It is mainly produced using Ziegler-Natta and single site catalysts in a solution or in suspension phase.



Dow revolutionized the EPDM industry in 1997 by producing EPDMs using INSITETM technology [1]. The INSITETM Technology utilized the single site catalyst and modern process technology to deliver clean and gel-free EPDMs that became the benchmark in the rubber industry. Recently, Dow further pioneered the evolution of catalyst technology by developing next generation of molecular catalysts [2], named as Advanced Molecular Catalyst (AMC). The AMC technology set the standards high in terms of catalyst efficiency, higher diene incorporation, and higher temperature stability of the solution process, while still maintaining the clean and gel-free EPDM characteristics. Using high throughput technologies [3], new catalysts were discovered which allowed the efficient manufacturing of newer EPDMs were developed with ultra-high molecular weight [4], higher diene content [5], higher long chain branching [6], and broader molecular weight distribution. In this paper, we will highlight the evolution of catalyst technology, EPDM sustainability footprint [7], new EPDM developments, and finally, some application examples.

TM Trademark of The Dow Chemical Company (“Dow”) or an affiliated company of Dow

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Polymer Brush Functionalized Magnetic Nanoparticle Clusters as Magnetic Blood Purification Agents

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Magnetic blood purification based on the use of functionalized and freely diffusing magnetic nanoparticles has demonstrated great potential for the capturing of toxins and pathogens from blood extracorporeally.¹ High surface area available for binding and fast extraction offer significant advantage compared to traditional blood purification techniques, which often suffer from membrane saturation and clotting.² However, the compromise between good dispersibility of the magnetic beads and high bead recovery poses a major challenge.

Here, we report on the synthesis and functionalization of 200 nm superparamagnetic magnetite cluster nanoparticles functionalized with cationic (co)polymer brushes grown using Surface Initiated Atom Transfer Radical Polymerization (ATRP). These nanoparticles form comparatively stable dispersions in physiological fluids (stable for more than 24hrs compared to minutes for the unfunctionalized nanoparticles) and can be fully recovered (>99.9%) in under three minutes. By appropriately selecting co-monomers, the colloidal stability and bead separation times can be further tailored. Introduction of mPEG monomers (1:3) reduces bead recovery times as well as the cytolytic activity of the polycationic brush-functionalized nanoparticles. Following in-depth studies on the colloidal stability as well as bead separability, we then demonstrate the quantitative extraction of free bilirubin from physiological media using cationic polymer brush-functionalized nanoparticles.

Taken together, we present tailorable functionalized magnetic nanoparticle systems that unify colloidal stability with high magnetic recovery rates. The demonstrated bilirubin capturing by the brush-functionalized magnetic nanoparticles has prospective applications in artificial liver support systems.

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3D Printing of Personalized Biodegradable Airway Stents via Vat Photopolymerization

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Stereolithography (SLA)-based 3D printing exhibits distinguished advantages including high resolution, good surface quality and relatively low cost. It is based on a vat photopolymerization process, taking place in a bath containing liquid (macro)monomers and photoinitiators. In combination with medical imaging techniques, this might provide enormous opportunities to design customized drug formulations and biomedical devices.^[1] Unfortunately, the lack of biomaterials suitable for SLA limits its medical applications, especially when the manufacture of biodegradable elastic devices is sought. As a typical elastic implant, airway stents are designed to simulate the airway anatomy, palliating symptoms in patients suffering from central airway obstruction. However, the clinical use of commercial one-size-fits-all stents is often constrained by the geometrical mismatching to the complex tracheobronchial anatomy of individual patients.^[2] Therefore, biodegradable airway stents with personalized geometry are highly desired. Here, we report the SLA printing of personalized airway stents from biodegradable polymeric materials (Figure 1). A series of polymers with various molecular weights were synthesized for 3D printing in a customized SLA printer. The printed specimens exhibited highly tunable mechanical properties, depending on the polymer chain length and on the feeding ratio of the different polymers. An airway stent prototype based on the computed tomography (CT) scan images of rabbit trachea was successfully printed from the optimized polymeric materials. It exhibited high flexibility and stretchability, which were comparable to those of commercial silicone products with the added advantage of being bioresorbable. This work opens new perspectives for developing biodegradable 3D printed personalized medical devices with adequate mechanical properties.

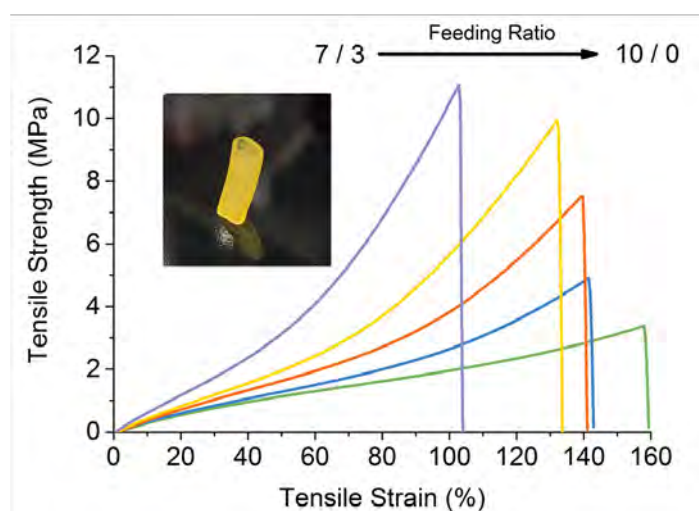


Figure 1. Representative tensile stress-strain curves of 3D printed specimens with highly tunable mechanical properties. Inset: 3D printed biodegradable stent based on CT scan images of rabbit trachea.

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Developing A Safe by Design Nanoagrochemical

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Safe by Design nano-agrochemicals promise higher efficiency than conventional pesticides, and therefore have a high potential in reducing the pollution penalty of these products. However, much has to be learned about the gain of efficiency compared to conventional products, the economical and environmental costs of a large-scale production, the willingness of farmers to adopt their practice, regulations, and the risk of directly applying such new types of yield enhancers on agricultural soil.



Here, we present the results of laboratory scale experiments to develop a bioinspired nanobiostimulant and compare its effects with conventional pesticide ingredients on the agricultural legume alfalfa (lucerne, *Medicago sativa*) and the model plant *Arabidopsis thaliana*. As a reference substance for conventional pesticides, the broadband fungicide tebuconazole was tested. Seed germination and infection tests, and plant growth tests as well as biochemical tests with pathogens as well as soil organism ecotoxicity tests were conducted. The release profile of the nanoparticle was quantified by an inductively coupled plasma - optical emission spectroscopy (ICP-OES) method developed in house [1], and its interactions with the plant were visualized in view of potential uptake and translocation using transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS).

The performance of the nanobiostimulant was found to be up to twice as high as for the conventional product. The use of nanobiostimulants promises to strongly reduce the organic pesticide burden of people and the environment.

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Amine functionalized nanofiber aerogel for efficient CO₂ captureS. Mousavi¹, S. Ko², C. Adlhart^{1*}

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Increasing CO₂ emissions mainly as the result of fossil fuel combustion are a key factor behind global warming (1). This gives the CO₂ capture and sequestration (CCS) technologies a priority in controlling and balancing the atmospheric CO₂. Currently, different technologies such as adsorption, distillation and membrane separation have been used for CO₂ capture (2, 3, 4).

Supported amine materials are an attractive group of solid adsorbents with some advantages compared to liquid amines (5, 6). Considering certain limitations such as clogging and recycling issues of particles and powders, different studies are recently indicating that amine modified aerogels with nonporous and three-dimensional structures are promising CO₂ adsorbents (7, 8). However, finding flexible and mechanically stable aerogels, which are providing the possibility of surface modification, is still challenging.

In the present work, we developed a 3D porous pullulan/PVA/PAA nanofiber aerogel impregnated with PAMAM dendrimer. It is a very efficient CO₂ adsorbent favoring the gas diffusion due to its porous architecture. The morphology, pore structure and chemical composition of the nanofiber aerogel were characterized. CO₂ capture was performed in a continuous CO₂ capture apparatus using dry CO₂/argon gas mixtures. Repeated adsorption/desorption cycles showed a significant regeneration capacity of the nanofiber aerogel rendering it a promising adsorbent for continuous CO₂ removal Systems.

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Mechanochemical Activation at Interfaces Driven by Swelling of Polymer BrushesJ. N. Bleich¹, M. M. Marcinek¹, H. A. Klok^{1*}¹Institut des Matériaux et Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Surface-initiated controlled radical polymerization (SI-CRP) is a powerful technique to grow densely graft chain-end tethered polymers from surfaces. These polymer assemblies are usually referred to as polymer brushes. SI-CRP allows to control grafting density and chain conformation. Immersed in a good solvent, polymer brushes swell and individual chains are forced into an extended conformation. This extended chain conformation is an important contributor to the non-fouling and low friction properties, which were reported for a number of hydrophilic polymer brushes. While for a long time surface grafted polymer brushes were considered very stable thin films, an increasing number of papers has been published within the last decade that report degrafting of hydrophilic brushes in aqueous media. Hence, the stretched chain conformation is not only an important factor for the brush properties, but also influences the chemical reactivity at the substrate-brush interface. A fundamental understanding of this phenomenon, however, is still lacking. In the field of polymer mechanochemistry external force fields are usually applied to alter the polymer reactivity using techniques such as ultrasound sonication, and turbulent or elongational flow fields. Mechanochemical activation by swelling of a polymer brush may offer an alternative tool with the advantage that no external stimulus is needed.

With the aim to better understand and predict the degrafting of polymer brushes, hydrophilic polymer brushes are prepared via surface-initiated atom transfer radical polymerization (ATRP) from silicon substrates modified with a dimethylchlorosilane-based ATRP initiator. Subsequently the polymer brush modified substrates are incubated in aqueous media and their degrafting behavior is monitored by ellipsometry. Apparent initial rate constants are determined from the degrafting profiles assuming pseudo first-order kinetics. We describe and discuss the analysis of these apparent rate constants and our attempts to correlate these with the swelling behavior of polymer brush films of different polymer molecular weights and grafting densities in different media. Moreover, strategies to investigate reactions other than the ester or siloxane hydrolysis mentioned above (e.g. primary sulfonate hydrolysis or reductive disulfide cleavage) are developed. The challenge herein lies in the development of hydrolysis stable platforms, which only undergo the reaction of interest. Next to hydrophobic-hydrophilic diblock polymer brush structures, hydrophobic polymer brushes incubated in dry organic media are investigated with the advantage that background hydrolysis of the present ester and siloxane functionalities is avoided.