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Leak-tight anastomosis hydrogel sealants using mutually interpenetrating networks

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Intestinal anastomotic leaking involving the release of chemically aggressive, microbially active fluids into the abdomen through defective suture or staple sites, remains one of the most dreaded postoperative complications of abdominal surgery. Depending on the site and the patient condition, incidence rates of up to 21% and mortality as high as 27% are reported. Currently available surgical sealants only poorly address the issue, with most commonly used fibrin-based glues failing due to insufficient adhesion and chemical instability.

In this work, a leak-tight, chemically highly resistive and mucoadhesive hydrogel sealant, which is grafted on the surface of the intestinal wall via the use of a mutually interpenetrating network, is presented. This latter traverses both hydrogel and tissue yielding tissue compatible, deep anchorage. In contrast to clinically used, fibrin-based sealants (such as Tachosil), the developed poly(acrylamide-methyl acrylate-acrylic acid) (P(AAm-MA-AA)) adhesive patch does not degrade and exhibits high performance tissue adhesion under the harshest digestive conditions present in the abdominal cavity. The biocompatible hydrogel patch effectively seals anastomotic leaks in human relevant, *ex vivo* intestinal models, greatly surpassing commercial sealants (time to patch-failure >24 hours compared to 5 minutes for commonly used Tachosil). Importantly, the developed adhesive patch paves the way for the application of both mechanically and chemically robust sealants suitable for the treatment and prevention of intestinal anastomosis leaks.

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Keywords: hydrogel, surgical sealant, leak-prevention, abdominal surgery, sepsis

Recycling of waste polypropylene into high-value liquid hydrocarbons

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The exacerbation of plastic pollution has escalated the necessity to devise efficient chemical valorization routes to meet global recycling goals. Constituting nearly 30% of all plastic waste, polypropylene (PP) poses a challenge to chemical processing due to its branched structure leading to greater chemical resistance.[1, 2] Among prospect chemical routes, hydrogenolysis of polypropylene on Ru-based systems exhibits promising activity but favors the formation of methane over high-value liquid products (**Fig. 1a**).[3] Unavailability of sufficient data on reactivity trends hinders the realization of the full potential of such catalysts. More specifically, the exclusive attention paid to the metal phase so far leaves behind the role of the carrier, which could be critical to unlocking effective catalyst design. We have developed Ru-based catalysts on various carriers unveiling the indispensable role of the latter in steering the cleavage away from demethylation towards backbone scission which helps achieve up to 90% liquid yield (**Fig. 1b**). We have quantified the relative occurrence of the two mechanisms by formulating the *scission preference* through use of product characterization data obtained using an accessible ^{1}H-NMR data. Titania (anatase), displayed up to 5 backbone scissions per demethylation event as opposed to 3 with its rutile polymorph and only 2 for ceria (**Fig. 1c**). This highlights that using ceria as carrier makes the formation of low-value methane thrice as likely as when using titania(anatase). Experimental correlations point to the distinct hydrocarbon affinity of the carriers as a reason for this phenomenon. This work paves the path towards practical Ru-based catalysts and provides universal tools for ranking of catalytic systems.

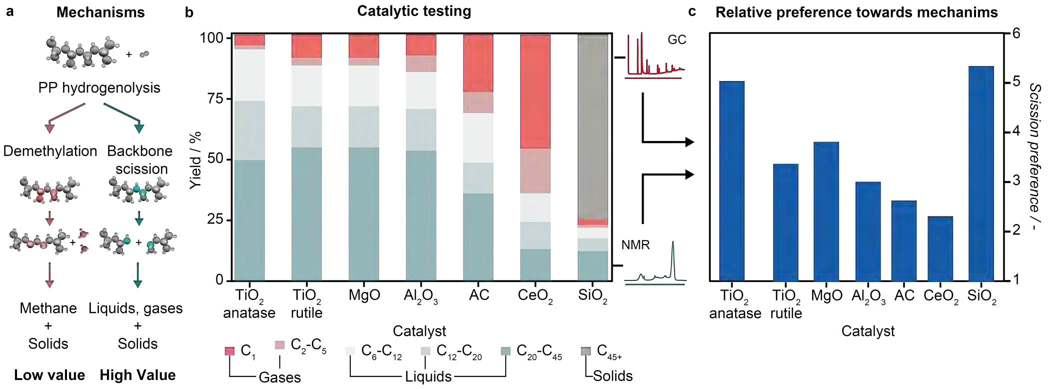

Fig. 1a Two main mechanisms hydrogenolysis of PP. Backbone scission is preferred as it forms the more-valuable liquid products **b** Yields for methane, gas, liquid products, and solid residue for tested catalysts. The extent of methane formation varies widely across systems with different carriers, highlighting their influence on hydrogenolysis by Ru. All catalysts were tested at T = 523 K, P = 20 bar H_2, t = 1 h and catalyst/plastic = 5 wt.%. **c** *Scission preference* of the tested catalytic systems quantifying the relative occurrence of the two cleavage routes followed for hydrogenolysis in each system.

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Colloidal synthesis of size and composition controlled alloy nanocrystals as selective alkyne semihydrogenation catalysts

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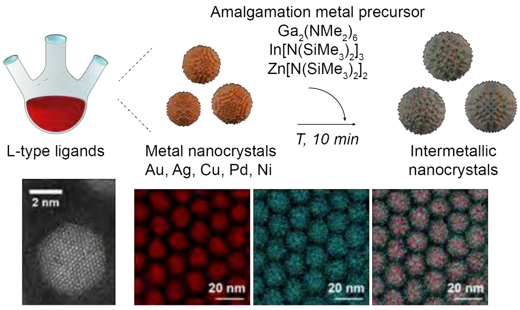
The selective hydrogenation of alkynes to alkenes is an important transformation with applications in both the fine chemical industry (synthesis of vitamins and natural products) and polymer industry (selective removal of acetylene), where alloys are often employed as heterogeneous catalysts. Yet, advances in catalyst formulations that feature high activity, selectivity, durability and broad functional group tolerance and where both noble metals (e.g. Pd, Pt) and metals of environmental concern (e.g. Cd, Pb) are replaced by earth abundant and non-toxic metals are highly desirable. Here, we present the synthesis of uniform Ni-alloy nanocrystals (NCs), which are 3-4 nm in size and feature narrow size dispersions [1]. The nanocrystals are synthesized via an amalgamation seeded growth procedure [2], a generalized colloidal synthesis method developed by us for size and composition controlled nanocrystals of a wide range of alloys. The resulting catalysts are pristine, capped with non-poisoning oleylamine ligands and work as dispersions which are at the interface of homogeneous and heterogeneous catalysis. We find that Ni_3Zn NCs are particularly active and selective for the liquid-phase semi-hydrogenation of alkynes in batch, operating under mild reaction conditions. Furthermore, Ni_3Zn NCs are tolerant to a wide range of functional-groups, allowing the selective conversion of a broad scope of alkynes as studied with high-throughput experimentation. In addition, we show that the investigated substrate scope covers the chemical space of commercial alkynes to a large extend, as evaluated with data science techniques [1].

Figure 1. Investigation of NiZn Nanocrystal Catalyzed Alkyne Semihydrogenation Driven by Data Science and High-Throughput Experimentation.

Figure 2. Size- and Composition-Controlled Alloy Nanocrystals via Amalgamation Seeded Growth.



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Increasing the coverage of photoactive ligands on the surface of nanocrystals through a hybrid metal-oxide-ligand shell

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Ligand exchanges on the surface of nanocrystals are ubiquitously employed for applications in photocatalysis, optoelectronics and biological imaging [1]. Particularly the positioning of polyaromatic hydrocarbons (PAH) ligands on semiconductor nanocrystals (NCs) has been crucial in harvesting or sensitizing molecular excited states obtained from multiexcitonic processes such as singlet fission and triplet fusion [3].

To maximally benefit from these processes the PAH density on the surface of NCs needs to be maximized. This is typically achieved through a one-for-one exchange driven by mass action between the PAH and native ligands [3]. However, the steric hindrance and limited solubility of the PAH-NC hybrids restricts the amount of PAH ligands that can be placed on NC surfaces.

Here, we demonstrate how to bypass this inherent limit by growing an alumina shell by colloidal atomic layer deposition (c-ALD) [4]. This is achieved by noting that the deposition of alumina locks the native ligands into the shell, and subsequently, new ligands can be added and are observed to selectively bind to new exposed binding sites on the alumina shell without displacing native ligands [5]. This process effectively increases the ligands density around the surface of NCs. We leverage this observation by growing alumina shells that embed a large number of PAH ligands allowing to significantly increase the PAH density. The formation of this metal-oxide-ligand shell promises to synergistically boost multiexcitonic processes while endowing enhanced stability to the NC core.

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Self-assembly of lead halide perovskite nanocubes into multicomponent nanocrystal superlattices

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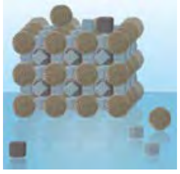
Colloidal lead halide perovskite nanocrystals (NCs) self-assembled into long-range ordered superlattices (SLs) with simple cubic packing of perovskite nanocubes have been shown to emit superfluorescent light, wherein coherent coupling among several NCs leads to collective emission, resulting in ultrafast bursts of photons. Co-assembly of perovskite NCs into multicomponent SLs with other building blocks might serve as a versatile platform for controlling their collective properties. We show that the use of cubic NCs instead of spherical ones changes the assembly outcome. $CsPbBr_3$ nanocubes combined with spherical Fe_3O_4 or $NaGdF_4$ NCs and truncated cuboid PbS NCs form binary SLs of six structure types, namely, NaCl-, AlB_2-, CuAu- as well as uncommon to all-sphere assemblies novel AB_2-, quasi-ternary ABO_3- and ABO_6-types. In these structures, the nanocubes retain orientational coherence. The co-assembly of $CsPbBr_3$ nanocubes with larger disk-shaped LaF_3 NCs (1.6 nm in thickness) results in the formation of six columnar structures with AB, AB_2, AB_4 and AB_6 stoichiometry. In the systems with comparable dimensions of nanocubes (8.6 nm) and nanodisks (6.5–12.5 nm), other, non-columnar structures are observed, such as ReO_3-type SL, featuring intimate intermixing and face-to-face alignment of disks and cubes. With large and thick $NaGdF_4$ nanodisks, an orthorhombic SL resembling CaC_2 structure with clusters of $CsPbBr_3$ NCs was obtained. We also explore an on-liquid assembly method using glyceryl triacetate as a subphase that allows obtaining free-floating SL films comprising perovskite nanocrystals.



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Order and disorder in inverse Opals

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In nature some animals make use for structural colours, instead of pigment colours, to interact or camouflage with the environment around them. Structural colour comes from the interaction of light with the structures in a material and for this reason does not fade like normal pigments do. Inspired by nature, these colours can be mimicked by arranging monodisperse colloids in crystals by making use of self-assembly. When the size of the colloids are on the order of visible light (400-700 nm) structural colours can be seen.

Colloidal crystals can be used as templates to create inverse opal structures. The amount of order and disorder in the crystalline structure allows structural colours to have different properties. In highly ordered photonic crystals the structural colour shows an angular dependence, when a low degree of disorder is introduced the structural colours begin to have a much lower angle dependence. However, once the disorder in the crystal becomes too large, the structural colour is lost and the surface appears to be white, as the light is scattered in all directions.

This project is looking at introducing disorder into self-assembled colloidal crystals by making use of non-spherical dimpled particles as templates. The particles with dimples introduce a different type of disorder into the system, with the idea that the order of the disorder can be controlled by the size of the dimple in the particle itself. Different self-assembly approaches are looked at, thin film evaporation deposition, gravitational sedimentation as well as confined self-assembly within a water-in-oil emulsion. The methods needed to create inverse opals as well as the viability of inverting these different self-assembled structures are also looked into. The final particle arrangements within the self-assembled structures and the visible light reflection spectra (in real and in reciprocal space) will be used to compare the methods.

The synthesis of the dimpled particles results in drastic changes of the surface properties of the particles, changing from hydrophobic polymeric particles to hydrophilic carbon based particles. These changes impact the self-assembly behaviour in the system, as the hydrophobicity of the particles play a role in the way particles self-assemble in evaporation deposition. This required modifications to the particle synthesis and a particle surface preparation with the assistance of surfactants, to enable the particles to be stable enough to form ordered crystalline arrangements.

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Creating chemistry for a sustainable future in a world of change

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As a leading chemical company, BASF combines economic success with environmental protection and social responsibility. To address pressing global challenges, we believe chemistry will be an enabler, and continued innovation necessary. In this presentation, I will describe how research topics are identified on that background and show examples how they are aligned in an industrial context between science, business and sustainability.

Transformer-Induced Metamorphosis of Polymeric Nanoparticle Shape at Room Temperature

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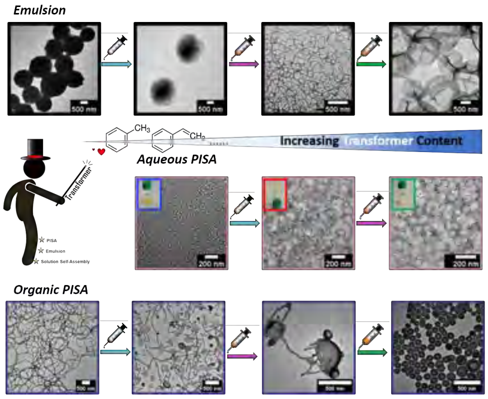
Controlled polymerizations have enabled the synthesis of a wide range of amphiphilic block copolymers which can form nanostructured materials with different shapes exhibiting distinct properties and performance.[1] Despite the importance of shape, current strategies that allow for the efficient morphological transformation are limited in polymer scope, often alter the chemical structure, operate at high temperatures, and can be fairly tedious and time-consuming. Herein we present a rapid and versatile morphological transformation strategy which operates at ambient temperature and without impairing the chemical structure of the resulting morphologies. By simply adding a small amount of a molecular transformer (i.e. small organic molecule) in an aqueous solution of polymeric nanoparticles, a rapid evolution to the next high-ordered morphology was observed within seconds, yielding a range of nanoparticles morphology from the same starting material. Significantly, this approach can be applied to nanoparticles produced by disparate block copolymers (i.e. with different cores and coronae) obtained by various synthesis techniques, including emulsion polymerization, polymerization-induced self-assembly and traditional solution self-assembly.[2,3]



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Mechanically morphing polymer systems

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Functional materials enable organisms to accomplish complex tasks in response to external or self-modulated stimuli with many examples of continuing function beyond the organism's lifetime. The resurrecting rose of Jericho *(Anastatica hierochuntica)* and the seed dispersion mechanism of conifer cones are two of the most well-known instances of post mortem tissue functioning in response to environmental changes. While variations in relative humidity and exposure to water are two of the most prevalent stimuli in nature, synthetic functional polymers frequently respond to temperature change, which can be controlled through irradiation with light, oscillating magnetic fields or electrically *via* Joule heating. These materials are important components of soft actuators used in complex soft robotic systems. For example, a thermally controlled bilayer bending actuator depends on anisotropic thermal expansion of the two joined layers, resulting in a bending or flattening motion. Semicrystalline polymers such as polyethylene exhibit considerable thermal expansion associated with the melt transition, which however cannot be readily used in bilayer bending actuators since melting would compromise the device's mechanical integrity. To avoid this, we developed segmented polyurethanes with a crystalline soft segment and a physically cross-linking hard segment that prevents flow beyond the melt transition of the soft segment.[1,2] These polymers enabled the development of electro-thermally controlled bilayer bending actuators with a high deflection and low switching temperature (55°C). To demonstrate the merit of these devices, we designed a cross-shaped robot with four individually controlled legs capable of performing complex tasks such as locomotion.

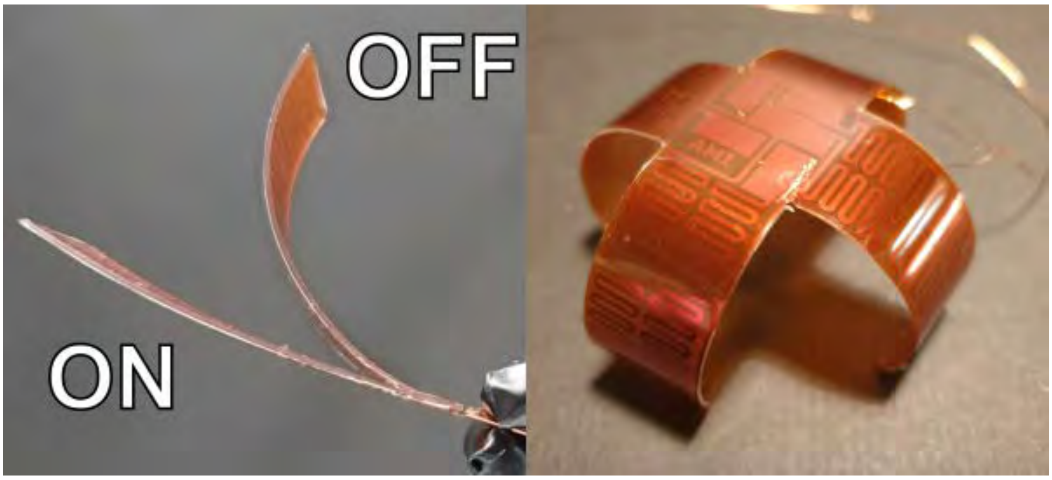

Photo overlay of a high thermal expansion polyurethane and polyimide bilayer bending actuator with integrated Joule heater in the flat (ON) and bent (OFF) state (left). Image of a cross-shaped soft robot in the resting state (right).

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Interfacial rheology of particles with matching convex and concave asperities

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Surface roughness of colloids highly influences their self-assembly behaviour, therefore dictating the mechanical properties in such systems. Here, we report the macroscopic interfacial rheology of microparticle networks in different ratios of topologically matching convex and concave surface asperities measured with a double wall ring (DWR) interfacial rheometer. In this set-up, a Langmuir through with an adapted DWR attached to a stress-controlled rheometer was used to probe the mechanical properties. The surface coverage and local events are investigated using a light microscope during the experiments.

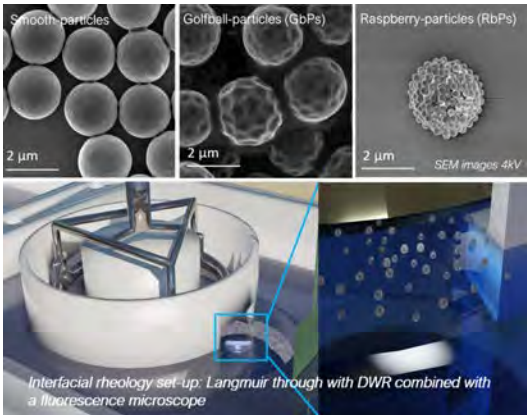
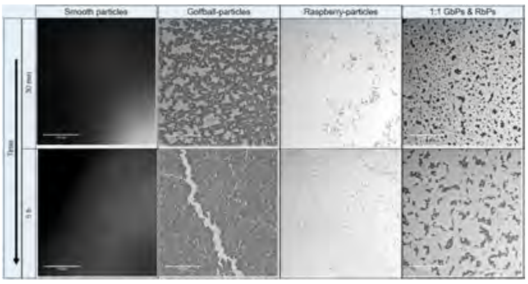


Fig. 1:SEM images 4kV, 30'000 x magnification, scale bar corresponds to 2 µm, below interfacial rheology set-up: Langmuir through with DWR combined with a fluorescence microscope

The organo-silica particles with concave features, also known as golf ball-like particles (GBPs) were synthesized following an approach from Liang et al. [1] The particles with a convex featured were synthesized following a novel one-pot synthesis, based on a co-condensation reaction of two organo-silane precursors. These particles consist of smaller corona particles condensed to a larger core particle and can be referred to as raspberry-like particles (RBPs) [2]. These particles were spread at a water-air interface in different ratios and compressed to different surface coverage to measure their interfacial mechanical properties. Preliminary results show a highly elastic and strong interface in the high frequency regime due to interlocking between particles compared to smooth particles with similiar surface chemistry.

Fig. 2: *Spreading of Particles at an Air-Water interface, 40 x magnification*



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Lipidic based-gel with tunable release properties as a platform for local delivery of biotherapeutics

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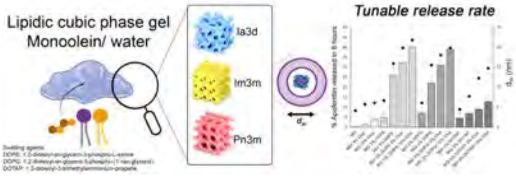
Lipid mesophases are able to incorporate and release a plethora of molecules, spanning from hydrophobic drugs to small hydrophilic proteins and therefore they have been widely used as drug delivery system. However, their water channels of 3–5 nm do not allow the release of large hydrophilic molecules such as monoclonal antibodies and therapeutic proteins. To overcome this major geometrical constrain, we designed a gel by mixing monoacylglycerol lipids, generally recognized as safe for human and/or animal use by FDA, and phospholipids, to obtain a material with swollen water channels suitable to host and further release macromolecules [1]. Apoferritin, a 12 nm nanocage protein with intrinsic tumour-targeting properties able to incorporate several molecules, was selected here as a hydrophilic model protein to be embedded in the biocompatible gel. When immersed completely in the release media, mesophases with a swollen water channel of 22 nm, composed of monoolein and doped with 5 mole % of DOPS and 10 mole % of Chol allowed us to achieve a protein release of 60 %, which is 120 times higher with respect to that obtained by employing non-swollen-LMPs composed only by monoolein. Swollen lipidic mesophase allow to administer locally biomacromolecules in those diseases easily reachable by a local application such as rectal or vaginal cancer, thus reducing the drawbacks associated with a parenteral administration. The system prompts a release profile suitable for a mucosal application paving the way for a local application of other biomacromolecules including monoclonal antibodies.



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Clusters of Hard-Soft Assembly for Bio-Applications

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The self-organization of nano-objects into complex architectures is a major strategy to produce novel systems with emerging properties and functionalities in fields such as chemistry, electronics and technology[1–3]. The DNA hybridization between synthetic assemblies (polymersomes, nanoparticles, micelles) represents an essential step in the development of interconnecting artificial organelles because they topologically favor cascade reactions between different catalytic compounds encapsulated/entrapped inside, and are capable to mimic cell signaling or interactions[4,5].

In this study, we investigate the self-organization of clusters between “hard” Janus nanoparticles (JNPs) and “soft” polymersomes which represents a new approach for developing a multifunctional hybrid system for specific bio-applications. These polymer-based JNPs with anisotropic composition and orthogonally addressable functionality providean asymmetric platform suited for directional interaction[6,7] with the soft polymersomes. The hybridization of complementary ssDNA strands attached to each components links them into clusters. The polymersomes are deformed upon adhesion to the “hard” JNPs surface but maintain their integrity, thanks to the inherent mechanical robustness of the block copolymer membrane. Importantly, the continued integrity of the vesicular architecture of polymersomes after assembly into JNP-polymersome clusters offers the possibility of encapsulating various kinds of functional cargo. Finally, the biocompatibility of the clusters and their interactions with cell surfaces, mediated by scavenger receptors, was investigated.

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Photo-crosslink bottlebrush polymers for voltage-driven artificial muscles

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Applications of dielectric elastomer actuators (DEA) in implantable soft robots need soft elastomers that allow the manufacturing of reliable, durable, adaptable, and low voltage responsive actuators. However, currently, DEAs do not meet the safety standard due to the high driving voltage. Reducing the thickness and elastic modulus allows for lowering the driving voltage. However, soft materials are prone to electromechanical instability (EMI), which causes electric breakdown. The elastomers made by cross-linking bottlebrush polymers are one of the most promising approaches to achieving DEAs that suppress EMI. Dielectric materials prepared by chemically cross-linking bottlebrush polymers using free-radical UV-induced polymerization have been reported, but molds were required to prevent oxygen inhibition leading to rather thick films. Therefore, the respective actuators are operable at voltages above 4000 V. Herein, designed monomers that can be efficiently polymerized by ring-opening metathesis polymerization and subsequently cross-linked via a UV-induced thiol-ene click reaction were used. The developed strategy allowed us to produce defect-free thin films cross-linked within 5 min. The dielectric films gave up to 12% lateral actuation at 1000 V and survived more than 10'000 cycles at frequencies up to 10 Hz.

SELECTIVE REMOVAL OF TOXIC ORGANIC DYES USING TRÖGER BASE-CONTAINING SULFONE COPOLYMERS MADE FROM A METAL-FREE THIOL-YNE CLICK REACTION FOLLOWED BY OXIDATION

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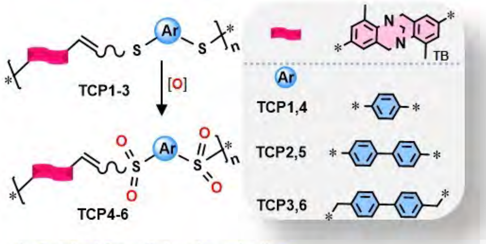
Three copolymers TCP1–3 bearing Tröger's base (TB) units intercalated with various thioether groups were synthesized using a catalyst-free thiol-yne click reaction. TCP1–3 display excellent solubility in common organic solvents allowing for their structural, and photophysical characterization. The thioether groups in TCP1–3 were selectively oxidized into their respective sulfone derivatives under mild oxidation reaction conditions affording the postmodified copolymers TCP4–6. Investigation of organic dye uptake from water by TCP1–6 proved their efficiency as selective adsorbents removing up to 100% of the cationic dye methylene blue (MEB) when compared to anionic dyes, such as Congo red (CR), methyl orange (MO) and methyl blue (MB). The sulfone-containing copolymers TCP4–6 display superior and faster MEB removal efficiencies with respect to their corresponding synthons TCP1–3.



- ✓ Catalyst-free click polymerization
- ✓ Selective oxidation and Selective cationic dye adsorption
- ✓ Oxidized polymers TCP4-6 enhances the dye adsorption

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Stimuli-responsive, functional, porous membranes for ultrafast and switchable gas separation applications

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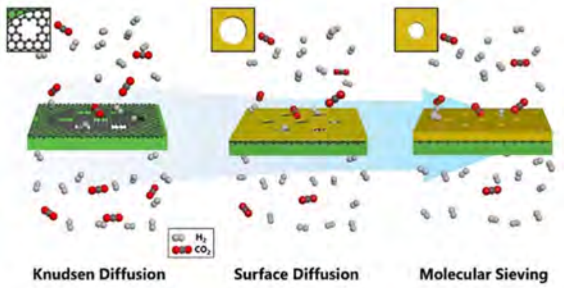
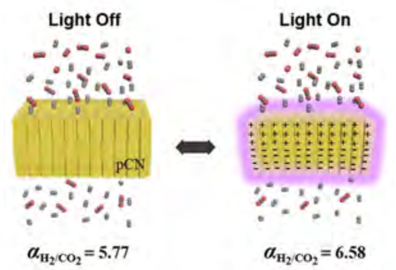
Membranes are an integral part of the industry due to their modular design, cheap production cost, and easy installation. However, membranes are subjected to a permeability (how fast the gases pass through the membrane) and selectivity (how pure is the component gas after the membrane) trade-off. To break this trade-off the membrane thickness needs to be reduced below the critical value (mean free path of the gas). In that regard, 2D materials such as graphene are considered as a holy grail of membranes due to million times higher permeability rates compared to conventional membranes, however, they suffer from low gas selectivity. Whereas decreasing the pore size below 3 nm is expected to increase the gas selectivity due to molecular sieving, it is rather challenging to generate a large number of uniform small pores on the graphene surface. We introduced the pore-narrowing approach via gold deposition onto a porous graphene surface to tune the pore size and thickness of the membrane to achieve a large number of small pores. Through the systematic approach, the ideal combination is determined as a pore size below 3 nm, obtained at the thickness of 100 nm, to attain high selectivity and high permeance. The resulting membrane shows a H_2/CO_2 separation factor of 31.3 at H_2 permeance of 2.23×10^5 GPU (1 GPU = 3.35×10^{-10} mol s^{-1} m^{-2} Pa^{-1}), which is the highest value reported to date in the 10^5 GPU permeance range. This result is explained by comparing the predicted binding energies of gas molecules with the Au surface, −5.3 versus −21 kJ mol^{-1} for H_2 and CO_2, respectively, increased surface–gas interactions and molecular-sieving effect with decreasing pore size.





Another approach is to prepare membranes prepared out of stimuli-responsive materials that can adapt to changing surrounding conditions. In that direction, switchable gas separation membranes are quite intriguing systems for controlling the transport properties of gases. However, existing stimuli-responsive gas separation membranes either suffer from very slow response times or require high-energy input for a switching event to occur. Accordingly, herein, we showed, for the first time, light-switchable polymeric carbon nitride (pCN) gas separation membranes with an ultrafast response time. The membranes with various thicknesses and porosity were prepared through in-situ formation and deposition of pCN onto a porous support using chemical vapor deposition by varying the amount of melamine precursor. Our systematic analysis revealed that the gas transport behavior upon light irradiation is fully governed by the polarizability of the permeating gas and its interaction with the charged pCN surface, and can be easily tuned either by controlling the power of the light and/or duration of the irradiation. We also demonstrated that gases with higher polarizabilities such as CO_2 can be separated from gases with lower polarizability like H_2 and He effectively with more than 22% increase in the gas/CO_2 selectivity upon light irradiation. The membranes also exhibited ultrafast response times (<1 s) and can be turned "on" and "off" using a single light source at 550 nm.

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Lipidic mesophases for local delivery of rapamycin to treat inflammation

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Hydration of certain lipids leads into formation of lipidic mesophases (LMPs): lamellar, hexagonal, cubic, and micellar cubic phases.[1,2] The lipophilic sections make LMPs an ideal material for local controlled delivery of hydrophobic drugs. In the present study we encapsulated rapamycin (RAPA) in monoolein (MO), which is generally recognized as safe by the FDA[3] and formulated an LMP subcutaneous injection. Recent research by our group showed RAPA's potential for prolonged treatment of localised inflammation,[4] but many of the formulations involve organic solvents and pose a risk of toxicity. We tested the drug release and characterised the system with small angle X-ray scattering (SAXS) and rheometer. Our results showed the release lasting over 30 days, which would significantly reduce the administration frequency. Furthermore, we demonstrated the system's ability to respond to the lipase overexpression - an inflammatory cue[5] and release the drug on demand (Figure 1). SAXS analysis showed that the injection precursor was comprised of a lamellar mesophase structure, while contact with water caused the change to a bicountinuous cubic mesophase.[1,2] Rheological assessment corroborated the easy injectability of the precursor and the high elasticity of the *in situ* formed cubic gel. This phase transition occurred within 1 h of LMP submersion into excess water, but this was not final, as the presence of lipases shifted the mesophase further to an inverted hexagonal structure.

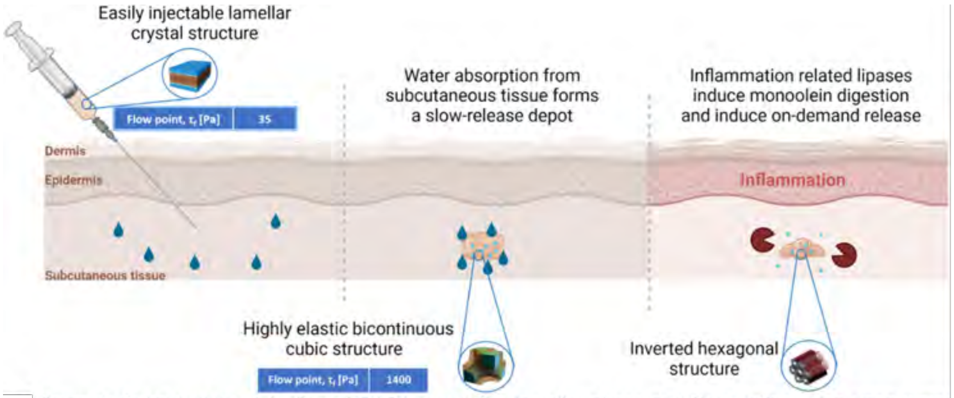

Figure 1: Subcutaneous injection of RAPA-containing lamellar phase and its transformation upon water absorption and on-demand release after an inflammatory cue.

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An Approach to Photoredox Catalysis Using Light-Harvesting Supramolecular Polymers

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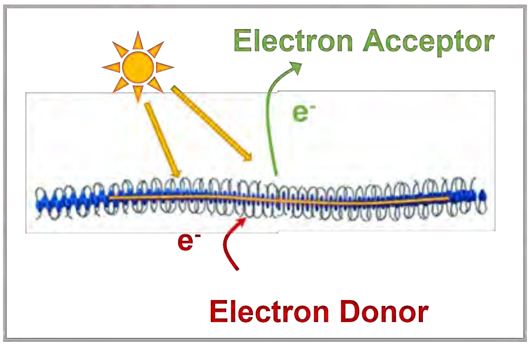
One promising approach to store the ubiquitous energy of the sun is to drive photoproduction of high energy fuels out of simple and abundant materials, such as water or CO_2. In natural photosynthetic systems, this process is done via large supramolecular assemblies of chlorophyll molecules that funnel excitons toward a reaction center which itself initiates a redox cascade toward the fuel production.[1] Mimicking this extremely efficient machinery is a quest that chemists have been addressing over the last decades. One possible approach is molecular and associates, in a single solar fuel device, an absorber (dye, quantum dots …) with a fuel production catalyst. If a huge amount of work has been dedicated to have more efficient catalysts for this technology,[2] little has been done to adapt the design of the absorber to a real antenna of chromophores. Light harvesting Supramolecular Polymers (SPs) could enable to reach that goal and their integration into photoredox schemes is indeed a rather unexplored field of research.[3] Building on a strong expertise in SPs chemistry and photophysics,[4] our group proposes to address this issue. We will present first results regarding photoinduced electronic transfers between SPs and suitable redox active centers.



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Hydrogel-liposome composite for local treatment of fibrosis

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Few therapeutic approaches are designed to effectively treat fibrotic diseases. Pirfenidone (PFD) is a small molecule drug approved for the treatment of idiopathic pulmonary fibrosis and exhibits anti-fibrotic and anti-inflammatory properties in a variety of different organs. Numerous preclinical and clinical studies using PFD are being conducted to treat local fibrotic disorders such as fibrotic scarring following spinal cord injury [1], intestinal fibrosis [2], diabetic foot [3], and localized scleroderma [4]. However, PFD is only available as oral dosage form and – due to the high dosage needed to achieve the therapeutic effect – it may be associated with significant adverse reactions including gastrointestinal and neurological complications. To improve PFD's safety profile, we developed a drug delivery system consisting of layer-by-layer PFD-loaded liposomes (LbL-LIP) embedded into a zinc alginate hydrogel (Fig. 1a). We envision the hydrogel for the treatment of endometriosis or intestinal fibrosis. A drug loading of 85% is obtained using a passive loading method to encapsulate PFD. The 150 nm sized liposomes are coated with up to 5 layers (Fig.1b) of biopolymers – alginate and chitosan, alternatively- to generate LbL-LIPs while any purification step needed during layering. Subsequently, LbL-LIPs are embedded into zinc alginate hydrogel to provide an instantly crosslinked ready-to-use drug delivery platform. To mimic the vaginal and intestinal environment, the release profile of PFD is monitored at both pH 4.5 and 7.4 (Fig.1c). The results of this study demonstrate one can reach highly concentrated PFD-liposomes while by adjusting the LbL thickness a controlled and tunable release of PFD can be obtained. In conclusion, our composite LbL-LIP-hydrogel offers a highly tunable PFD release ranging from h to several days by simply adjusting the LbL thickness for local and sustained release of the drug directly to the fibrotic site. Further study will prove the ability of the system to bioadhere to the fibrotic site.

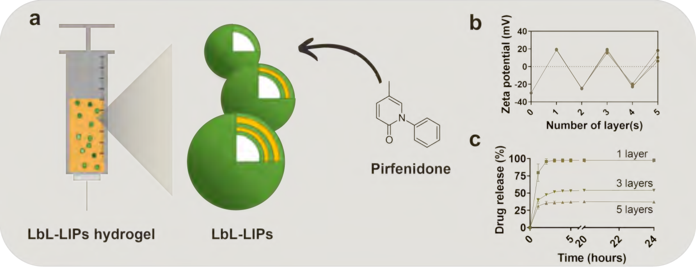

Figure 1. a) Schematic representation of the composite hydrogel; b) Changes in ζ-potential at each biopolymer deposition; c) *in vitro* release studies of LbL-LIPs hydrogels at pH 7.4

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Polyion sensing based on the polarization of various optical reporters

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Polyions such as protamine (arginine-rich polycation), heparin (polyanionic saccharide), DNA, RNA and phosphorylated protein play important roles in nature. In spite of the development and improvement of polyion-selective electrochemical sensors, optical sensing of polyions in nanoscale by nanoparticle sensor has remained a challenge due to the limited choice of a polyion ionophore (a selective ligand) and its poor selectivity, which make the conventional nanoparticle-based polyion sensors not applicable to polyion quantification in biological samples.[1] Recently, we have demonstrated new strategy of optical polyion sensing by nanoparticles based on solvatochromism.[2] In this nanoparticle sensor, dinonylnaphthalenesulfonate ($DNNS^-$: protamine ionophore) strongly polarized the solvatochromic dye $X3^+$, resulting in solvatochromism of $X3^+$ absorption. In the presence of protamine, $DNNS^-$ no longer polarizes $X3^+$ but rather binds to protamine, which resulted in protamine extraction into the nanoparticle and optical signal change. This novel sensing mechanism has demonstrated excellent selectivity and finally enabled protamine sensing in human blood plasma.

In this work, we have collected data to further understand the details of the new sensing mechanism, and based on the understanding, we have designed a new nanoparticle sensor for the direct “polyanion” detection in order to demonstrate the universality of the polarization-based sensing mechanism. Interestingly, we have found that tridodecylmethylammonium ($TDMA^+$: heparin ionophore) polarizes quantum dots (Qdots), see Figure 1 left, and quenches Qdot fluorescence. As this quenching effect is canceled in the presence of heparin due to $TDMA^+$-heparin complexation, the increased heparin level enhances fluorescent signal (Figure 1 center). As a result, this Qdot-nanoparticle composite sensor showed sensitive solvatochromic response to heparin. Thus, solvatochromism based on ligand polarization can be harnessed not only for polycation sensing but also for polyanion quantification.

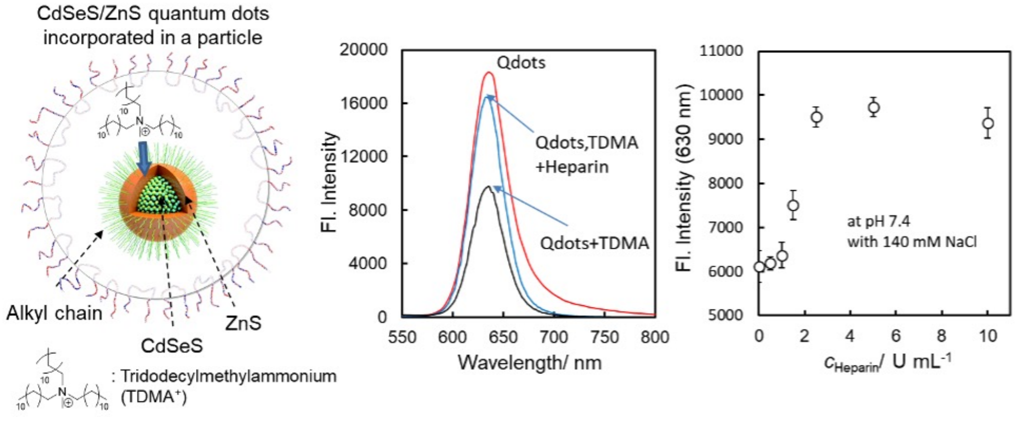

Figure 1. The composition of the Qdot-nanoparticle sensor (left), the fluorescence signal change with/without $TDMA^+$ and heparin (center) and the calibration curve for heparin with 140 mM NaCl background (right).

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All solvent-free synthesis of dielectric elastomer transducers

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Dielectric elastomer transducers (DET) manufacturing requires conductive as well as dielectric inks, which are *co*-processed by various techniques.[1,2] Each processing technique requires suitable viscosity of the two inks, often achieved by diluting them with a solvent. Especially, DET made from composites require a significant amount of solvent. Here we introduce the synthesis of a conductive, soft, stretchable, and flexible electrode material using anionic polymerization of cyclosiloxane monomers in the presence of graphene nanoplatelets.[3] The synthesis approach allows tuning the viscosity of the uncured material to suit various processing techniques such as screen-printing, spray-coating, slot-die coating or direct ink writing. Additionally, it can be transferred to the dielectric composite, making this a versatile approach. Since the composites are synthesized solvent-free, stack DET can be easily manufactured and problems like delamination and swelling on the underneath layers are prevented. The entire process from synthesis to device manufacturing requires no solvent. The developed DET are not only efficiently manufactured but are also environmentally friendly.

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Thermo-responsive smart gating wood membranes

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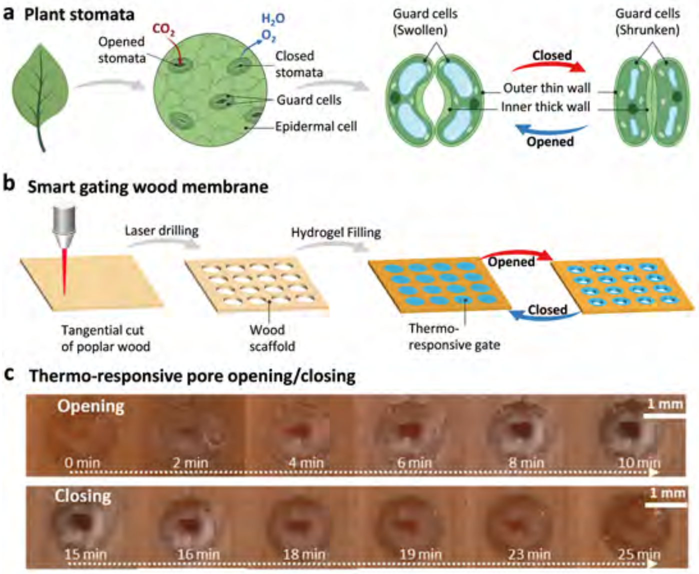
Smart membranes that can open and/or close their pores in a controlled manner by external stimuli possess potential in various applications such as water flow manipulation, indoor climate regulation, and sensing. The design of smart gating membranes with high flux, immediate response, and mechanical resistance is still an open challenge, limiting their versatility and practical applicability. Inspired by the controlled opening and closure of plant stomata, we have developed here a smart gating wood membrane, taking advantage of the unique wood scaffold with its hierarchical porous structure to carry thermo-responsive hydrogel gates.

We have established a facile strategy for preparing a wood-based smart gating membrane. With laser drilling, wood fibers and vessels were cut open and the three-dimensional interconnected wood scaffold with well-aligned order, uniform pore size, and superior mechanical strength was employed as the fixed boundary of the smart gating membrane. A thermo-responsive domain was introduced into the wood scaffold by in situ polymerization of PNIPAM hydrogels. Hydrogels prepared above its LCST showed a heterogeneous microstructure with micro-gel clusters, resulting in remarkable deswelling ratio and rapid swelling. Moreover, the methacrylation pretreatment and a suitable microstructure of the wood scaffold played an important role in promoting the good interfacial strength between the responsive domain and fixed boundary ensuring proper pore actuation. Since the thermo-responsive behavior of PNIPAM depends on its hydration state, in its current configuration our smart gating wood membrane requires high relative humidity or moist conditions.

The wood-based smart gating membranes exhibited reversible and stable pore opening/closing under heating/cooling stimuli. The achieved rapid response and feasibility of scale-up open the venue for various practical applications. In this work, we demonstrated their potential for indoor light regulation and as water flow manipulator [1].



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Assembly of functionalized supramolecular polymers

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A growing interest for tunable nanoscale polymers has been observed in the past decade. The main interests are their ability to act as light-harvesting devices and their nonclassical optoelectronic behavior which find application in a variety of fields. It was previously shown that phosphodiester di-alkynyl-substituted pyrene trimers[1,2] allowed the formation of 2D supramolecular polymers. In this work, we have functionalized the initial building blocks with a cyclooctyne, allowing us to perform post-assembly modifications with azides through strain promoted azide-alkyne click chemistry. The aggregation process of the pyrene building blocks will be presented through spectroscopic measurements.

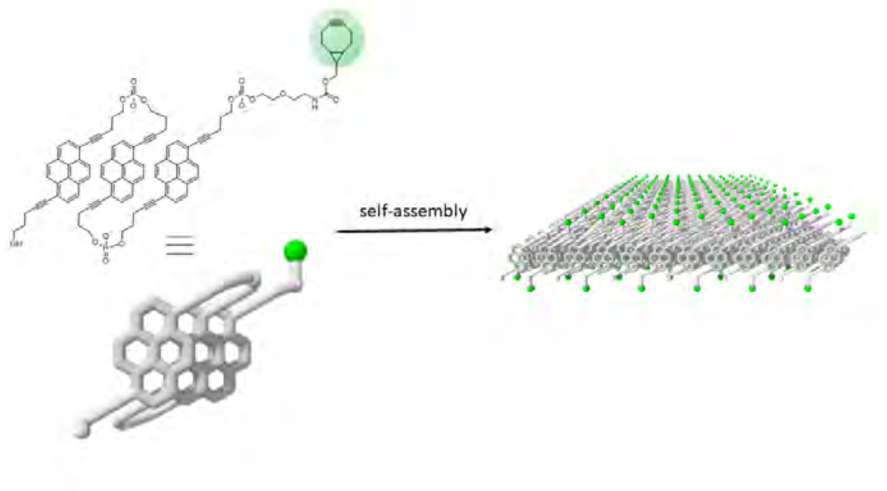

Figure 1: Self-assembly process of cyclooctyne modified pyrene trimer.

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Characterisation of New Self-Plasticised Redox Polymer based on 3,4-Ethylenedioxythiophene

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Over the last few years, conductive polymers have gained significant interest due to their use in supercapacitors, rechargeable batteries, bioelectronics, sensors and also photovoltaic cells. This breakthrough was mainly supported by an increasing number of new available materials. The most well-known conductive redox polymers include poly(3-octylthiophene) (POT), polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT), which has been extensively studied due to its versatility.

Owing to a simple synthetic pathway, a wide variety of EDOT derivatives can be synthesised and have been reported in biosensors, conducting hydrogels and many others [1]. Our group has already investigated the use of modified EDOT monomers intended as transducers in ion-selective electrodes. The simple constructing bloc was modified with a long alkyne chain to enhance the lipophilicity of the resulting polymer upon electropolymerisation [2].

We present here the novel synthesis of a 3,4-ethylenedioxythiophene derivative with a triazole analogue of phthalate based on “click” chemistry. It is believed that grafting a plasticiser-like sidechain to the initial EDOT molecule will generate smoother polymer films upon electropolymerisation. We evaluate the hydrophobicity of different EDOT monomers and also compare their structural and electrochemical properties

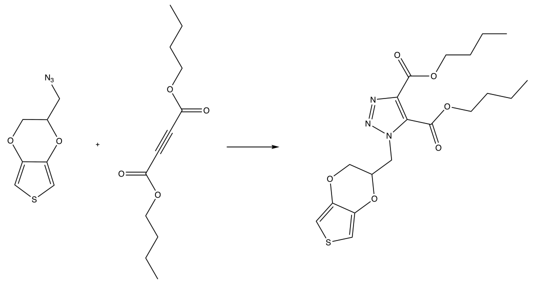

Figure 1: Huisgen 1,3-dipolar cycloaddition to synthesise a 3,4-ethylenedioxythiophene derivative with a triazole analogue of phthalate.

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Design and characterization of pH-responsive lipid biointerfaces from bacteria-derived bio-surfactants

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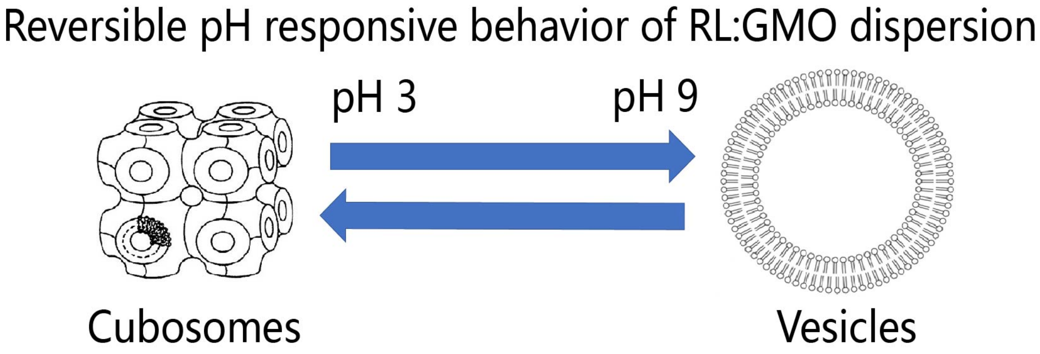
Functional colloids have gained much attention as advanced nutrient delivery systems in the recent years. Their response to external factors such as pH, temperature and ionic strength can be used to trigger nutrient uptake and release [1]. Of particular interest are lipid-based self-assembled structures. In this context, rhamnolipids (RL) are sustainable natural biosurfactants that are extracted from bacteria [2]. However, their self-assembly in water, that is crucial for their further design into functional food materials, has not been analyzed in detail yet.

This presentation demonstrates the pH-dependent phase behavior of RL in buffer. It further discusses the self-assembly of RL with the food-grade surfactant, glyceryl monooleate (GMO) for the design of advanced nutrient delivery systems. Small angle X-ray scattering (SAXS), cryogenic transmission electron microscopy (Cryo-TEM) and dynamic light scattering (DLS) are used in an integrative approach to study colloidal structures and their composition- and pH dependent transformations in solution. RL:GMO dispersions were found to form cubosomes at pH ≤ 5 that reversibly transformed into vesicles at pH ≥ 7 (Graphical abstract). The further application of the pH-triggered colloidal transformations for controlled release application was demonstrated through the encapsulation and release of a hydrophobic dye. The results can guide the design of novel nutrient nanocarriers that respond to pH variations in the gastro-intestinal tract. These structures can protect encapsulated degradation-sensitive nutrients or drugs from degradation in the harsh environment of the stomach, and release them at higher pH in the small intestine for absorption into the circulatory system of the body.



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A modular silica core-shell synthesis particle platform: rough, sticky and yet reversible colloidal gels.

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Colloidal gels derive part of their technological interest from the ability to undergo a solid-liquid transition, and the microstructural causes underlying this have been intensively researched using various rheological and structural characterization methods in the past. The propensity to gel or break up depends both on the suspending media properties and primary particle features such as shape, size, surface roughness and surface functionalization. In the present work, we developed a synthesis approach where we can independently tune these different particle features, with particle topography as an additional non trivial complexity. Silica particles are synthesized using a standard Stöber method, with an option to add surface roughness by electrostatic hetero-aggregation of smaller particles. To arrive at a reproducible and scalable functionalization, these cores are first functionalized with secondary-amines through silane chemistry. The click-like (amine -yne) chemistry enables the grafting of different kinds of functional molecules to the surface of the particles, such as hydrocarbons, polymers or fluorophores. These functional molecules have been modified beforehand with an alkynoate group, using the Fischer esterification process of an -OH group with propiolic acid. The amount of grafting agent to the particle surface can be tuned by the reaction conditions. This synthesis approach was used to fabricate both smooth and rough particles, where the thermoreversibility of the steric repulsion can be used to build aggregate networks to investigate their influence on the gels mechanical properties. Rheological measurements show how surface roughness delays the structural yielding due to interlocking of the particles, in addition to influencing the thixotropy as roughness counteracts flow induced cluster densification.

Union Carbide Polymerization Catalysts: from Uncovering Active Site Structures to Designing Molecularly-Defined Analogs

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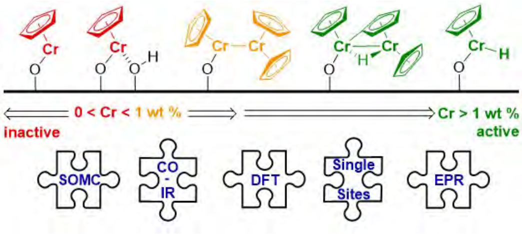
The ethylene polymerization Union Carbide (UC) catalyst is one of the first catalysts prepared through surface organometallic chemistry (SOMC) using chromocene dispersed on silica. In contrast to the Phillips catalyst, based on CrO_3/SiO_2, it produces polymers with narrow molecular weight distribution and allows for chain length control by co-feeding H_2.[1-2] Despite the importance and the uniqueness of this catalyst, the identification of surface and active site structures, as well as the initiation mechanism for ethylene polymerization are still under debate due to the variety of surface sites and the low number of catalytically active sites (few %).

Based on a combination of IR, EPR spectroscopies, labeling experiments, and modeling at the DFT level, we identified monomeric surface-supported Cr(III) hydrides as the active sites of the UC catalyst.[3] These sites initiate polymerization, yielding Cr(III) alkyl species that insert ethylene monomers through a Cossee–Arlman-type mechanism, as evidenced by labeling and spectroscopic studies. Furthermore, we designed a well-defined analog by grafting $CpCr(CH(SiMe_3)_2)_2$ on partially dehydroxylated silica that shows similar spectroscopic signatures and supports the presence of similar active sites in the UC catalyst, opening the way to generate new classes of catalysts.



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Interpenetrated Elastomeric Networks containing Supramolecular Motifs

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Interpenetrating polymer networks (IPNs) are composed by a combination of interlaced polymer networks that do not share any chemical connectivity. These materials have received growing attention by the scientific community, thanks to the wide range of applications and the remarkable mechanical properties, including increased toughness and stiffness, and enhanced extensibility and tensile strength.[1][2]

In the last years, different IPNs systems containing covalent motifs have been investigated, while very few studies have covered the supramolecular counterparts. Nevertheless, supramolecular motifs show some advantages compared to traditional systems. The resulting interactions represent a powerful tool and their introduction bestows polymer materials with stimuli-responsive behaviour, dynamicity, tunability, and self-adjusting abilities.[3] Moreover, the reversible nature of supramolecular interactions should result, in principle, in easier processing, recyclability, and unique properties such shape memory effect, and self-healing behaviour.[4] All the discussed reasons justify the interest and curiosity to create IPNs featuring supramolecular interactions, both as fundamental research question and for the construction of materials for tailored applications.

Here we report the synthesis of different types of polymer networks comprising either covalent or supramolecular cross-links (Fig. 1). The covalent system consists of a poly methyl acrylate network (PMA) synthesized by UV-initiated free-radical polymerization (UV curing) of MA in presence of a covalent crosslinker (Fig. 1, red).[5] The supramolecular polymer networks are based on poly ethyl acrylate (PEA), instead. These materials were prepared by reversible addition−fragmentation chain-transfer (RAFT) polymerization, and feature different cross-link densities. The supramolecular cross-links are introduced through either the 2-ureido-4[1H]pyrimidinone (UPy) motif (Fig. 1, orange), which is capable of forming quadruple H-bonds, or the 2,6-bis(1′-methylbenzimidazolyl)pyridine (MeBip) tridentate ligand (Fig. 1, blue), which forms complexes with Zn^{2+} ions in a 2:1 stoichiometry.[6][7][8] The thermal and mechanical properties of the individual networks and their combinations (Fig. 1, left) have been investigated.

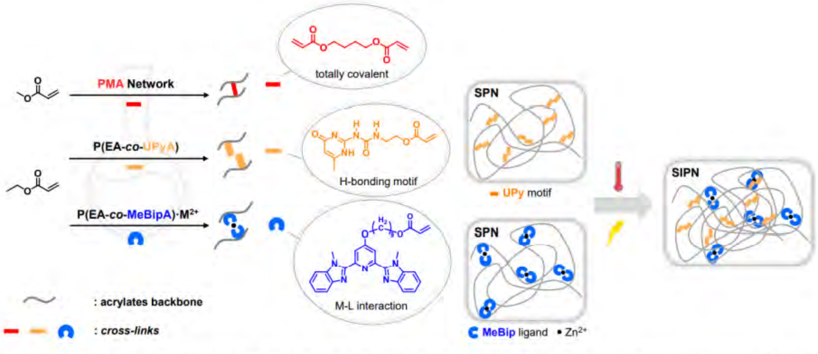

Figure 1. Synthesis of a covalent PMA network (obtained by UV free-radical polymerization), and supramolecular UPyA and MeBipA networks (obtained by RAFT polymerization) synthesized with ethyl acrylate as monomer (right). Synthesis of supramolecular interpenetrating polymer networks (IPNs), obtained by the combination of the two supramolecular polymer networks displaying different supramolecular interactions (M-L complexes and H-bond motif) (left).

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Insights into Engineered Protein Condensates and their Applications

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Recent discoveries in biology have shed light on a class of intrinsically disordered proteins which can spontaneously undergo liquid-liquid phase separation to form membraneless organelles. In vivo the composition and environment of these compartments is carefully controlled in space and time, therefore allowing them to fulfill several important functions. Inspired by these observations, here we attempt to mimic such protein-based condensates in vitro using engineered fusion proteins with the aim of developing high-performance open microreactors, with promising applications in biocatalysis and bioseparation.

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Supramolecular Self-Assembly of Pyrene-DNA Conjugates into Vesicles

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Recently the supramolecular assembly of DNA conjugates has caught attention in supramolecular chemistry. DNA offers some unique characteristics allowing the design of complex nanostructures. The DNA framework allows the defined spatial arrangement of modifications. In previous work DNA was modified with phenanthrene sticky ends forming vesicular supramolecular assemblies with light-harvesting properties.[1] Interestingly, *E*-tetraphenylethylenes modifications at the 3’-ends of DNA led to aggregation-induced emission (AIE) active assemblies.[2] In this work, we modified a DNA strand at the 3’- and 5’-end with 2,7-pyrene (Figure 1A). AFM measurements of the 2,7-pyrene-DNA conjugates revealed their self-assembly into vesicles (Figure 1B). In addition to AFM studies, fluorescence and UV-vis spectroscopy measurements will be presented and discussed.

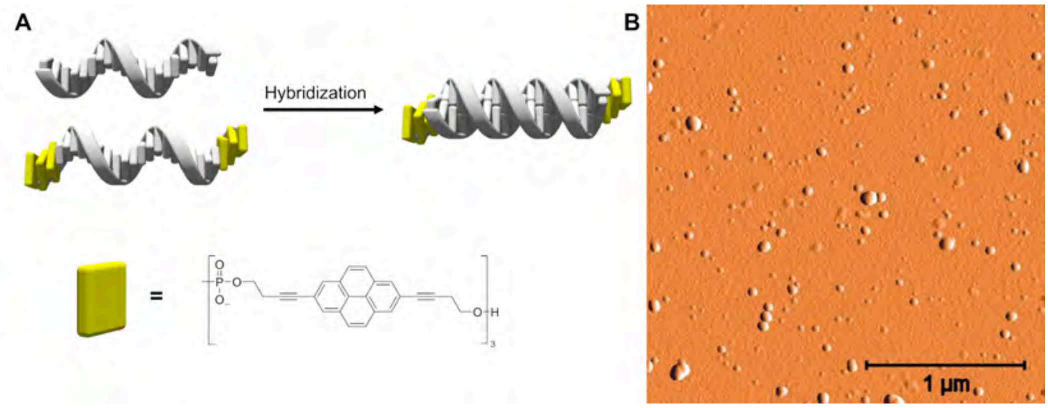

Figure 1 (A) Illustration of single strands forming a pyrene-modified DNA duplex. (B) AFM image of vesicular objects formed by supramolecular self-assembly of amphiphilic DNA.

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Reversing RAFT Polymerization: Near-Quantitative Depolymerization into Monomer via a Catalyst-Free Approach

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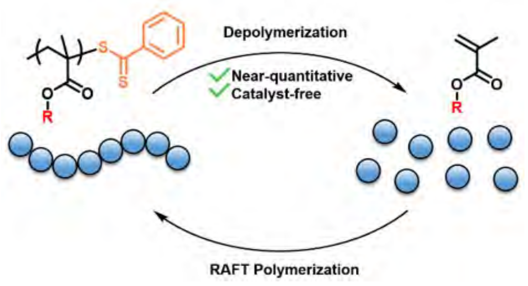
The ability to reverse controlled radical polymerization and regenerate monomer would be highly beneficial for both fundamental research and applications, yet this has remained very challenging to achieve. Herein, we report a near-quantitative (up to 92%) and catalyst-free depolymerization of various linear, bulky, cross-linked, and functional polymethacrylates made by reversible addition–fragmentation chain-transfer (RAFT) polymerization.[1] Key to our approach is to exploit the high end-group fidelity of RAFT polymers to generate chain-end radicals at 120 °C. These radicals trigger a rapid unzipping of both conventional (e.g., poly(methyl methacrylate)) and bulky (e.g., poly(oligo(ethylene glycol) methyl ether methacrylate)) polymers. Importantly, the depolymerization product can be utilized to either reconstruct the linear polymer or create an entirely new insoluble gel that can also be subjected to depolymerization. This work expands the potential of polymers made by controlled radical polymerization, pushes the boundaries of depolymerization, offers intriguing mechanistic aspects, and enables new applications.



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In situ Characterization of Viruses Colloidal Systems for Design of Antiviral Solutions

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Viruses are a class of pathogens that have a high burden on humanity. Waterborne viruses, such as rotavirus and norovirus, have their biggest toll on young infants in developing countries. Whereas airborne lipid enveloped viruses, such as influenza virus and SARS-CoV2, have worldwide consequences. Viruses are self-assembled colloidal particles. To design antiviral solutions, the interactions and effect on their self-assembled structure needs to be understood. Bacteriophages Qbeta and Phi6 were used as surrogates respectively for non-enveloped and enveloped viruses pathogens. Their interactions and structures were characterized by small angle X-ray scattering, dynamic light scattering and cryogenic transmission electron microscopy.

This allowed to show, (i) the pH-dependent adsorption of viruses on cationic modified nanocellulose as well as the viruses' structural integrity upon interacting, subsequently allowing to design a regenerable virus adsorption filter for water purification. [1] (ii) The mechanism of ethanol inactivation of enveloped viruses is via the separation of the outer lipid envelop from the inner nucleocapsid, hence separating the host-cell recognition function from the genetic material. [2] In situ characterization of the virus colloidal systems allows a bottom-up design of effective antiviral solutions.

Keywords: Virus, SAXS, disinfection, filtration, ethanol, nanocellulose

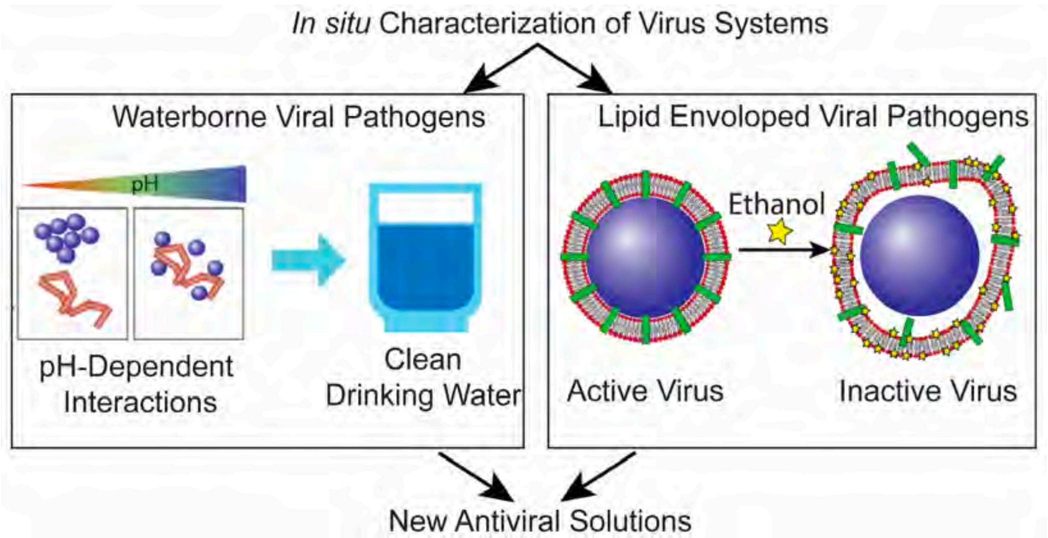

Figure 1: Graphical abstract

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Novel Polyphosphazenes for Dielectric Elastomer Applications

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Dielectric elastomer actuators (DEAs) use external electricity to transform electrostatic energy into mechanical energy by the deformation of a soft dielectric elastomer. The simplest device is constructed by placing two electrodes on a thin, soft elastomer film. When a voltage is applied, one of the electrodes is charged positively while the other is negatively charged. Columbic attraction of these opposite charges as well as repulsation of alike charges on the same electrode lead to the compression and lateral expansion of the dielectric film [1]. This muscle-like behavior of the DEAs has gained significant attraction among both academic and industrial communities. Therefore, research efforts to enhance these devices increases day by day. The main challenge of DEAs is to combine high permittivity and a rather low Young's modulus for a large range of temperatures. Lowering the thickness of the dielectric film by using appropriate processing methods leads to smaller operating voltages. The elastic modulus can be tuned by the nature of the polymer backbone and its functionalization. It can furthermore be adjusted by controlling the network density. Dielectric permittivity can be tailored by introducing different polar groups [2]

Polyphosphazenes have interesting mechanical and dielectric properties, however, their potential has never been explored in DEAs. Polyphosphazenes are macromolecules composed of an alternating single and double bond between phosphorous and nitrogen atoms, bonded with two organic side groups.Compared to silicones, its polymer backbone shows higher polarizability leading to an increased permittivity. Substitution by alkoxy units of polyphosphazene backbone provides many advantages such as low glass transition temperature, high elasticity, and moisture stability [3]. Herein, polydichlorophosphazene is synthesized and modified with different alkoxy units. With the help of a thiolene reaction, the polymers are crosslinked into a film. The polymers are characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The dielectric permittivity and mechanical properties of the crosslinked films are analyzed.

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