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3D Printing of Living Structural Biocomposites

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Nature has a remarkable ability to create composite materials by combining organic and inorganic elements under benign conditions. Surprisingly, these natural composites often exhibit superior mechanical properties compared to their individual building components. The key to this evolutionary feat lies in nature's unique capability to precisely control the structure and composition of materials. This control is achieved through the compartmentalization of reagents, which can be selectively released in specific locations. Drawing inspiration from nature, we have developed an energy-efficient process that harnesses compartmentalization to fabricate porous composites based on CaCO_3 , exclusively using materials derived from nature. Remarkably, these composites exhibit compressive strength similar to trabecular bones.

The unique combination of nature-derived materials, 3D printability, and good mechanical properties is achieved through the formulation of these materials: We utilize microgel-based granular inks, which possess inherent 3D printing capabilities. In addition, we leverage the potential of engineered living materials to induce the formation of biominerals by bacteria. By combining these elements, we successfully create biomineral composites with a porous trabecular structure.

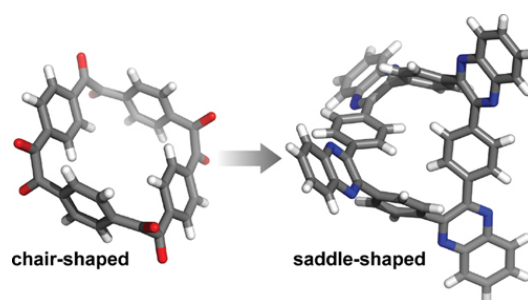
The potential applications of this system are vast. It can be utilized in art restoration, providing an innovative solution for repairing damaged artworks. Furthermore, these composites can serve as artificial corals, aiding in the regeneration of marine reefs. With further development, this technology may even enable the repair of fractured or deteriorated mineral-based materials found in natural structures such as certain bone components.

By leveraging the ingenuity of nature and utilizing cutting-edge techniques, we envision a future where our system revolutionizes various fields, offering sustainable and effective solutions for diverse challenges.



Porous Organic Polymers for Advanced Gas Separation ApplicationsT. Ashirov¹, K. S. Song¹, A. Coskun^{1*}¹Department of Chemistry, University of Fribourg, Chemin du Musee 9, 1700 Fribourg Switzerland

Ever-increasing greenhouse gas emissions led to the development of novel functional adsorbents that can show remarkable gas uptake and separation efficiencies. In that regard, porous organic polymers (POPs) have gained tremendous attention due to their thermal and chemical stabilities, structural tunability, and control over textural properties. Two main parameters define the POPs' performance a large abundance of micropores and the presence of functional groups that selectively bind the target gas molecules. In this direction, we have synthesized various POPs containing macrocycles for advanced gas separation applications. The resulting POPs showed incredible CO₂ uptake capacities and IAST CO₂/N₂ selectivities of 137. We also tested various solvent uptake properties of larger macrocyclic POPs. Moreover, we also explored controlling the textural properties of POPs under solvothermal conditions. We used readily available and cheap table salt as a hard template to control the ratio of porosity of the final POP. Not only the BET surface area but also the ratio of the micropores and mesopores can be easily tuned by using different amounts of templates. The resulting salt-templated polymers were tested at high pressures, where the difference in the diffusion of gases to the pores was observed. While linear molecules such as CO₂ can go quickly in the pores, larger and bulky ones such as CH₄ and N₂ have very slow diffusion rates. Thus, high selectivity values were achieved.

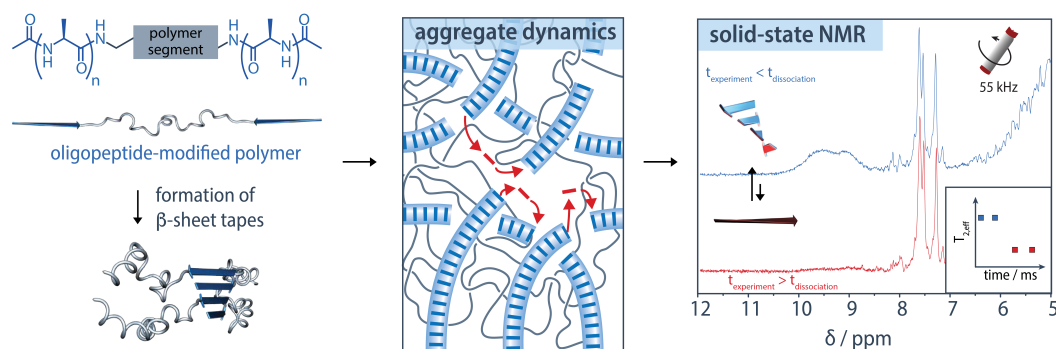


Insights into the Dynamics of Supramolecular Materials from Semicrystalline Polyesters by Solid State NMR

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Supramolecular network materials exhibit broadly tailorable thermomechanical properties which is important to adjust the processability, final product performance, or recyclability of contemporary polymer materials. These materials are typically based on the thermoreversible formation of well-defined aggregate structures from self-complementary hydrogen-bonding ligands that serve as physical crosslinks to the polymer matrix. The intrinsic dynamic behavior of these aggregates often gives further rise to self-healing properties, shape-memory effects, or stimuli-responsiveness. This dynamic behavior arises from the scission-reaggregation events of the ligands at the molecular level, the timescale of which directly influences their macroscopic behavior. Site-specific studies on the dynamic kinetics of supramolecular crosslinks on a molecular scale are limited to dilute solution states, leaving a fundamental gap in our understanding of structure-dynamics-property relationships in technologically relevant solid-state polymer materials.



In this study, we investigate the aggregation-scission dynamics of helical one-dimensional network junctions from β -sheet forming oligopeptide end groups of a telechelic polyester using solid-state NMR for the first time. By employing Carr-Purcell-Meiboom-Gill relaxation dispersion experiments, we monitor the dissociation events over time and at different temperatures, including room temperature when the polymer matrix is semi-crystalline. Our results reveal that the amide dissociation in the crystallized polymer matrix occurs between 0.15–0.45 ms, and is accelerated to a range of 0.08–0.15 ms in the polymer melt at 60 °C. This methodology eliminates the need for additional chemical modifications, can site-specifically detect dissociation events down to 1 wt% of supramolecular linker content, and is applicable at variable temperatures, even in semi-crystalline polymer states. Our approach therefore holds promise for advancing the understanding of supramolecular network dynamics and for accelerating the development of next-generation functional materials.

Emmanuel Croisier *et al.*, *Nature Communications*, **2014**, 5, 4728.

Developing Non-Native Cascade Reactions by Means of Catalytic Nanocompartments

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Compartmentalization is fundamental in nature, where the spatial segregation of biochemical reactions within and between cells ensures optimal conditions for the regulation of cascade reactions. Reproducing, but also manipulating hierarchically organized compartments with regard to their responsiveness and communication provide crucial information towards understanding biological systems. One of the most promising strategies to mimic nature compartmentalization is to combine synthetic nano-compartments with biomolecules in order to develop artificial organelles and to organize them into more complex architectures with cell mimetic functionality.

We present an exquisite spatiotemporal control of catalysis in polymeric nanosized compartments by means of a periodate sensitive linker that controls the opening of outer membrane protein OmpF (OmpF) channels inserted in the compartment membrane.[1] Being able to precisely time confined reactions pave the way to controlling multifunctional cluster activity when specific substrates or products need to be made available at a specific site and with precise timing.[2] In addition, the combinatorial and functional diversity of catalytic nanocompartments (CNCs) assembled into various supramolecular architectures can be exploited either in bulk or on a surface, whereby surface immobilization offers the advantage of highly controlled spatial organization. As an example, we developed CNC-functionalized DNA microarrays where individual reaction compartments are kept in close proximity by a distinct geometrical arrangement to promote effective communication.[3] Our work represents a significant advance in the field of communicative networks by combining compartmentalization with controlled inter-compartment distance to promote efficient cascade reactions.

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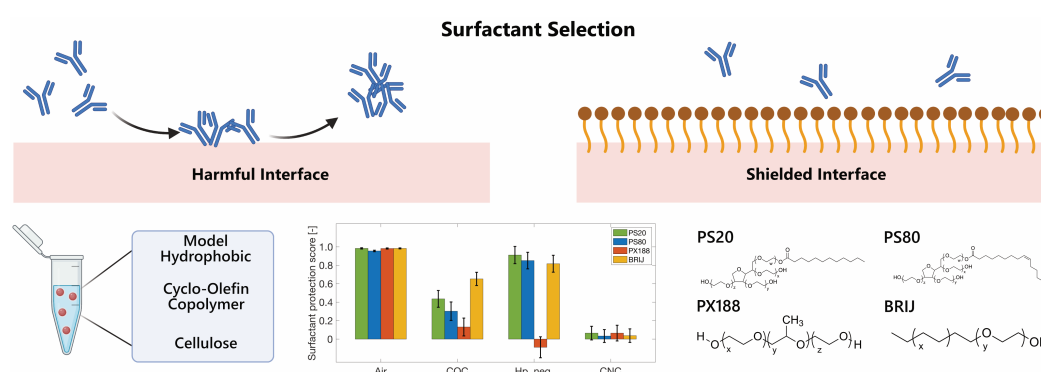
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Comparison of the Protective Effect of Surfactants on Antibody Stability Against Different Interfaces

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Maintaining the structural integrity of therapeutic proteins during their lifecycle is crucial for their efficacy and safety. However, interactions with various interfaces can compromise protein stability and lead to aggregation. During development, protein molecules and buffer composition must be optimized to ensure favorable physicochemical properties, but assays that systematically probe interfacial stability are lacking. To address this challenge, we have developed and applied a highly controlled nanoparticle-based method based on realistic and model interfaces to evaluate the stability of four monoclonal antibodies in the presence and absence of commonly used surfactants.



While all the surfactants demonstrated stabilizing effects against the hydrophobic air-water interface, none of them could safeguard the antibodies from hydrophilic charged cellulose. Additionally, polysorbates and Brij 35 provided a certain level of stability against COC and the model hydrophobic interface, while Poloxamer 188 had minimal impact on stability across these interfaces.

By rapidly evaluating the stability of therapeutic proteins against various interfaces using limited amounts of sample, this method can accelerate the selection of molecules and formulations during early development and formulation design.

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Unraveling the electrochemical doping in semiconducting polymers

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Organic mixed ionic-electronic conductors (OMIECs) are a class of organic materials that efficiently support both ionic and electronic transport. Due to this remarkable property, a broad range of emerging technologies, from energy storage to bioelectronics, rely on OMIECs. [1] A key property of these materials is their ability to be electrochemically doped, which is an efficient and reversible method to increase the materials electric conductivity. This process relies on the injection of carriers into the organic film, while the counterions from an electrolyte infiltrate the film and maintain charge neutrality. The electrochemical doping relies on a complex interplay between multiple factors, from electrolyte choice to molecule design and film morphology, and due to the increasing number of applications that rely on this process, there has been great interest in further understanding its properties and fundamental mechanisms. [2]

In this work, we explore the impact of the polymer film morphology on the electrochemical doping. We use time-resolved visible-near infrared (Vis-NIR) and in-situ Raman spectroscopy combined with electrochemical measurements to show that the ordered and disordered domains of poly(3-hexylthiophene) (P3HT) are doped through different mechanisms and kinetics. We demonstrate that for intermediate doping levels, polarons and bipolarons (singly and doubly charged species) coexist exclusively in the disordered domains. In the ordered domains, only polarons are observed until there are no more ordered undoped chains, and only at this point bipolarons start to be formed at these domains. We propose a kinetic model that described the reactions that take place and show that the ordered phase is doped faster than the disordered for all doping levels.

To confirm our propositions, we used in-situ electrochemical Raman spectroscopy, a technique very sensitive to local conformation. We obtained good agreement with the trends observed with Vis-NIR spectroscopy. Additionally, we compared the doping of P3HT films with different degrees of morphology. We use regiorandom P3HT to investigate the doping in purely disordered films, and the results strongly correlate with our proposed kinetic model. Finally, by measuring the Thz conductivity of our films, we investigate how the polarons and bipolarons impact electronic conductivity.

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The future of polyurethane adhesives

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Due to their high versatility and well-balanced cost/performance ratio, polyurethanes are the first choice for many applications like CASE and foams. However, reactive polyurethane systems as for example adhesives and sealants have constantly been under regulatory pressure. This will reach its latest peak in September 2023 with the introduction of the new REACH regulation concerning the content of monomeric diisocyanates in finished goods.

As one of the largest producers of reactive polyurethane products for construction and industrial applications, Sika undertook great efforts in the past years to develop polyurethanes adhesives and sealants with the lowest possible monomeric content. This could be achieved by cleverly designing our prepolymers as well as their production process.

We will outline the key points of the new prepolymer design and examples on how it was possible to translate the benefits into new product properties.

Block Copolymer Photonic Pigments for Optical Materials

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The natural world is a colorful environment. Stunning displays of coloration have evolved throughout nature to optimize camouflage, warning, and communication, and the resulting flamboyant visual effects and remarkable dynamic properties – often caused by an intricate structural design at characteristic sizes in the order of visible light wavelengths – continue to inspire scientists to unravel the underlying physics and to recreate the observed effects. Photonic materials could bring tremendous benefits to society as their capability to emit, detect, manipulate and control light is expected to be accompanied by several technological breakthroughs. In this context, photonic pigments consisting of dispersible solid microparticles displaying vibrant, long-lasting structural coloration have been attracting more and more attention as they possess great potential to substitute traditional pigments – either organic or inorganic – henceforth having a growing economic significance in various industrial products and end-user applications. Structural pigments are superior to pigmentary colors in many ways, because of their tunability, resistance to photo- or chemical bleaching, reduced dependence on toxic materials, and capability to create spectacular unconventional effects [1].

Here, we report on the fabrication of photonic microparticles via the three-dimensional confined self-assembly of block copolymers (BCPs) in emulsion droplets [2]. The accurate selection of the BCP properties and the emulsification conditions leads to either highly ordered (i.e., concentric lamellae) or quasi-random (i.e., presenting only a short-distance order) structures comprised of alternated domains with refractive index mismatch showing strong light reflection. Here, the bandgap spectral position can be finely tuned by using “swelling agents” enabling the formation of supramolecular comb-like assemblies that consent to control the domain spacing thus altering light-matter interactions. Therefore, photonic pigments with color brightness, full-spectrum tunability, and adaptive optical properties are rapidly and easily achieved. Finally, we demonstrate the possibility to combine these structurally colored particles with different nanomaterials – such as plasmonic and oxide nanoparticles or emitting quantum dots – that enable the unlocking of additional functionalities with promises in several breakthrough applications [3].

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Structural diversity in superfluorescent multicomponent nanocrystal superlattices comprising lead halide perovskite nanocrystals

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Self-assembly of colloidal nanocrystals into long-range ordered superlattices is a versatile platform for materials engineering, wherein the functionalities of the mesostructures may result not only from the combination and enhancement of size-dependent properties of constituent building blocks but also from synergistic effects and emergent interactions between neighboring nanocrystals. The assembly of steric-stabilized colloidal nanocrystals coated with hydrocarbon ligand chains relies on relatively weak (van der Waals, dipole-dipole, magnetic, Coulombic) interactions with the considerable role of entropic contributions, with the nanocrystal shape anisotropy often being the decisive factor determining self-organization into diverse structures. Cesium lead halide perovskites, being synthetically available as uniform, monodisperse nanocrystals and owing to their outstanding properties (high oscillator strength of bright triplet excitons, slow dephasing, minimal inhomogeneous broadening of emission lines), are promising building blocks for creating functional superlattices exhibiting collective luminescence phenomena, namely superfluorescence. We present a broad structural diversity in binary and ternary, long-range ordered superlattices obtained by shape-directed co-assembly of highly luminescent CsPbBr₃ nanocrystals with the spherical and shape-anisotropic building blocks. We also demonstrate the effect of superlattice structure on the emergence of collective optical properties.

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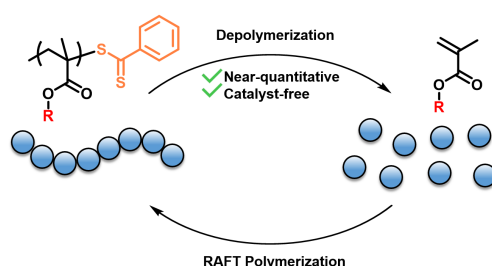
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Low-Temperature Chemical Recycling of Polymethacrylates Synthesized by RAFT Polymerization

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Reversing polymerizations and regenerating the monomer is highly beneficial for both fundamental research and applications, yet this has remained very challenging to achieve.^[1] Herein, we report a near-quantitative (up to 92%) and catalyst-free depolymerization of various linear, bulky, cross-linked, functional, and thermally unstable polymethacrylates synthesized by reversible addition-fragmentation chain-transfer (RAFT) polymerization.^{[2],[3]} 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.



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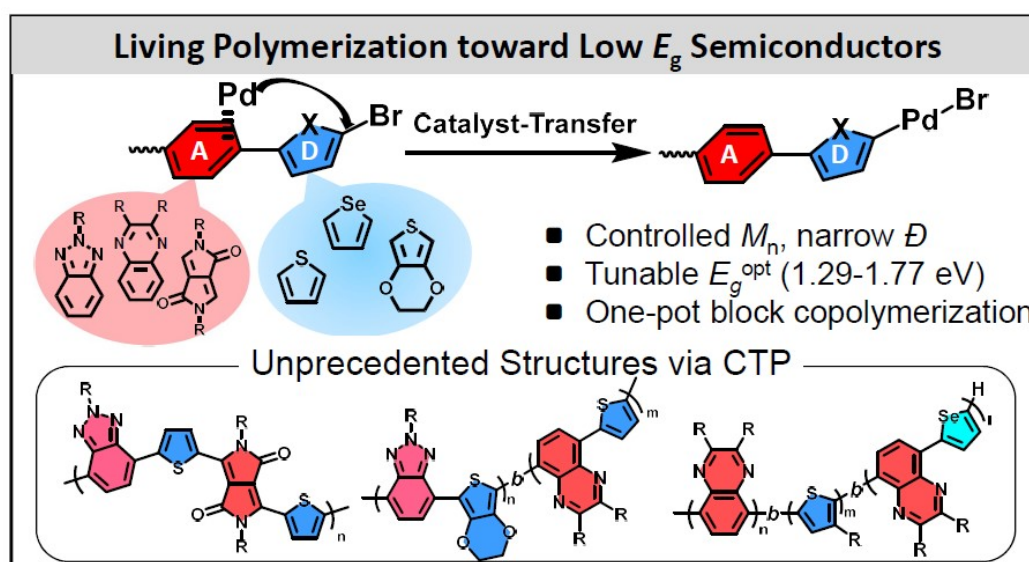
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Precision Synthesis of Various Low-Bandgap Donor-Acceptor Alternating Conjugated Polymers via Living Suzuki-Miyaura Catalyst-Transfer Polymerization

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In this study, we present the living Suzuki-Miyaura catalyst-transfer polymerization (SCTP) using a RuPhos Pd G3 precatalyst as a versatile approach for the precision synthesis of several types of donor-acceptor alternating conjugated polymers (DA ACPs). Initially, we optimized the living SCTP process for biaryl monomers with varying electronic characters of both strong and medium electron-donating (D) and electron-accepting (A) groups. This optimization allowed us to obtain DA ACPs with controlled number-average molecular weight (M_n), narrow dispersity (\mathcal{D} , 1.05-1.29), and high yields (>87%). Furthermore, we successfully expanded this method to the controlled polymerization ($M_n = 9.2 - 40.0 \text{ kg mol}^{-1}$) of a quateraryl monomer (A₁-D-A₂-D) containing diketopyrrolopyrrole (DPP; a strong acceptor). Additionally, the living SCTP technique facilitated the efficient one-step synthesis of various diblock and triblock copolymers. Lastly, the resulting DA ACPs exhibited adjustable optical band gaps (E_g^{opt}) ranging from 1.29 to 1.77 eV and varied highest occupied molecular orbital (HOMO) levels (from -5.57 to -4.75 eV), while their block copolymers displayed wide absorption spectra and demonstrated promising light-harvesting properties in the visible range.



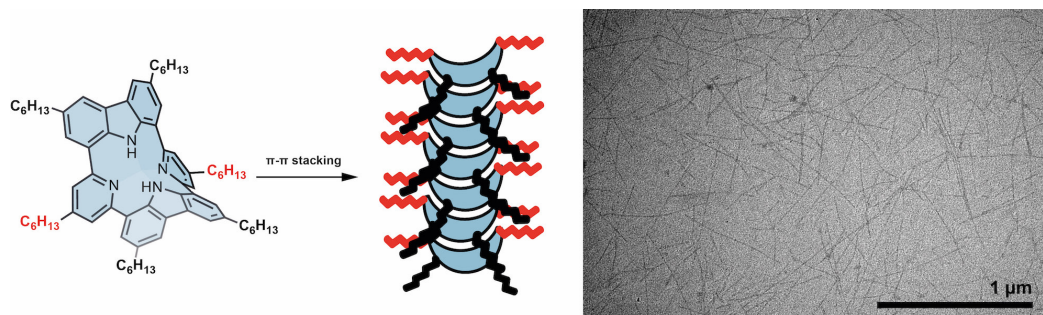
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Restricting the Shape-Assisted Self-Assembly of Carpyridines to One Dimension

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Shape-Assisted Self-Assembly (SASA) is a process in which the shape of a monomeric unit enforces the order between monomeric units needed for supramolecular assemblies in the absence of strong non-covalent interactions such as H-bonding.¹⁻³ Saddle-shaped molecules stand out for these processes due to the translational and rotational rigidity of the monomers within the stacks. Carpyridines (CPs) are porphyrin-related metal-containing macrocycles bearing two carbazole and two pyridine units alternately connected through ortho aryl-aryl bonds.^{1,2} This arrangement results in a saddle-shaped structure, where prefunctionalized building blocks allow the synthesis and tuning of properties of these macrocycles. These units have shown to be effective towards supramolecular assembly purely based on p-p interactions and assisted by the shape of the monomers, demonstrating the significance of shape in self-assembly processes. Alkyl substitution onto the carbazoles has allowed us to study 2D sheet formation,^{1,2} which combined with substitution onto the pyridines with different side chains allows us to study the mechanism of assembly of the monomers into oligomers, and ultimately, into micrometer-long fibers.⁴



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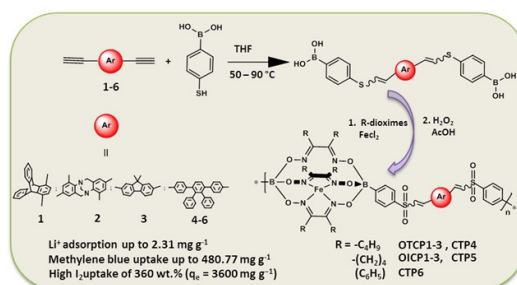
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Metalorganic Copolymers From Iron(II) Clathrochelates: Versatile Materials and Conspicuous Adsorbents of Lithium Ions, Iodine, and Organic Dyes

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The organometallic copolymers with butyl, cyclohexyl and phenyl lateral groups were made from a one-pot complexation of iron(II) clathrochelate units that are interconnected by various thioether-containing contorted groups and tetraphenylbenzene units. The resultant copolymers were converted into their poly(vinyl sulfone) derivatives OTCP1-3, OICP1-3 and CTP4-6 quantitatively via the selective oxidation of the thioether moieties into their respective sulfones using mild oxidation reaction conditions. The target copolymers were characterized by various instrumental analysis techniques. The copolymers were tested as potent lithium ions adsorbents revealing a maximum adsorption (q_m) value of 2.31 mg g⁻¹ for OTCP2. Furthermore, this same copolymer was found to be a promising adsorbent of methylene blue (MEB); an isothermal adsorption study divulged that OTCP2's uptake of MEB from an aqueous solution (following the Langmuir model) was, at maximum adsorption capacity, (q_m) of 480.77 mg g⁻¹; whereas the kinetic study divulged that the adsorption follows pseudo second-order kinetics with an equilibrium adsorption capacity ($q_{e,cal}$) of 45.40 mg g⁻¹. The iodine uptake studies of copolymers disclosed excellent iodine properties, reaching a maximum of 360 wt.% ($q_e = 3600$ mg g⁻¹). The adsorption mechanisms of the copolymers were explored using pseudo-first-order and pseudo-second-order kinetic models. Furthermore, regeneration tests confirmed the efficiency of the target copolymers for their iodine adsorption even after several adsorption-desorption cycles.



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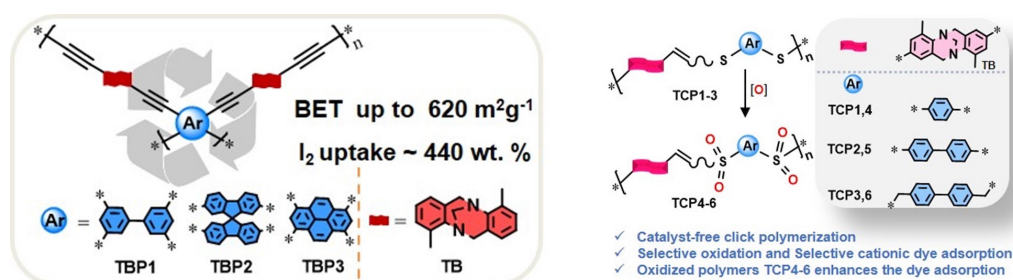
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Revisiting Tröger's Base: Microporous Copolymers Via Sonogashira Cross-coupling and Thiol-Yne Click Reactions For Superior Iodine and Dyes Uptake

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Copolymers bearing Tröger's base were synthesized in very good yields using either a Sonogashira cross-coupling reaction or a catalyst-free thiol-yne click reaction[1,2]. Instrumental analysis of the target copolymers reveals their high chemical stability. Nitrogen adsorption measurements of some copolymers reveal Brunauer-Emmett-Teller (BET) surface areas ranging from $\sim 586 \text{ m}^2 \text{ g}^{-1}$ to $\sim 620 \text{ m}^2 \text{ g}^{-1}$. Inspection of the iodine adsorption properties of the copolymer networks made using Sonogashira cross-coupling reaction reveals their high iodine vapors uptake up to 440 wt% and removal of iodine from a hexane solution reaching $\sim 77\%$ ($q_e = 192 \text{ mg g}^{-1}$). On the other hand, the thioether units of the copolymers made from the thiol-yne click reaction were selectively oxidized into their respective sulfone derivatives under mild oxidation reaction conditions. Investigation of organic dyes uptake from water of the thiol-yne copolymers proves their potential application as selective adsorbents as proven by the quantitative removal 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 display superior and faster MEB removal efficiencies with respect to their corresponding synthons.



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One-dimensional carbon-based nanostructures via the droplet-assisted growth and shaping (DAGS) mechanism

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One-dimensional (1D) polymeric nanostructures e.g. nanofibers, nanotubes, and nanowires are nanomaterials with a typical diameter ranging from 1 to 100 nm which can be fabricated via several techniques including electrospinning, self-assembly, and template methods.¹⁻⁴ The droplet-assisted growth and shaping mechanism (DAGS) belongs to one of the approaches for the production of (1D) nanomaterials.⁵ Conceptually similar to the VLS method, the DAGS mechanism uses water nanodroplets that have formed on the substrate surface to react with a precursor generating unidimensional polymeric nanostructures namely, based on silicone, alumina, and germanium oxide.⁵⁻⁷ However, the DAGS mechanism has not been used to fabricate organic polymeric unidimensional nanomaterials. In this work, we demonstrate that the DAGS technique can also be applied to organic precursors such as ethyl cyanoacrylate to obtain (1D) nanostructures. This opens up new avenues for developing (1D) nanomaterials, which, for instance, could be exploited in superhydrophobic coatings, optoelectronics, and biomedical applications.⁸⁻¹⁰

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Granular Elastomers for 3D Printing Applications

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The rising interest in the field of soft robotics demands for elastic soft materials whose mechanical properties can be locally varied to design materials that can deform in a pre-defined fashion while bearing significant loads. Such materials have the potential to enable the design of a soft robot that possesses high dexterity, can interact safely with humans and adapt itself to different environments. The stiffness-toughness compromise inherent to elastomers can, at least in parts, be addressed if they are formulated as multi-network materials.¹ However, the elastomeric liquid precursors are difficult to process, limiting the complexity of shapes they can be processed into. The involved processing of a second network further reduces the shape control and hence applications of these elastomers.²

In my poster, I will present a strategy to 3D print elastomers with a high spatial resolution. This is achieved by loading elastomer-based microparticles with a precursor solution. I will discuss how the composition and microstructure of the 3D-printed elastomers influence their mechanical properties.

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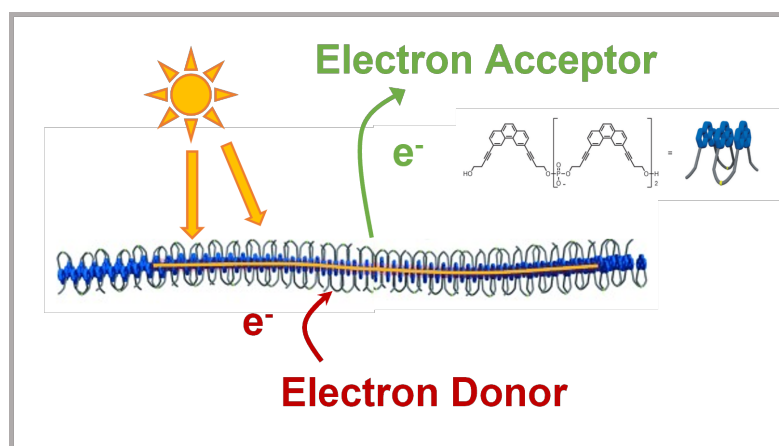
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Phenanthrene-based Light-Harvesting Supramolecular Polymers for photoredox catalysis

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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 CO₂. In natural photosynthetic systems, like green bacteria, this process is done via large self-standing supramolecular assemblies of chlorophyll molecules - the so-called chlorosomes - 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 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] less 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] we propose to address this issue. We will present first results regarding photoinduced electronic transfers between phenanthrene-based SPs and suitable redox active centers.



Photoinduced electronic transfers mediated by light-harvesting supramolecular phenanthrene polymer (in blue)

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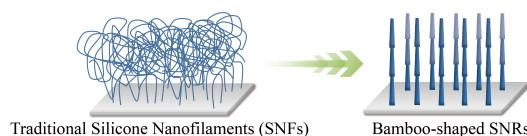
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Dynamic Synthesis of Bamboo-Shaped Silicone Nanorods to Control Water Repulsion and Collection

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Design and synthesis of regular and morphologically controllable silicone micro and nanostructures have long been a topic of great interest in materials and surface science. Although there has been extensive research on the fabrication of ordered and uniform structures, most of the methods such as chemical etching and lithography are limited to long-term treatment under harsh conditions, hazardous chemicals, environmental impact, and high cost. Our research systematically investigates the synergistic influence of various growth parameters for silicone nanorods (SNRs) and proposes the dynamic Droplet Assisted Growth and Shaping (d-DAGS) strategy to achieve one-step synthesis and in-situ shape control of SNRs.¹ The periodic dynamic regulation of growth parameters, such as relative humidity, precursors, and reaction time, contributes to the fabrication of highly regular bamboo-shaped SNRs with an adjustable number of segments, which provides novel insights into the mechanism of the traditional chemical vapor deposition method and the "tip-growth" model. Compared with the conventional 1D silicone nanofilaments and wires, which are usually fragile and irregular due to their soft mechanical properties,² the bamboo-shaped SNRs have enhanced mechanical stiffness and, therefore, can keep growing into the straight ultra-long rods with super-high aspect ratio and perfect superhydrophobicity with nearly 180° static water contact angle. Based on the strong chemical stability and water resistance properties, the versatility of bamboo-shaped SNRs is presented in the improvement of buoyancy, self-cleaning, and water harvesting. Meanwhile, the d-DAGS strategy promotes more possibilities to fabricate specially designed bamboo-shaped structures through the regulation of each independent, distinct segment. Further chemical modifications on the specific segments of the bamboo-shaped SNRs to endow them with unique physical and chemical properties are promising and will allow their applications to be extended to a broader range of fields.

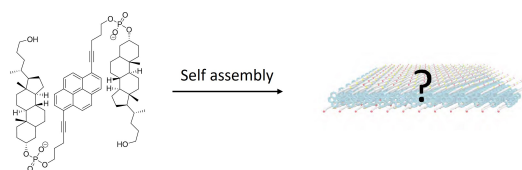


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Self-assembly of cholane-pyrene oligomersE. Ehret¹, M. Thiede¹, S. M. Langenegger¹, R. Häner^{1*}¹University of Bern

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 studied the possibility of replacing the polyaromatic residues present in the construct with cholane moieties. One pyrene unit was kept to investigate the photophysical properties of the oligomer. The aggregation process of the oligomer will be presented.



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Synthesis of hollow square macrocycle as nanochannels and hollow square helices

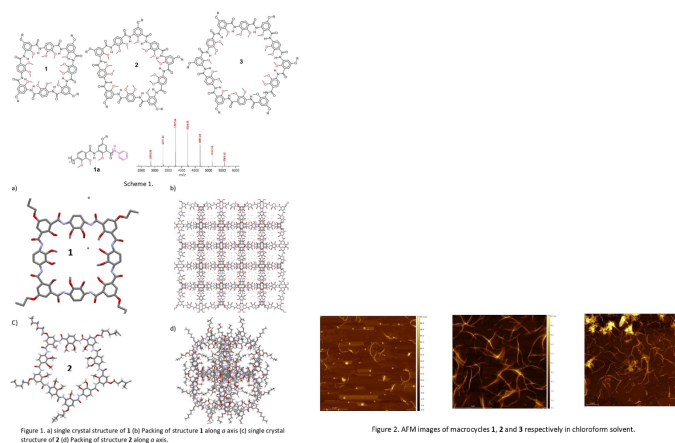
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Macrocycles and foldamers with substantial tubular cavities are intriguing and have captured significant attention. Foldamers and macrocycles with non-collapsible hydrophilic cavities have demonstrated exceptional properties in areas such as cation recognition and highly conducting membranes.¹ Conversely, helical foldamers and macrocycles that are rich in hydrophobic interior surfaces have shown exceptional performance in the field of water permeation.² Recent work by Takuzo Aida's group³ has highlighted how these hydrophobic interior surfaces in macrocycles act as artificial water channels responsible for water permeation, using a densely fluorinated interior surface system. However, the yield of these macrocycles is low, 0.0055-0.16%, which limits their potential for use in membrane technology for water purification. Furthermore, the diacid and diamine monomers used in this system restrict the ability to synthesize helices of a specific length with narrow dispersity.

We have developed a novel category of hollow square macrocycles (1) with an internal diameter of 0.9 nm, as well as helices (1a) (Scheme 1) that feature a non-collapsible cavity of roughly 0.9 nm, and possess hydrophobic interior surfaces. Additionally, we obtained macrocycles with a diameter of 1.5 nm (2) and 2 nm (3) (Scheme 1). The square shape of the macrocycle (1) was confirmed by the solid-state structure (Figure 1a). Dynamic light scattering (DLS) of these macrocycles and helices revealed significant aggregation in chloroform solution, which increased with increasing concentration. Evidence of nanochannels was found in these macrocycles, based on the crystal structure packing of 1 and 2 (Figure 1). Furthermore, the linear stacking of macrocycles 1, 2, and 3 was confirmed by atomic force microscopy (AFM) analysis (Figure 2)

The water permeability and salt rejection tests of macrocycles and polymers, both in vesicles as well as in fabricating the membranes using interfacial polymerization, are under investigation.



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Quantifying Förster-type energy transfer from single perovskite quantum dots to organic dyes

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Colloidal quantum dots (QDs) are promising photoredox catalysts that offer broadly tunable potentials, high absorption coefficients and regenerability. These properties have prompted QDs to be examined for various photocatalytic reactions, from water splitting and CO₂ reduction to various organic transformations [1]. An even wider parameter space emerges upon coupling QDs with other homogeneous catalysts – transition metal complexes or organic dyes – in hybrid nanoassemblies exploiting energy transfer (ET). Such nanoassemblies could significantly exceed the performance of the individual constituents thanks to the very large absorption cross section of QDs combined with the long-lived triplet states of co-catalysts [2]. However, understanding the complex behavior arising in hybrid nanoassemblies requires methods with high spatio-temporal resolution [3]. Here, we probe ET from single lead halide perovskite QDs to organic dye molecules employing single-particle photoluminescence spectroscopy with single-photon resolution. We identify ET by spatial, temporal, and photon-photon correlations in the QD and dye emission. Exploiting the high temporal resolution of our experiment as well as the discrete quenching steps due to photobleaching of individual organic dyes, we observe a characteristic Förster-type ET, with efficiencies higher than 70% in the sole case of a strong donor-acceptor spectral overlap. Our work sheds light on the processes occurring at the QD/molecule interface and demonstrates the feasibility of sensitizing organic catalysts with QDs.

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Tetraoxa[8]circulene-Based Porous Materials

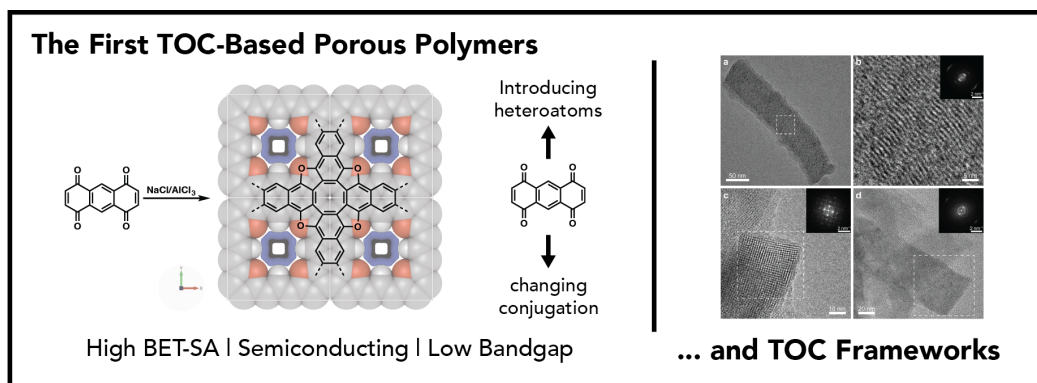
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Tetraoxa[8]circulenes (TOCs) are a subclass of hetero[8]circulenes featuring a planar cyclooctatetraene core, endowing them with unique aromatic features, that influence their electronic properties, which made them the subject of several experimental and computational studies.^[1,2] Despite this interest in small-molecule TOCs and ample interest by the computational community, extended TOC structures had not been reported in the literature.

Recently, we reported the first extended polymeric TOC (pTOCs) based on an acid-mediated cyclization procedure.^[3] The obtained semiconductive polymers featured tunable porosity and could be post-synthetically modified or doped to further control their conductive properties. Based on these findings, we developed further protocols to change the degree of conjugation and to introduce heteroatoms into the pTOCs, thus further altering their physical and charge/electron transport properties.

Besides such porous organic polymers, TOC-based framework materials are exciting due to their ordered structures and more isotropic properties. To that end, we have developed suitable TOC-based linkers and prepared Cu-based metal-organic frameworks and boronate-ester-linked covalent organic frameworks. These materials exhibit excellent semiconducting properties and are currently being investigated as supercapacitors and ion conductors.



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3D Printing of functional organoids at room temperatureR. M. García Montero¹, E. Amstad^{1*}

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Organoids derived from stem cells represent a powerful tool to study the growth, development and function of normal and pathologic human tissues. In addition, they have the potential to serve as excellent models to test drugs, thereby reducing the need for animal tests. Unfortunately, it is still challenging to fabricate organoids that display a similar functionality as natural tissues *in vitro*. Organoids are typically grown from hydrogel-based scaffolds with well-defined 3D shapes. To obtain tight control over the 3D structure, hydrogels are frequently 3D printed. Matrigel, the most commonly used scaffold that can be 3D printed, must be processed at low temperatures and the printing duration is very limited because the rheological properties of Matrigel change over time.

In this poster, I will outline a possible route to address this limitation by using cell-loaded viscoelastic capsules that can be processed into 3D printable inks. Importantly, this formulation would enable room temperature 3D printing for an extended time, thereby addressing the most stringent limitations of Matrigel.

Scale-up strategy for lipidic mesophases production

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Ulcerative colitis (UC) is a chronic inflammatory disorder involving the colon and rectum which has no cure. The severe dose-dependent side effects caused by oral therapies combined with the favourable localization of the disease encouraged the development of local therapies using enemas and foams as dosage forms. However, the efficacy of these formulations is limited due to insufficient retention time in the rectum. In this scenario, our research group developed an in situ forming gel, named TIF-Gel, for the treatment of UC aiming for high local retention and low systemic drug exposure [1]. TIF-Gel is a lipidic mesophase (LMP)-based formulation characterized by a low viscosity lamellar phase at room temperature, which provides an easy application by the patient, and a high viscosity cubic phase at the rectal temperature, providing high drug retention. The TIF-Gel process flow chart is shown in Figure 1, which is the method commonly used for the preparation of LMP-based drug delivery systems. In such a method, however, critical process parameters (CPP) that could affect the quality of the final formulation were identified. Quality deviation due to CPP becomes a bigger issue when larger batches, for example, for preclinical studies, need to be produced.

We aimed thus to develop a more reproducible and robust production method for LMP. With our optimized approach, we could avoid lyophilization and the use of organic solvents, making the large-scale production of LMP more sustainable. In this study we used a Quality by Design approach based on a Design of Experiments to select the best conditions to produce the TIF-Gel. We selected the mixing and equilibration times of the formulation as independent variables, and the LMP phase geometry, the drug homogeneity within the syringe, and the drug release rate as dependent variables. We evaluated the versatility of our optimized approach by incorporating five drugs with diverse physicochemical properties into the TIF-Gel. Overall, using the new production method, we obtained LMP with lamellar phase geometry at 25 °C and cubic phase at 38 °C, high drug homogeneity within the syringe and drug release rates comparable to the formulation produced by the standard methodology.



Figure 1. Process flow chart and the critical process parameters that could affect the quality of the final product using (A) a standardized method and (B) the dual syringe method.

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Hyperbranched polyarylethenes synthesized by successive C-H vinylation

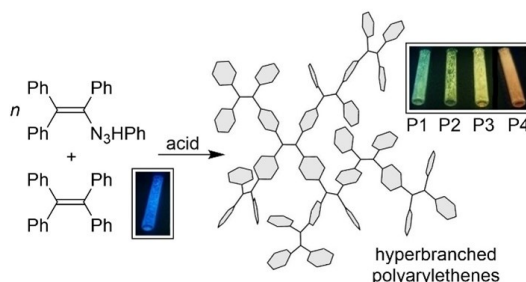
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Since the aggregation-induced emission (AIE) phenomenon was discovered for tetraphenylethene (TPE) in 2007,¹ polymers based on tri- and tetraphenylethene have received renewed interest.² These polymers stand out for highly functional properties such as enhanced AIE, high luminescence quantum yield in the solid state, high porosity, and response to additives. As a consequence, polyarylethenes were applied as effective sensors for explosives and metal ions, as gas sorption compounds, and as light-emitting materials.^{3,4}

Polyarylethenes are generally synthesized from monomers featuring reactive functional groups (halogens, boronic acids, terminal alkynes) using C–C coupling reactions,² reductive olefinations, or cyclotrimerizations.⁴ The existing approaches are effective and high-yielding. However, the final polymeric products remain chemically unstable due to the presence of the functional groups on the ends or in the periphery.

Here we show a novel procedure for the synthesis of polyarylethenes. As coupling polymerization, we employ a C–H vinylation of aromatic cores mediated by acid-induced cleavage of a triazene (Scheme 1).



Scheme 1. Synthesis of polyarylethenes via C–H polyvinylation.

The methodology allows obtaining 'inert' polyarylethenes without reactive functional groups in good yield. The branched polyarylethenes were characterized by NMR, HRMS, GPC, TGA, and elemental analysis. They show a size-dependent luminescence and a double emission in the solid state and in aggregates. The unusual AIE behaviour allows ratiometric detection of metal ions in water solutions.

The authors are sincerely grateful for financial support from the Swiss National Science Foundation (SNSF) and the EPFL.

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Switchable asymmetric water transport in dense nanocomposite membranesL. Grillo¹, C. Weder^{1*}¹Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

Directional transport of water has technological relevance in several applications, from separation processes^[1] to functional clothing^[2] and smart packaging^[3]. While this feature has been widely implemented in asymmetric porous materials to achieve directional wetting,^[4] studies on non-porous membranes with directional water transport are rather limited. As part of a renewed interest in this topic, our group recently developed dense nanocomposite membranes inspired by plant cuticles that exhibit asymmetric water transport characteristics.^[5]

Here we report compositionally asymmetric membranes based on a hydrophobic poly(styrene)-*block*-poly(butadiene)-*block*-poly(styrene) (SBS) copolymer and hydrophilic polyvinyl alcohol (PVA) nanofibers. The water-induced plasticization of PVA, combined with the asymmetric structure, results in directional water transport when the membranes are exposed to large relative humidity (RH) gradients. The directionality can easily be tuned by varying the composition of the membranes, enabling the development of a wide variety of new materials with switchable asymmetric water transport that may be useful for packaging applications.

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The key role of reaction engineering in catalytic recycling of HDPE and PP

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High-density polyethylene (HDPE) and polypropylene (PP) account for nearly 50% of all plastic waste produced. Life cycle assessments point at their catalytic hydro-conversion into light alkanes as a potential long-term environmentally and economically viable solution.^[1] Investigations have largely focused on catalyst development, despite the presumably large relevance of reaction engineering due to the distinctive nature of plastic as reactants. As non-Newtonian fluids when melted, their highly viscous and shear-thinning nature (**Fig. 1a.**) may dictate mass transport properties not properly described by classical theories for internal and external mass transport limitations, underscoring the role of rheology to assess catalyst-feedstock contact^[2]. Systematic studies over a reference Ru/TiO₂ catalyst revealed and rationalized distinctive responses to fluid velocity, flow pattern, and catalyst sieve sizes. Distinctive flow patterns imposed by stirrer geometry are described by cyclic motion of the feedstock in axial flow, bringing about greater catalyst-feedstock contact, leading to higher conversion, whereas sideways motion in radial flow leads to the catalysts being settled at the bottom (**Fig. 1b**). Multiphase CFD simulations and high-speed imaging revealed that the lower viscosity of PP under operating shear (**Fig. 1a**) favour a more homogeneous distribution of catalyst particles in the reactor, in contrast to the more viscous HDPE, for which catalyst sieve size becomes key (**Fig. 1c**). The aforementioned observations indicate that reaction engineering is thus of utmost importance for the evaluation of catalytic performance. Consequently, this study also identifies operating conditions characterized by non-dimensional numbers for minimizing the influence of viscosity of HDPE and PP, under which catalyst are recommended to be evaluated (torque > 10 N.cm with axial flow, T > 473 K).

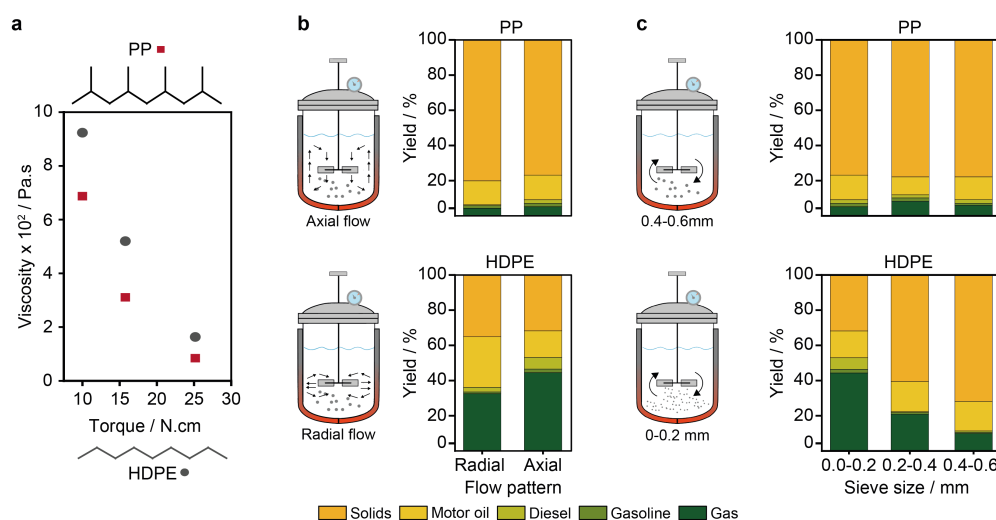


Fig. 1a Chemical structure and viscosity (under changing torque) of the two feedstocks (PP, MFI = 4, HDPE, MFI = 2.2). **b** Yields of different fractions for PP and HDPE under varying mixing patterns **c** Yields of different fractions for PP and HDPE under varying sieve size. Reaction conditions: $T = 498$ K, $P = 20$ bar H₂, $t = 4$ h and catalyst/plastic = 5 wt.%

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Enabling reprocessability and flame retardancy of fiber reinforced epoxy composites via reactive approach

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The increasing amount of fossil-based plastic waste ending up in our environment is one of the most pressing issues of the oncoming decades. Thus, development of re-usable polymers with a prolonged useful lifetime heralds the switch for a transition towards a more circular economy.[1] A novel class of dynamic phosphonate ester bonds containing thermoset has been designed and synthesized, via a simple one-pot and two-step procedure.[2] The resulting material has been used to fabricate natural fiber reinforced polymer composites (FRPCs), which demonstrated exceptional reparability, recyclability and flame retardancy. The chemical structures and compositions of the chemical precursor and thermosets are confirmed by solution and solid phase NMR spectroscopy, elemental analysis, and Fourier transform infrared spectroscopy. The covalent incorporation of monomer/polymer phosphite moieties in the thermoset matrix introduced sufficient dynamic P-O ester bonds, and promoted the exchange of network strands under moderate heating condition, resulting in scratch reparability and recyclability. Due to the presence of phosphorus in the structure, the thermoset also exhibited excellent flame retardancy in varied fire tests. Applications of the thermoset as fire protective coating on wood samples and polymer matrix in FRPC were explored. Fire tests confirmed their excellent fire performance via intumescent mechanism.

In order to improve the recyclability of thermosetting materials, various recyclable materials have been synthesized via incorporation of wide variety of covalent exchangeable bond.[3, 4] Some of these materials containing sufficient carboxylic ester, disulfide, siloxane, imine, diketoenamine, Diels–Alder adduct, dioxaborolane bonds etc., can "flow" again like thermoplastics through network topological rearrangement by thermally triggered catalytical bond exchanges. Such network structures are fixed at product operating temperatures when the exchange reaction kinetics are frozen. Among the various dynamic covalent bonds, phosphorous ester based transesterification reaction may provide a multifaceted solution, this functionality not only offers excellent fire protection, but also has industrial relevance due to ready availability of monomers and straightforward synthesis procedure. Phosphate triester based thermosets brought new inspirations into multifunctional vitrimer material.[5] If we could replace the phosphate with phosphonate, the P-C bond will theoretically bring even better material stability and flame retardancy, as it is a chemically and thermally stable analog of a P-O bond.

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Silicone Nanofilament Coatings as Flexible Catalyst Supports for a Knoevenagel Condensation Reaction in Batch and Flow Systems

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In this work, the application of silicone nanofilament (SNF) coatings as catalyst supports for amino moieties from (3-aminopropyl)triethoxysilane (APTES) was investigated. During the past years, our group has established a highly facile method to grow SNF on substrates via a droplet-assisted growth and shaping (DAGS) approach at room temperature [1]. With the optimized coating conditions identified, the Brunauer-Emmett-Teller surface areas of a bare glass filter substrate and bare glass beads after the coating have increased by 5-fold and 16-fold, respectively. The SNF-coated filters were readily functionalized with amino groups via a liquid-phase deposition process, and their catalytic activities for a Knoevenagel reaction were evaluated using a batch reactor and a packed bed reactor. In both reactors, the as-prepared filters demonstrated superior catalytic performance over the functionalized filters without SNF coatings. Notably, the unique flexibility of the SNF coatings allowed the facile preparation of a packed bed reactor and a scalable catalytic system. It is expected that the packed bed system established in this study will support the development and the use of various SNF-supported organocatalysts and catalytic materials.

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Charge-Selectively Permeable MicrocapsulesC. Li¹, E. Amstad^{1*}¹Swiss Federal Institute of Technology in Lausanne (EPFL)

Microcapsules with a selectively permeable shell are attractive delivery vehicles, containers for sensing, and micro-reactions. While capsules displaying a size-selective permeability have been frequently reported¹⁻⁴, capsules with charge-selectivity are much rarer. Here, we introduce a new type of capsule possessing viscoelastic shells that display a charge-selective permeability. The capsules are composed of chelator-functionalized surfactants that have been crosslinked with appropriate ion clusters. We demonstrate that these capsules can repeatedly uptake and release selected reagents. These capsules have the potential to be used, for example, for wastewater treatment, or as picoliter-sized reaction vessels to selectively conduct chemical reactions only within capsule cores.

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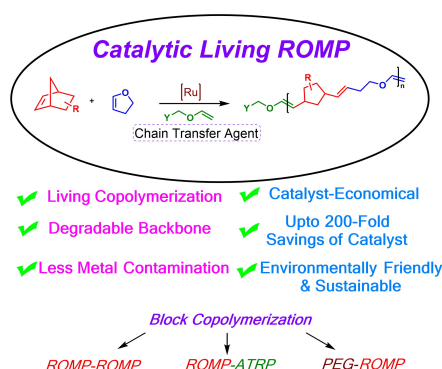
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Degradable Polymers via Catalytic Living ROMP

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The development of degradable polymers has commanded significant attention over the past half-century.¹ Since most of the metathesis polymers lack backbone degradability, recent efforts have been directed toward expanding the family of degradable polymers accessible via olefin metathesis polymerization for their potential applications in drug delivery, therapeutics, technology as well as for environmental sustainability. Although several routes have been developed to synthesize degradable polymers via ring-opening metathesis polymerization (ROMP), they all rely on the utilization of stoichiometric amounts of ruthenium-based metal catalysts, which bestow a ruthenium carbene on each polymer chain during the polymerization. This often results in high catalyst loading, which is quite expensive and leads to toxic metal contaminants in the synthesized polymers, potentially hindering the industrial and biomedical applications of these materials. The design of ROMP methods that require only a catalytic amount of ruthenium catalyst is desirable to realize lower costs and the most sustainable syntheses compared with ROMP using a traditional amount of catalyst. But, finding a catalytic ROMP protocol that will facilitate the synthesis of living and degradable polymers has always been a challenging issue. Herein, we have demonstrated a new catalytic living ROMP mechanism exploiting the regioselectivity and high metathesis activity of vinyl ethers as chain transfer agents (CTAs) to synthesize narrowly dispersed degradable polymers by copolymerizing 2,3-dihydrofuran (DHF) with several norbornene derivatives.^{2,3} All characteristics of a living polymerization such as narrow dispersity, excellent molar mass control, and the ability to form block copolymers are achieved by this method. This simple and one-pot approach allows the use of up to 200 times less ruthenium complex than traditional living ROMP. Narrowly dispersed ROMP-ROMP diblock copolymers, ATRP from a ROMP macro-initiator, and living ROMP from a PEG-based macro chain transfer agent were also synthesized quite straightforwardly by this strategy. We believe that this cost-effective, sustainable, and environmentally friendly synthesis of degradable polymers and block copolymers enabled by this method will find various applications in bordering fields.



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A Handful of Sustainable Routes for Catalytic Ring-Opening Metathesis Polymerization

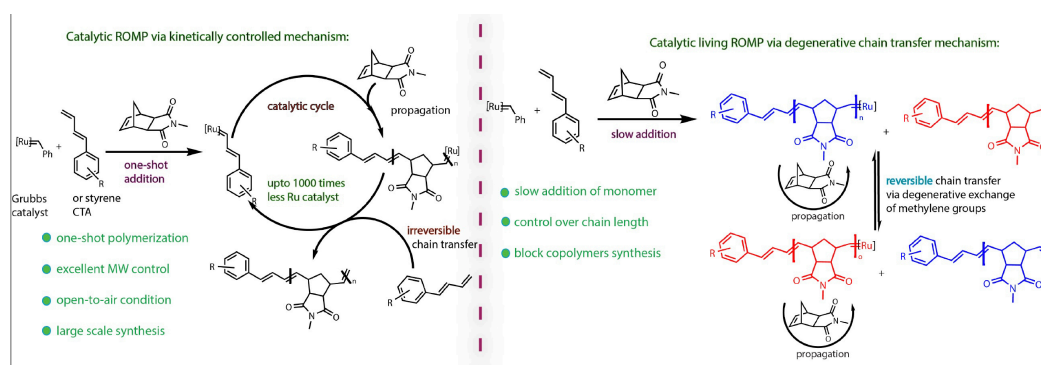
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For many decades, the ring-opening metathesis polymerization (ROMP) using Grubbs complexes has been a well-known technique. However, stoichiometric amounts of toxic and expensive Ru complexes are required with respect to the number of polymer chains formed for typical ROMP. In 2022, our group discovered that conjugated 1,3 dienes¹ and styrenes² can act as effective chain transfer agents (CTAs) that catalytically allow for polymerization, reducing the required amount of Ru complex by up to 1000 times compared to classical syntheses. Our detailed mechanistic analysis uncovered a new kinetically controlled chain transfer mechanism. Furthermore, our catalytic method allows access to structurally new block copolymer combinations that were previously unachievable³.

Moreover, we have recently revealed that using the same CTAs under slow monomer addition conditions can achieve a degenerative exchange mechanism⁴. This mechanism involves the reversible exchange of vinyl groups (derived from CTAs such as styrene), giving the macroscopic impression that all polymer chain ends can propagate quasi-simultaneously. It turns out that virtually all ROMP polymers prepared over the last 50 years have carried the correct end-group for degenerative exchange, meaning they could be activated again and turned into block copolymers with only sub-stoichiometric quantities of Grubbs catalysts.

This discovery has exciting implications for the field of ROMP and may pave the way for more sustainable and cost-effective polymer synthesis.



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Hierarchical Self-organization of Polymersomes and Janus Nanoparticles Mediated by DNA

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A significant approach in various fields such as chemistry, electronics, and technology is the self-organization of nano-objects into complex architectures. This strategy aims to generate novel systems with unique properties and functionalities [1-3]. An important step in creating interconnected artificial organelles is the DNA hybridization between synthetic assemblies, including polymersomes, nanoparticles, and micelles. These assemblies facilitate cascade reactions among different encapsulated catalytic compounds and can imitate cell signaling and interactions [4,5].

In this study, we explore the self-organization of clusters formed by "hard" Janus nanoparticles (JNPs) and "soft" polymersomes, presenting a universal approach to developing a hybrid system with multiple functions for specific bio-applications. The polymer-based JNPs possess anisotropic composition and orthogonally addressable functionality, making them an asymmetric platform suitable for directional interactions [6,7] with the soft polymersomes. These clusters are formed through the hybridization of complementary ssDNA strands attached to each component. While adhering to the surface of the "hard" JNPs, the polymersomes undergo deformation but maintain their structural integrity due to the robustness of the block copolymer membrane. Notably, the polymersomes retain their vesicular architecture even after assembly into JNP-polymersome clusters, allowing for the encapsulation of various types of functional cargo [8]. Lastly, the study investigates the biocompatibility of these clusters and their interactions with cell surfaces, facilitated by scavenger receptors.

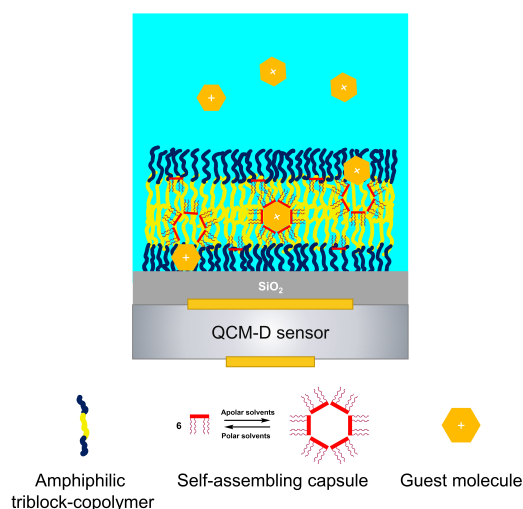
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Insertion of dynamically self-assembling capsules into planar polymer membranes for specific guest uptake

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Solid-supported membranes offer great potential in material and life sciences. Especially the use of amphiphilic block-copolymers introduces many advantages over lipid membranes. Due to their robustness and compatibility for the combination with biomacromolecules, polymers are good candidates for the generation of functional surfaces with biomimicking properties. However, there is still a need for novel strategies which allow for adaptation of the systems to specific requirements, such as selective molecule recognition and permeability. In this study, we used a solvent-assisted approach for polymer hybrid membrane deposition and show the successful insertion of a synthetic host for specific guest complexation: Resorcinarenes, which assemble into hexameric capsules in apolar solvents, were inserted into a solid-supported, planar PMOXA-PDMS-PMOXA triblock copolymer membrane. Their functionality was assessed by a Quartz-Crystal Microbalance with Dissipation (QCM-D)-based guest uptake assay. Physicochemical characterisation is provided by Atomic Force Microscopy (AFM). The membranes containing resorcinarenes were able to specifically take up a guest molecule from the aqueous flow, proving the capsule assembly inside the polymer membrane and furthermore indicating the ability of a hydrophobic polymer layer to partially mimic bulk properties of organic solvents. Resorcinarene capsules, which provide a large cavity with specific encapsulation affinity for cationic and polyhydroxylated molecules via specific host-guest interactions, could in the future serve as novel, dynamic membrane transporters with specificity for cations and certain sugars, which makes them interesting as well for biological applications.



Combating multidrug-resistant bacterial infections with peptide-loaded lipid-polymer hybrid nanoparticles

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Antimicrobial resistance is a global health concern that is rising to dangerously high levels. Antimicrobial peptides (AMPs) have emerged as promising alternatives to antibiotics due to their high efficacy and low resistance rates against several bacterial strains¹. However, the clinical application of AMPs is hampered by their toxicity, immunogenicity and rapid degradation *in vivo*. This study aims to develop a novel AMP delivery system based on non-toxic and non-immunogenic nanocarriers with tunable physicochemical properties to improve the stability and therapeutic efficacy of AMPs *in vivo*.

Lipid-polymer hybrid nanoparticles (LPNPs) that combine the advantages of both liposomes and polymeric nanoparticles² were developed for the encapsulation of two antimicrobial peptides, cathelicidin (LL-37) and Human beta-defensin 3 (hBD3). These peptides present the main defense response of the respiratory system and are known for their broad-spectrum antibacterial activity against multidrug-resistant Gram+ and Gram- bacterial strains³.

The peptide-loaded LPNPs were prepared by emulsion-solvent evaporation method using both sonication and microfluidic mixing. The formulations were characterized for their physicochemical characteristics (DLS), their morphology (AFM, TEM), as well their stability after lyophilization and storage under different conditions. Finally, their antimicrobial efficacy towards *E. Coli* and *B. Subtilis*, was tested and compared to the peptide solutions.

The LPNP formulations that were developed demonstrated an optimal size (~150 nm), and polydispersity index (PDI < 0.2) with a spherical morphology. Compared to liposomes, they maintained their physicochemical characteristics after lyophilization and storage in different temperatures. In addition, they demonstrated enhanced antimicrobial activity towards the *E. Coli* and *B. Subtilis* bacterial strains.

In summary, a novel lipid-polymer hybrid nanoparticle system was developed that exhibited optimal physicochemical properties, stability and improved antimicrobial efficacy compared to the peptide solutions, indicating that they could be an important alternative tool for the fight against bacterial resistance. Further *in vitro* and *in vivo* studies are needed to exploit the potential of this novel LPNP system.

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Responsive supramolecular cross-links for healable double polymer networks

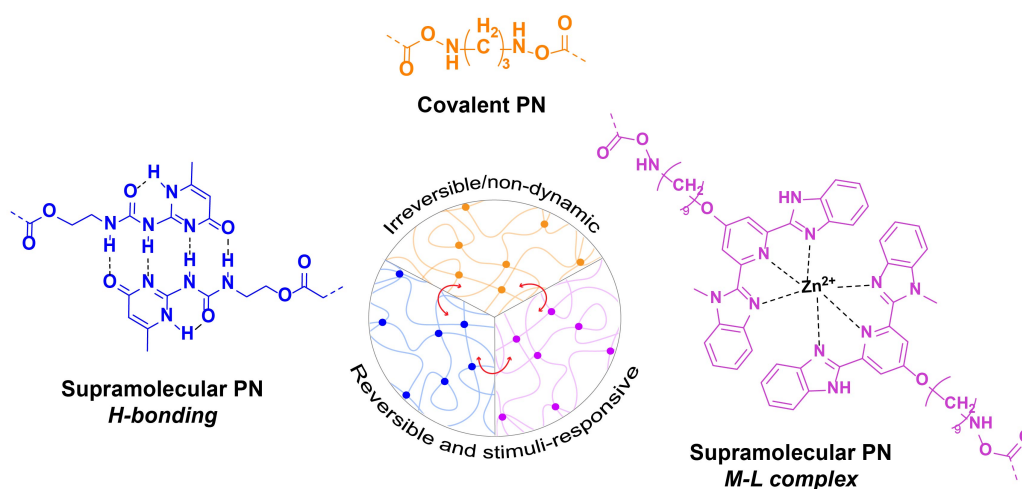
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Double polymer networks (DNs) consist of two polymer networks that usually exhibit different physical properties. These materials are of great interest thanks to the remarkable mechanical properties (toughness, elasticity) that one can achieve, and they can find direct applications in engineering or the medical field.[1]

DNs comprising covalent cross-links synthesized either in the presence or absence of a solvent have been deeply investigated.[2][3] little attention has been dedicated to DN containing *supramolecular* cross-links. Supramolecular bonds can be highly dynamic and DN containing such motifs can offer ease of (re)processing and recyclability as well as the possibility of being healable.

Here, we report the synthesis of different DN elastomers based on poly(butyl acrylate) (**PBA**) that comprise covalent and dynamic cross-links in different molar feeds (**Fig. 1**). The supramolecular polymer networks are made by reversible addition–fragmentation chain-transfer (RAFT) co-polymerization of butyl acrylate (**BA**) with either 2-ureido-4[1H]pyrimidinone (**UPy**) motif, which dimerizes by quadrupole hydrogen bonding interaction, or the 2,6-bis(1'-methylbenzimidazolyl)pyridine (**MeBip**) tridentate ligand, which forms complexes with Zn²⁺ ions in a 2:1 stoichiometry.[5][6][7] The covalent polymer network (**PBA-BDA**) comprises 1,4-butanediol diacrylate (**BDA**) as a covalent cross-link, and is prepared by UV-initiated free-radical polymerization (UV curing).[8] The thermomechanical properties of the individual networks and their multiple combinations are investigated. In addition, we investigated the responsiveness of **PNs** comprising dynamic cross-links by healing studies.



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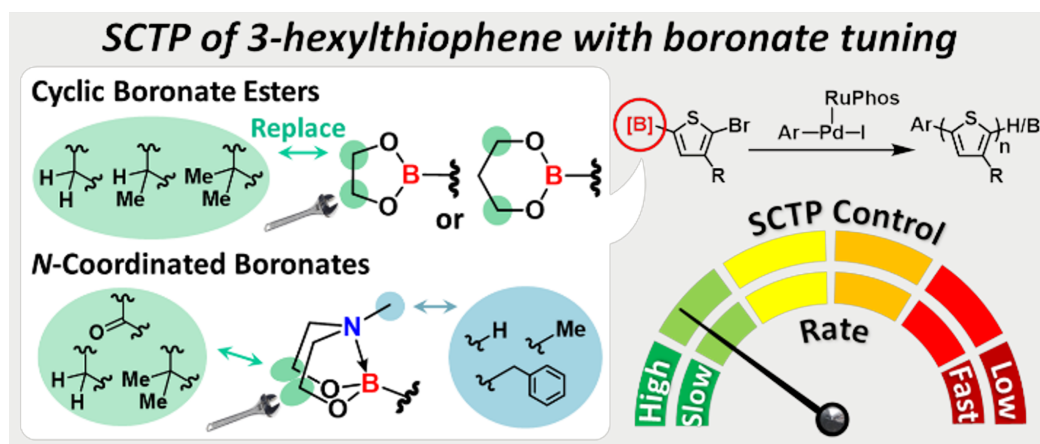
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Modulating the Rate of Controlled Suzuki-Miyaura Catalyst-Transfer Polymerization by Boronate Tuning

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Despite the remarkable breakthroughs in catalyst-transfer polymerization (CTP) technology in the precision synthesis of conjugated polymers, modulating the monomer reactivity is still challenging. We report that, by boronate tuning, we can modulate the rate of the Suzuki-Miyaura CTP (SCTP) of 3-hexylthiophene with high control. First, cyclic boronate esters showed different polymerization rates depending on their diol subunit structure. Additionally, the rates of the *N*-coordinated boronates were differentiated by tuning their *O*- or *N*-substituents. Notably, the origin of the difference in reactivity could be explained by the N → B bond lengths. The detailed structural analysis of the resulting polymers by ¹H NMR and MALDI-TOF spectrometry showed that the slower and more stable boronate monomers were less prone to homocoupling and protodeboronation, thereby producing poly(3-hexylthiophene) (P3HT) with higher control (i.e., molecular weight, dispersity, end-group fidelity, and yield). By rational optimizations to suppress homocoupling and protodeboronation, well-defined P3HT were prepared at various monomer-to-initiator ratios (M/I ratios).



Unraveling the synthesis, structure, and properties of zirconia nanocrystals

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Energy and memory storage systems play a vital role in numerous applications, ranging from consumer electronics to renewable energy. Ongoing research aims to enhance the performance and capabilities of these technologies while enabling new applications. One promising avenue for advancement lies in materials with switchable polarization behaviors, such as ferroelectricity, which have the potential to significantly improve developments in this field. Nanomaterials possess unique physical, chemical, and biological properties that differ from their bulk counterparts, making them highly attractive for many applications. However, their properties are often determined by size, shape, and structure, so understanding the relationship between synthesis and structure is crucial for optimizing their properties. In this work, we investigate the formation mechanism of zirconia nanocrystals using a powerful combination of techniques, including X-ray scattering, NMR spectroscopy, quantum chemical calculations, and chromatography.^{1, 2} Through these methods, we identified the active precursor species and amorphous intermediate in the reaction mixture and hypothesized an alternative mechanism for precursor decomposition and nanocrystal formation. By using various precursor combinations, we demonstrated several strategies for controlling the kinetics of the reaction and achieving size tuning, which is particularly challenging for group 4 and 5 metal oxides. Furthermore, we conducted a thorough structural characterization of zirconia nanocrystals using pair distribution function analysis, which revealed a distinct local structure distortion in the material. Intriguingly, this distortion induces switchable polarization properties in ZrO₂. Overall, our study sheds new light on the formation and properties of zirconia nanocrystals and opens up new possibilities for the design of novel energy and memory storage systems based on switchable polarization behaviors.

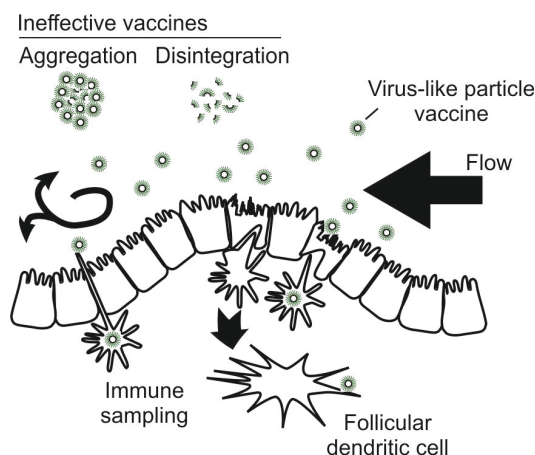
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What we learnt from PEGylation of virus-like particles for vaccination

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Virus-like particles (VLPs) have shown great potential in vaccination and drug delivery as nanocarriers of antigenic and therapeutic molecules [1]. VLPs are soft (~ 100 pN/nm) and proteinaceous colloidal particles (20–200 nm) that are susceptible to bio-mechanical and chemical stress leading to aggregation and disintegration, c.f. figure below for an example of VLP vaccines and Ref. [2]. These susceptibilities are expected to limit their application in various indications. We have very recently shown that polyethylene glycol (PEG) crosslinking of surface amine groups of a VLP assembled from *Acinetobacter* phage coat protein AP205, namely AP205 VLP, modulated the VLP's resistance to mechanical stress [3]. Building on this observation, here we present that the other stability profiles of AP205 VLP, including resistance to enzymatic degradation and pH-induced aggregation, are also modulated after PEG-crosslinking. In an *in vitro* model of human nasal tissue with motile cilia (representing mucosal administration), PEG-crosslinked as well as native AP205 VLPs were cleared via mucociliary clearance, thereby PEG-crosslinking did not make a noticeable difference. In *in vivo* mouse vaccinations, interestingly, PEG-crosslinking increased immune activation against the coat protein in addition to producing anti-PEG serum IgG. It is expected that by understanding the biophysical and immunological limits of VLPs, the VLP-based vaccine and drug delivery technology will present highly effective nanocarriers leading to reduced administration dosage and/or number of schedules.



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Surface functionalization strategies for optimal DNA biosensor performance

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The emergence of the COVID-19 pandemic highlighted the need for rapid, accurate and massive virus detection techniques to control the circulation of infectious diseases. Surface DNA-biosensors are interesting candidates for this purpose as they provide a high sensitivity detection, are affordable and can be implemented in microfluidic systems for automated detection.¹

The design of such surfaces must address a number of parameters, such as the density and orientation of immobilized single-strand DNA (ssDNA) probes, which have been identified as key factors to control the performance of the biosensing device.^{1,2} The available binding sites should be maximized to provide a large number of anchoring sites for the targeted gene, in order to increase the sensitivity of the sensor.

We suggest a variety of strategies to immobilize ssDNA probes on glass surfaces. The resulting sensing surfaces displayed different DNA probe densities, geometrical configurations and behaviours. A first simple system was obtained by conjugating ssDNA probes to amino-coated surfaces via a short succinic linker. Later, branched-peptides were developed to reach a higher immobilization density on borosilicate surfaces.³ Then, the use of spacers of different lengths were developed to study the effect of the DNA/surface spacing on the hybridization density. Finally, ssDNA probes were conjugated through a stimuli-responsive polymer to obtain DNA biosensors with antifouling properties.

Overall, diverse surface functionalization strategies were developed for the conjugation of ssDNA probes on glass surfaces to obtain DNA biosensors with tailored configurations and behaviours. The resulting sensing surfaces were further implemented in a microfluidic screening platform for the detection of unamplified viral RNA from saliva samples. As a proof-of concept, with a simple functionalization pattern, a detection limit of 10 aM was reached for the identification of SARS-CoV-2 RNA by fluorescence readout, in 10 minutes from human saliva with a high specificity.⁴ The detection efficiency of the newly developed sensing surfaces is under study for several viral RNAs.

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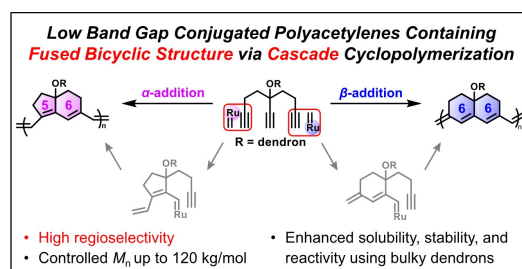
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Cascade Cyclopolymerization of 5-Ethynyl-1,8-Nonadiyne Derivatives to Synthesize Low Band Gap Conjugated Polyacetylenes Containing a Fused Bicyclic Structure

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Cyclopolymerization is a powerful method for synthesizing polyacetylenes containing four- to seven-membered rings. However, the structure of the repeat unit only consists of mono-cycloalkene due to the single cyclization of diyne monomers. Herein, we demonstrate a novel cascade cyclopolymerization to synthesize polyacetylenes containing fused bicyclic rings from triyne monomers containing bulky dendrons via sequential cascade ring-closing metathesis. These dendrons provided solubility and stability to the rigid bicyclic polyacetylene backbone. In addition, we controlled the regioselectivity of the catalyst approach by altering its structure and synthesized polymers containing fused bicyclo[4,3,0] or [4,4,0] rings with high molecular weights of up to 120 kg/mol. Interestingly, the resulting polymers showed narrower band gaps (down to 1.6 eV) than polymers with mono-cycloalkene repeat units due to the planarization of the conjugated segment resulting from the fused bicyclic structure.



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Solution-processed phase-change memory from molecular telluride inksE. M. Schenk¹, M. Yarema^{1*}

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The demand for data storage and processing increases exponentially, projected to reach 175 zettabytes in 2025.^[1] With the inability of silicon memory to meet this demand, we must turn to alternative solutions. Phase-change memory (PCM) is among the most mature emerging technologies, offering faster read and write times, non-volatility at elevated temperatures, and multibit analog-type data storage potential, making it particularly suitable for neuromorphic computing and artificial intelligence applications. PCM stores information using the stark electrical resistance contrast between high-resistance amorphous and low-resistance crystalline phases. To write the data, the PCM material is heated locally above the crystallization temperature (SET process); amorphization via melt-quenching erases the data (RESET process).^[2] Traditionally, PCM devices are fabricated via sputtering techniques, lithography, lift-off, and etching steps. Solution-phase deposition of chalcogenides at ambient temperature and pressure provides a low-cost and scalable alternative, while simultaneously giving access to a wider range of compositions. Moreover, thin film fabrication from the liquid phase unlocks new geometries of PCM devices (i.e., high-aspect ratio and multilayer arrays)^[3], in addition to low-cost high-throughput printing methods.

In this talk, we report the fabrication and performance of the first high-performing liquid-based PCM devices. While reaching state-of-the-art characteristics, our devices hold potential to substantially undercut the price-per-bit, thereby removing the last roadblock towards wide-scale implementation of PCM as the mainstream memory technology. We synthesize a range of PCM material inks by dissolving bulk tellurides in an amine/thiol co-solvent. While this approach has been reported for several technologies,^[4-6] it has not yet been demonstrated for state-of-the-art PCM applications. Upon subsequent purification steps, our telluride inks can be deposited to form high-quality thin films with tunable thickness, low surface roughness, and high crystallinity. We highlight the possibility to obtain stoichiometric binary PCM materials (i.e., Sb₂Te₃ or GeTe) and composition-tunable ternary tellurides (i.e., Ge₂Sb₂Te₅). Our approach allows for a wide range of tellurides, including ultra-fast Sc-Sb-Te, while ensuring highly homogenous thin films due to mixing on the molecular scale. We then emphasize the added value of liquid-phase engineering through infilling of nanoscale vias, the use of flexible substrates, and multilayer deposition. Finally, we demonstrate fabrication and characterization of prototype devices and quantify critical performance metrics, including threshold switching, SET/RESET switching, resistance contrast, power consumption, and cyclability of liquid-engineered PCM devices.

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Co-assembly of Shape Anisotropic Lead Halide Perovskite Nanocrystals into Functional Binary Superlattices

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Over the last few decades, the development of new approaches in colloidal chemistry enabled the synthesis of various colloidal nanocrystals in the monodisperse form. This, in turn, opened a new avenue for extensive research and application possibilities of novel nanomaterials. To this end, nanocrystal self-assembly holds great promise for creating metamaterials with tunable functionalities which originate not only from ensemble-average properties but also from diverse synergistic and collective effects, including conductivity enhancement, exchange coupling effects as well as collective light emission–superfluorescence [1]. The last was recently exhibited on the lead halide perovskite nanocrystal superlattices [2]. Such peculiar optical properties, together with a high degree of monodispersity, size tunability, and shape anisotropy of perovskite nanocrystals, stimulated research in exploring multicomponent superlattices, wherein perovskite nanocubes are combined with non-emissive nanocrystal spacers [3]. Thus, a whole plethora of superlattice types has become accessible, encompassing the superlattices comprised of perovskite nanocubes and spherical, truncated cuboid, or disc-shaped nanocrystals [4]. Not only were the perovskite superlattices obtained as films on the flat substrates including at the liquid-air interface, but also as spherically confined 3-dimensional supraparticles. Apart from superlattice type and morphology diversification, we managed to vary the superlattice composition by employing mixed halide and hybrid organic-inorganic perovskite nanocrystals [5]. A particular interest lies in studying superlattices containing a few light emitter types, wherein promising collective phenomena are expected to emerge.

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Lithium niobate nanoparticles functionalization with proteins for cancer active targeting

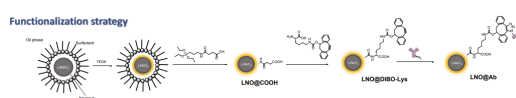
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Nowadays, cancer is a major health burden and has become the second leading cause of death in industrialized countries. Cancer mortality can be reduced through early stage detection and appropriate selective treatment. Conventional imaging techniques and cancer treatments lack sensitivity for early detection and show poor specificity, causing adverse side effects. Nanomedicine has emerged as an appealing tool to support early diagnosis and targeted tumor therapy^{[1],[2]}.

Harmonic nanoparticles (HNPs) are known for their efficient non-linear optical response by generation of second and third harmonic signals under ultrafast laser irradiation, which makes them appealing probes for bioimaging applications^[3]. The HNPs can be functionalized with i) imaging probes for multimodal imaging; ii) photocaged cargos for controlled drug delivery; and iii) targeting ligands for active targeting of cancer cells. We herein present a functionalization strategy based on the silanization of LiNbO₃ (LNO) HNPs through water-in-oil microemulsion^[4] to introduce surface reactive moieties followed by post-conjugation to targeting ligands, such as anti-EGFR antibodies. In order to enhance covalent immobilization over unspecific protein adsorption, surface covering with peptide mimics was investigated and showed promising anti-fouling properties. A small library of peptides was designed through solid phase peptide synthesis (SPPS) for further conjugation to antibodies using click reactions.

The long-term perspective of the project is to use protein-coated nanoparticles as theranostic nanoplatforms, focusing on the active targeting feature, through the use of monoclonal antibodies, or smaller engineered protein fragments, such as affibodies. Several grafting strategies will be investigated in the future. Potentially, these nanocarriers, simultaneously decorated with targeting ligands, anti-cancer drugs and imaging probes, could combine early detection and *in vivo* cancer treatment.



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Supramolecular Assembly of Pyrene-DNA Conjugates into Columnar Vesicles

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The arrangement of structural subunits plays a crucial role in the shape of both natural and artificial supramolecular assemblies. In DNA nanotechnology, the well-defined DNA framework is utilized to achieve the spatial organization of functional groups.^[1] In previous work DNA was modified with phenanthrene sticky ends forming vesicular supramolecular assemblies with light-harvesting properties^[2] and *E*-tetraphenylethylenes modifications forming aggregation-induced emission active assemblies.^[3-4] In this work, we modified two complementary DNA strands with 1,6-dialkynyl-pyrenes at the 3'-end (Figure 1a). Cryo-EM were performed after self-assembly revealing columnar vesicles (Figure 1b). In addition, the self-assembly was analyzed and discussed with fluorescence spectroscopy, UV-vis spectroscopy, and AFM.

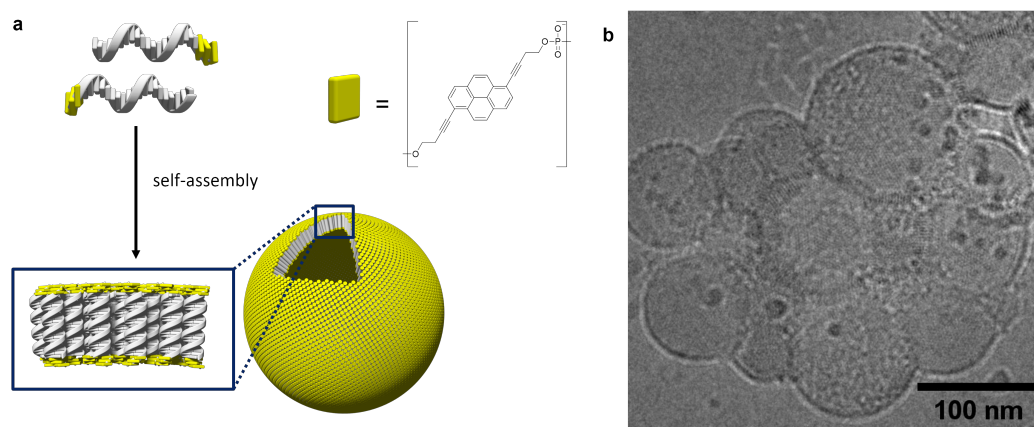


Figure 1 (a) Schematic representation of the self-assembled vesicles formed from 1,6-dialkynyl-pyrene-modified single strands and chemical structure of the pyrene-modification. (b) Cryo-EM image of vesicular assemblies.

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Unraveling Structure Formation in Tailor-Made Buriti Oil Emulsion during Simulated Digestion

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

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

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

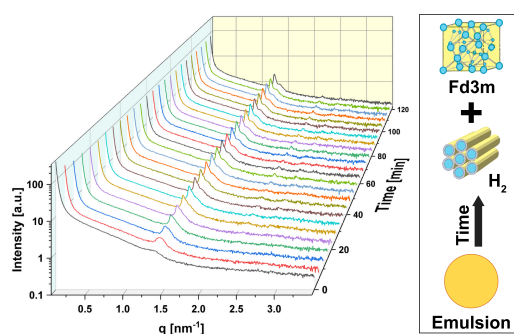


Figure 1. Time-resolved *in situ* SAXS curves of simulated intestinal digestion of buriti oil emulsion and artistic representations of the observed structures.

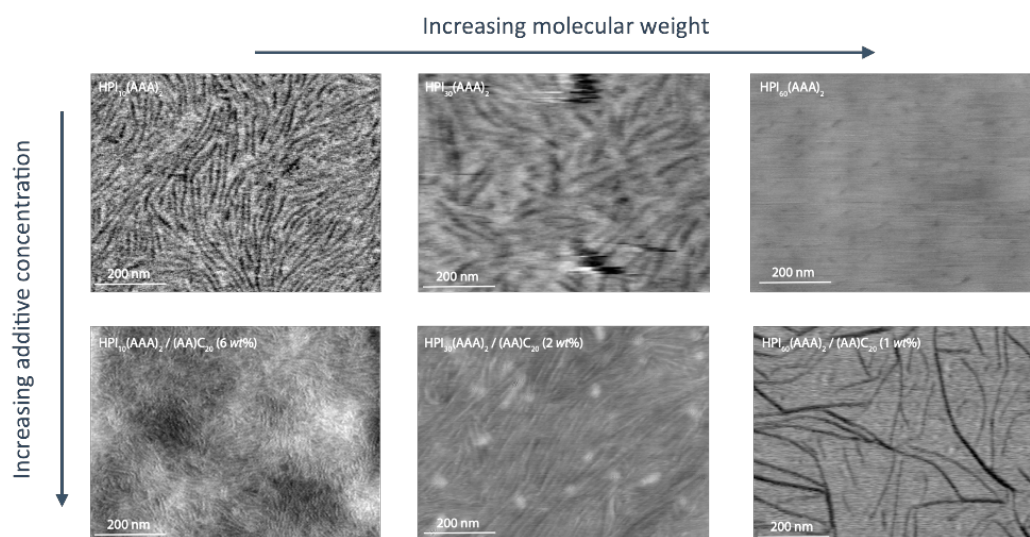
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Bio-Inspired Hierarchical Structure Formation in a Supramolecular PolymerM. Wendling¹¹Ecole Polytechnique Fédérale de Lausanne (EPFL). Institute of Materials. Laboratory of Macromolecular and Organic Materials (LMOM)

Supramolecular polymers are based on discrete building blocks that thermoreversibly self-assemble into defined architectures through non-covalent interactions such as hydrogen bonding, often resulting in materials with tailored structure, dynamic behavior, properties and function. The attachment of supramolecular ligands to polymer chains is, however, almost exclusively restricted to low molecular weight polymer segments, which consequently lack entanglement and exhibit brittle failure under low loads in tension. We have developed a supramolecular modification strategy that persists even when high molecular weight base polymers are employed, which is based on the co-assembly of bioinspired oligopeptide end groups with a matching low molecular weight additive into highly dispersed, polymer-tethered nanofibrils. The resulting supramolecular network gives rise to a variety of new melt properties that promise drastic improvements in materials processability or recyclability, but a detailed structural characterization of these nanofibrils and a profound understanding of their formation is required for a universal applicability of this approach to various technologically important base polymers.

Here we investigate the structure formation behavior of a hydrophobic amorphous model polymer of three different molecular weights using the supramolecular approach aforementioned. We show that the hydrogen-bond-driven co-assembly of additives and end-groups result in a new phase which we were able to describe with a thermodynamic analytical model. This phase is composed of anti-parallel beta sheets, of which a defined number stack to form helical nanofibrils that, due to the self-limiting lateral aggregation thus have a defined and uniform diameter. As a result of the tethering and bridging of the nanofibrils with the attached polymer segments, they are periodically placed in an hexagonal arrangement in the bulk material.



Structural elucidation of shape-assisted self-assembled nanosheets from π -saddles

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Questioning how molecular topography can govern supramolecular ordering is a relatively unexplored avenue of thought and one which poses great synthetic challenge that could lead towards new functional materials. “Carpriidines” (Fig. 1a) — saddle-shaped macrocycles fused from carbazoles and pyridines — are an underdeveloped example of a simple system bearing negative Gaussian curvature that could hold such promise.¹

Derivatisation of these non-planar systems through peripheral functionalisation of the aromatic core has yielded supramolecular assemblies (Fig. 1b, c) in the form of 2D sheets on surface with the thickness of a single molecule and fantastic edge definition.¹ Varying the length of alkyl chain in the macrocycle has then resulted in different types of nanosheet,² which hints at the subtle interplay between weak forces alongside the assisting role of shape. Using a combination of diffraction techniques, including micro-electron diffraction, the composition of these nanosheets can be elucidated to examine what effect shape has upon supramolecular ordering within the assembly.²

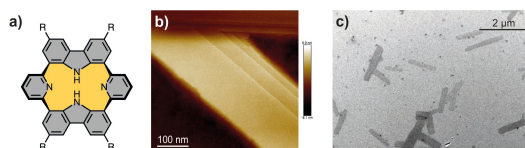


Fig. 1. a) Structure of Carpyridine (2H-Car-R) functionalised with R groups, and when R = n -C₆H₁₃, assemblies were visualized under b) AFM and c) TEM as 2D sheets.

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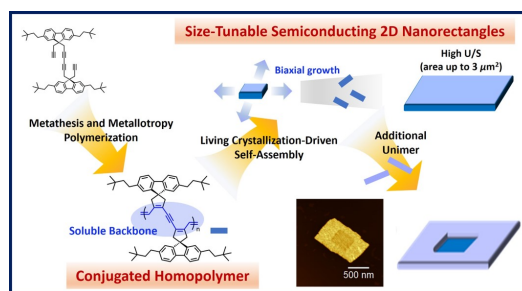
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Size-Tunable Semiconducting 2D Nanorectangles from Conjugated Polyenyne Homopolymer Synthesized via Cascade Metathesis and Metallotropy Polymerization

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¹ETH Zurich, ²Seoul National University

Size-tunable semiconducting two-dimensional (2D) nanosheets from conjugated homopolymers are promising materials for easy access to optoelectronic applications, but it has been challenging due to the low solubility of conjugated homopolymers. Herein, we report size-tunable and uniform semiconducting 2D nanorectangles via living crystallization-driven self-assembly (CDSA) of a fully conjugated polyenyne homopolymer prepared by cascade metathesis and metallotropy (M&M) polymerization. The resulting polyenyne with enhanced solubility successfully underwent living CDSA via biaxial growth mechanism, thereby producing 2D nanorectangles with sizes precisely tuned from 0.1 to 3.0 μm^2 with narrow dispersity mostly less than 1.1 and low aspect ratios less than 3.1. Furthermore, living CDSA produced complex 2D block comicelles with different heights from various degrees of polymerization (DPs) of unimers. Based on diffraction analyses and DFT calculations, we proposed an interdigitating packing model with an orthorhombic crystal lattice of semiconducting 2D nanorectangles.



Namkyu Yun, Cheol Kang, Sanghee Yang, Soon-Hyeok Hwang, Jun-Mo Park, Tae-Lim Choi, *J. Am. Chem. Soc.* **2023**, 145, 9029-9038.

Enhancing Volumetric Capacitance in pgBTTT Polymers through Ethylene Glycol Side Chain Variation and Blending Approaches

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The development of efficient electrochemical devices necessitates a comprehensive understanding of how polymer structure influences their performance. In this study, we investigated the impact of ethylene glycol side chains on the volumetric capacitance of pgBTTT, a regiochemistry-driven organic electrochemical transistor¹. Inspired by prior research on polymer design and mixed conductors², we synthesized a series of pgBTTT polymers with varying percentages of hydrophilic, ethylene glycol side chains, ranging from 50% to 100%. Our findings revealed a positive correlation between the percentage of ethylene glycol side chains and the volumetric capacitance of the polymers, except at 90% side chain content.

Building upon these findings, we further explored the potential of blending as a method for enhancing the volumetric capacitance of the polymers³. Two distinct blending approaches were employed: pgBTTT with pBTTT (OR)₂, and pgBTTT with pgBTTT-OEG-OR. The volumetric capacitance of the blend with pBTTT (OR)₂ was found to increase in accordance with the trend established by the varying side chain percentages. However, the blend with pgBTTT-OEG-OR demonstrated a consistent volumetric capacitance across the same ratios⁴, with both blends exhibiting lower volumetric capacitance than copolymers, except at a 90% ethylene glycol side chain ratio.

Additionally, we examined the effect of film thickness on the kinetics of doping and dedoping⁵. We discovered a direct relationship, with increased thickness leading to longer doping and dedoping times. This observation holds potential for future investigations into the interplay between side chain modifications and doping kinetics.

Our study provides valuable insights into the manipulation of polymer structure for improved electrochemical performance, serving as a foundation for the design of high-performing organic electrochemical transistors and mixed conductors.

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